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이재웅

(주)코오롱 중앙기술원 산자연구소

Antimicrobial Agents and Applications on Polymeric Materials

Jaewoong Lee

Industrial Materials Research Institute, Kolon Industries, Inc., Gumi, Republic of Korea

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Abstract— A wide variety of materials including aldehydes, cationic agents, alcohols, peroxygens, phenols and chlorinated phenols, metal ions are being employed as biocides. Among three levels for biocidal functions (sanitization, disinfection and sterilization), disinfection is an enough level for antimicrobial textiles. In terms of antimicrobial agents for textile applications, quaternary ammonium salts (QAS), chitosan, metal and metal salts, N-halamine based materials are developed with numerous research and the positive ions of those materials may result in disinfection of microorganisms. Photocatalysts, especially titanium dioxide (titania) produces the hydroxyl radical (· OH) which causes inactivation of microorganisms after UV radiation, have been used for antimicrobial applications.

Keywords: *biocide, antimicrobial, antimicrobial fiber, antimicrobial textile, antimicrobial finishing*

1. Introduction

Inactivation of microorganisms causing odor as well as contagious diseases is the goal of antimicrobial agents. Numerous materials have been developed over to the years as mankind has moved toward this goal. The recent concern over pandemics and terrorism has prompted increased emphasis in antimicrobial materials. Thus, it is valuable to understand antimicrobial materials as well as the inactivation mechanism.

There are three major concepts for biocidal functions, described in terms of the strength of the treatment: sanitization, disinfection and sterilization. Sanitization is defined as the process to kill or inactivate microorganisms up to the level that permits a safety for public health. It requires reducing microorganisms in the environment by significant numbers, but it is not a mandatory to eliminate all of microorganisms[1)].

Disinfection applies to the process to destroy or eliminate fungi and bacteria but not necessarily their spores. The three levels of disinfection and disinfectants are suggested with specific intended uses[1-3)]:

Low-level; Quaternary ammonium compounds and 70-90% isopropyl alcohol

Medium-level; Phenolic compounds and 70-90% ethyl alcohol

High-level; Sodium hypochlorite (1000 ppm) and 8% formaldehyde

Sterilization is the eliminating or killing of all forms of microorganisms including their spores. Spores are the most difficult to be destroyed of all forms of microorganisms. Hence, sterilization is the best function to inactivate microorganisms. Conventional sterilization systems include three methods:

†Corresponding author. Tel.: +82-54-469-3843; Fax.: +82-54-461-6113; e-mail: leejaew@kolon.com

Steam under pressure (autoclaves), dry heat (ovens) and chemical[1,4]. Non-conventional and more recent methods include plasma and gamma irradiation[4,5]. Ethylene oxide (ETO) gas or chemicals such as peracetic acid and glutaraldehyde are typical chemical sterilization agents. ETO gas is also very toxic unlike heat and steam, and in addition, residues of ETO in contact with water create ethylene glycol, which is also toxic. Even though heat is non-toxic, during repeated exposure to high temperature of dry heat, decomposition of fabrics or polymers can occur, and steam does not effectively penetrate specimens when they are stuck[1].

Unless disinfectants or sterilizers remain on specimens after disinfection or sterilization, the risk of recontamination still exists[6,7]. Thus, shelf life may be maintained by impermeable packaging. In case of antimicrobial clothing material, retention and reusability of antimicrobial functions after washing are a primary concern. With all agents, safety to the environment is important. For personal safety against contagious microorganisms, antimicrobial functions should be required at least at the disinfection level.

2. Structure and Inactivation Mechanism of Bacterial Cells

Bacteria, are unicellular organisms, and can be separated into two categories: gram negative and gram positive. Gram-negative is identified by absorption and retention of the Gram stain (Gram's Iodine, a kind of mordant dye). Gram-positive colorless after exposure to the Gram stain followed by washing with alcohols. Due to the outer membrane of Gram-negative bacteria (Fig. 1), they are normally less sensitive to biocides. A biocide, which inactivates both types of bacteria, can be defined as a broad-spectrum biocide. *E. coli* and *S. aureus* are conveniently handled and are frequently used to represent Gram-negative and Gram-positive, respectively.

The process of interaction between biocide and cell occurs in the following sequence

1. Attachment to or uptake of biocide by cell

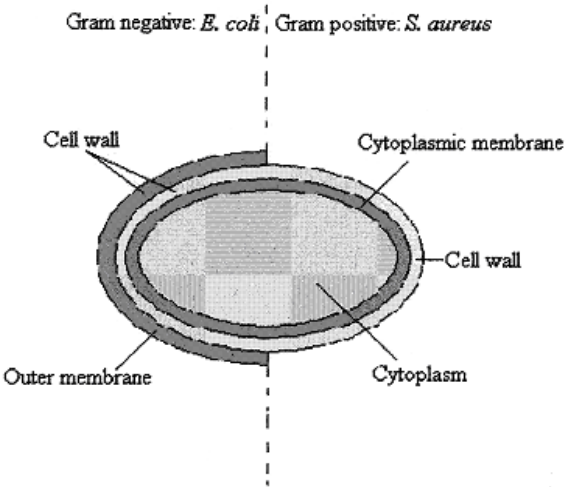


Fig. 1. Structure of the Two Types of Bacteria.

2. Penetration of biocide to target(s)
3. Concentration of biocide at target(s)
4. Damage to target(s)
5. Inactivation of the bacteria

The interaction of a biocide with bacteria induces an initial binding of a biocide to the bacterial cell surface. A deformation of the bacterial outer layer may allow a biocide to permeate the cell and reach target(s)[8-10].

Some cells may recover from metabolic injury after removing or neutralization of the biocide[11].

This is referred to as a bacteriostatic action. Bactericidal action is caused when the damage is to vital cellular structure or function and is irreversible. The penetration of biocide into cells is influenced by several factors affecting biocide chemistry and/or microbial physicochemistry. For example, bactericidal activity is influenced by pH. Weak acids are most active at pHs below their pKa, where they are less dissociated. Cationic surfactants have their most powerful biocidal activity at pHs which ensure the surface negative charge of cells[12]. In general, the target regions of cells are the cell wall, cytoplasmic membrane and cytoplasm. Damaging events at each target region are well defined and summarized below.

Cell wall: Structural/functional changes; disrupts of wall components; initiation of autolysis

Cytoplasmic membrane: Loss of structural organization and integrity, selective increase in

permeability to protons and other ions, inhibition of membrane-bound enzymes

Cytoplasm: Inhibition of cytoplasmic enzymes; interaction with functional biomolecules, coagulation and precipitation of cytoplasmic constituents

The most available target region is the cytoplasmic membrane, due to its fundamental metabolic and structural role within the cell. It also provides large surface area for interaction with biocides. The damage of the membrane integrity may result in the leakage of enzymes, nucleotides and nucleosides, and sugars. After leaking of vital components, the cell will die. A wide range of biocides in different chemical classes will damage cytoplsamic membrane by a variety of different mechanisms[8].

A few species of bacteria have the ability to produce highly resistant structures known as endospores (or simply spores) to help them survive through tough conditions. A bacterial spore is a complex entity, being composed of several different layers (Fig. 2), resistant to inactivation by variety of chemical and physical agents.

Bacterial spores basically consist of spore core, cortex and spore coats. A spore has an outermost layer known as, exosporium. Beneath the exosporium, there is the spore coat, which includes the layer(s) of modified peptidoglycans. Due to limited permeability of the spore coat, the spore has high resistance to chemical disinfection, heat, radiation and drying. The cortex exists within the spore coat.

The cortex has the normal, but small cell wall and cellular constituents. The resistance of spores against solvents is much higher than that of bacterial cells. Some spores can survive at high concentration of ethanol solutions and even withstand boiling in hydrochloric acid for 30 minutes.

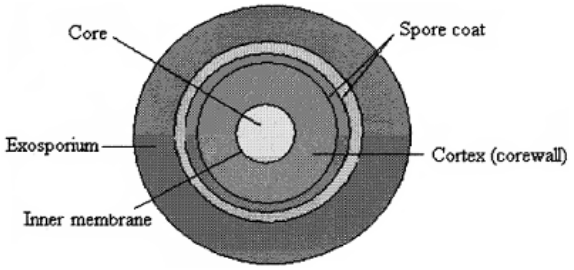


Fig. 2. Structure of Bacterial Spore.

The spore presents several sites at which interaction with an antibacterial agent is possible, e.g., the inner and outer spore coats, cortex, spore membranes, and core. However, it is also obvious that the spore has barriers, which limit biocide penetration[13].

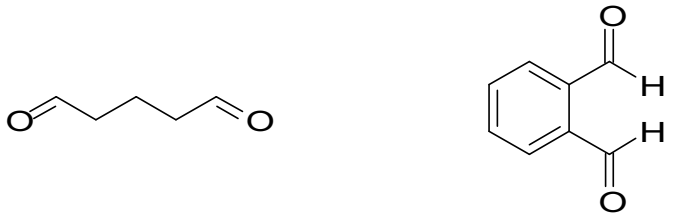
3. Biocides

Numerous biocides are active against bacteria. Normally, aldehydes, cationic agents, alcohols, peroxygens, phenols and chlorinated phenols, metal ions and halogens (in a variety of oxidation states including *N*-halamines) are being used as biocides[9,10,14-17].

Aldehydes inhibit the metabolism and replication cycles of proteins, RNA and DNA by alkylating with the amino, imino, amide, carbonyl and thiol groups. They can also harm some cell/spore wall constituents and may have effectiveness against fungi and yeast. Vapor of formaldehyde has been used as a sanitizer for poultry, and farm animal housing facilities and non-food contact surfaces. Formaldehyde has been used for preserving dead bodies: however, it is a carcinogen and is persistent in the environment. Strains of formaldehyde-resistant *E. coli* and *Serratia marcescences* are known[18]. Glutaraldehyde (GTA) acts as crosslinking agent on amino groups in bacteria proteins[19]. Ortho-phthalaldehyde (OPA), an aromatic dialdehyde, has been investigated with Gram-positive bacteria and Gram-negative bacteria, and has shown less effectiveness in crosslinking than GTA[20](Fig. 3).

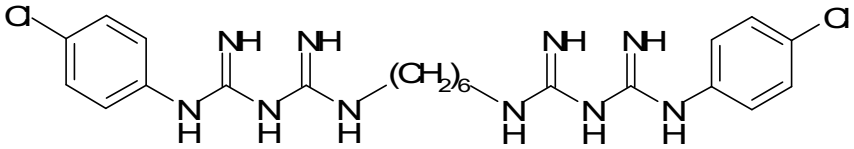
Cationic biocides induce severe membrane damage in various kinds of microorganisms, including Gram-positive and Gram-negative bacteria.

Chlorohexidine (CHX) (Fig. 4) and quaternary ammonium compounds (QACs) (Fig. 5) are good examples of cationic biocides[21]. CHX leaves a residual antimicrobial function after application to a variety of materials. Antimicrobial soaps, mouthwash and antiseptic hand-gels are common applications of CHX. After repeated exposure under CHX, microorganisms may develop resistance[22]. Biguanides such as CHX and alexidine may be applied in a polymeric form and the polymeric biguanides have been studied. Their mechanism of attack has been shown to result noticeable damage on the inner



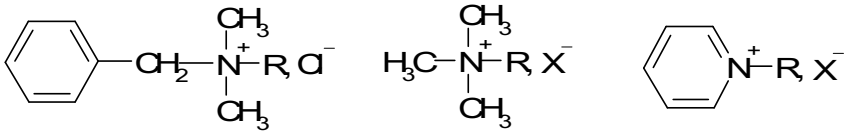
Glutaraldehyde (GTA) *o*-phthalaldehyde (OPA)

Fig. 3. Structure of Glutaraldehyde and o-phthalaldehyde.



Chlorohexidine (CHX)

Fig. 4. Structure of Chlorohexidine.



R= C_8-C_{19} alkyl group
X= Cl or Br

Fig. 5. Structure of Quaternary Ammonium Salts.

membrane of *E. coli*[23]. QACs such as benzalkoium chloride, dodecyltrimethyl ammonium bromide (DTAB) and cetylpyridinium chloride (CPC), destroy outer membrane surfaces on many pathogens. The key feature of antimicrobial QACs is at least one long hydrocarbon chain substituted at the nitrogen. Normally the range of the chain is from C_8H_{17} to $C_{19}H_{39}$, with a best activity around $C_{14}H_{29}$[24]. The suggested mechanism is electrostatic interaction between N^+ in QACs and negatively chargedcell surface increases a defect in the bilayer allowing the hydrophobic chain to permeate into the cell wall, which produces disruption. QACs are a kind of ionic surfactants and act as disinfectants and detergents. However, QACs are only weakly effective against Gram-negative bacteria and are ineffective against spores[22,25].

Alcohols usually have biocidal activity. They show rapid bactericidal properties, even in some cases, acid-fast bacteria. Alcohols can make hydrogen bonds with proteins/enzymes, denature them and render them inactive. However, they are ineffective to bacterial spores even at high concentrations. Ethanol and isopropanol disrupt membranes of bacteria cells. Ethanol inhibits DNA, RNA, protein and peptidoglycan synthesis in *E. coli*[26]. Because absolute alcohols (without water) can not denature bacteria as well as when water is included, a solution of around 70% iso-propanol or ethanol is typically used. These are widely used by hospitals, biological laboratories, in antiseptic gels and hand decontamination products. Due to volatility, they can only supply relatively short-period protection with no residue[27].

Peroxygens are strong biocides. The major peroxygens are hydrogen peroxide (H_2O_2), peracetic acid (CH_3COOOH) and ozone (O_3). They disrupt enzymes and proteins by oxidizing thiol groups.

Because of depolymerization of collagen or gelatin, they are used against spores, and they also destroy biofilm with oxygen bubbles assisting the penetration of the active agent. Hydrogen peroxide is a straightforward oxidizing agent. The hydroxyl radical (· OH), which oxidizes thiol groups in target microorganisms, is the main feature of peroxy-biocides. Peracetic acid is the most powerful peroxygen, and it is bactericidal, fungicidal and sporicidal. The free radical oxidation of enzymes and protein thiol groups is believed as its major action. Hydrogen peroxide and peracetic acid are readily vaporized under hot air condition, and they are also decomposed into oxygen and water, which are harmless to environment.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Ozone is a powerful bactericidal, sporicidal and fungicidal agent however, ozone does not remain in water long enough to supply a residual protection against latent contamination. In addition, ozone is very harmful to humans and decomposes polymers and corrodes metals on contact[28].

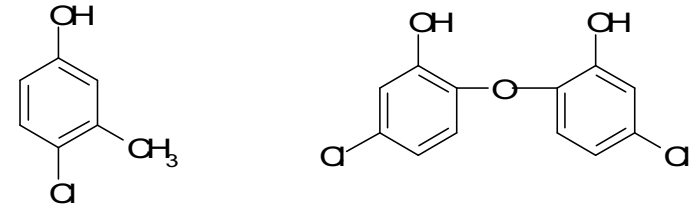
Phenols and chlorinated phenols are used for disinfectants or preservatives. Phenol induces effective loss of intracellular components from bacteria, and germination is inactivated by low phenol concentration. However, phenols are ineffective against bacterial spores even at higher concentrations[26]. Chlorocresol and triclosan are good examples of chlorinated phenols (Fig. 6).

They readily permeate into a phospholipid bilayer, then membrane integrity of bacteria is disturbed. They promote leakage and intracellular coagulation of bacteria. Even though triclosan inactivates bacteria on contact, the effectiveness is not very good.

Triclosan is basically bacteriostatic or fungistatic in action. Chlorinated phenols are predominantly applied for sanitation of floors, garbage cans, toilet facilities and several surfaces. Due to relatively non-corrosive properties, triclosan has been used as the active ingredient for antimicrobial soaps, deodorants, body-wash and antiseptic hand- gels. However, triclosan resistance has been found in *E. coli* (Gram-negative) and *S. aureus* (Gram- positive)[22].

Heavy metals such as Ag, Hg, Zn, As, Cu, Sb and their salts, or organomercury and organosilver compounds have toxicity to living organisms. Metal ions complex with proteins and may precipitate proteins after cleavage of disulphide bonds within proteins. Thus, the configuration of the enzymes and proteins to bind to DNA are inhibited. Silver and mercury are not effective against spores, but may be effective in preventing bacterial growth from the spores. Since heavy metal salts are inexpensive and biocidal, they have been applied as the active ingredient in anti-fouling formulations. Mercuric chloride is sporicidal, but applications of mercuric chloride are inhibited due to environmental problems, and some research has suggested that repeated exposure induced bacteria resistance to metal salts. For instance, silver-resistant Pseudomonas has been reported[29].

Halogen biocides such as Cl_2, Br_2, I_2, HOCl, HOBr, NaOCl, and ClO_2 are powerful antimicrobial agents. Halogen compounds readily halogenate amino groups in proteins. Since chlorine can oxidize the sulphydryl group of triosephosphoric dehyrogenase, the enzyme that supports the oxidation of triose-phosphoric acid to phosphoglyceric acid, enzymatic activity is destroyed[30]. Halogen compounds, especially hypochlorites, are inexpensive and broad spectrum biocides.



Chlorocresol Triclosan

Fig. 6. Structure of Chlorinated Phenols.

They are widely used and powerful oxidizing agents having bactericidal, sporicidal and fungicidal activity. Halogen compounds are referred to as multi-target reactors: acting on cell walls and the amino groups in proteins. Chlorine dioxide has been shown to have activity against bacteria, fungi, protozoa and algae[31]. In water systems and swimming pools, chlorine has been the predominant biocidal agent.

Stabilized halogen biocides such as monochloroamine have been shown to more effectively penetrate and destroy biofilms than free halogen such as free chlorine[32]. Hypochlorous acid (HOCl) is the reaction product of chlorine and water.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

$$HOCl \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H^+ + OCl^-$$

The pKa value of hypochlorous acid is 7.6 at room temperature[33]. Hence, most hypochlorous acid could reside in its neutral form, HOCl at pH<7.6. At pH> 7.6, most hypochlorous acid resides as the hypochlorite ion, OCl^-. Both HOCl and OCl^- are considered as "free" chlorine. HOCl is known to be more effective against microorganisms, and is 150~300 times more antimicrobial than OCl^-. Even if halogen compounds are powerful biocides, chlorine is still corrosive. In addition, chlorinated hydrocarbons such as trichloromethane and oxidized organic compounds are produced after using chlorine, and those products may be toxic. Indeed, trihalomethanes are suspected carcinogens[34-37].

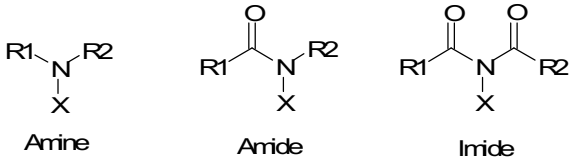
4. N-Halamines

N-halamine materials have debuted as antimicrobial agents over the last few decades. An *N*-halamine is a compound which has covalent bonding between nitrogen and halogen. In general, the halogen is bromine or chlorine (seldom iodine) and can be released into aqueous media as "positive halogen" from the compounds.

The outstanding feature of the compounds is a relative stability and very small amount of released halogen over a long time period. The general structure of *N*-halamine is shown below.

In an *N*-halamine, R and R′ can be an organic group (alkyl group, carbonyl group), inorganic group (phosphate, sulfate), hydrogen, or halogens. When R or R′ is an inorganic group, or both are hydrogen or halogens, it is considered as an inorganic *N*-halamine. Some inorganic *N*-halamine structures are depicted in Fig. 7.

If one of R groups is an organic group, it is considered as an organic *N*-halamine, and major structures are amines, amides and imides. The type of organic *N*-halamine determines stability of halogen and biocidal efficacy.



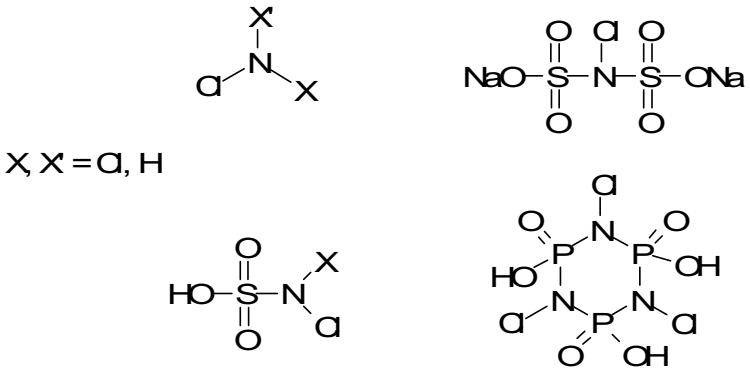


Fig. 7. Structures of Inorganic N-halamine Compounds.

In the amine case, an electron donating alkyl group adjacent to the nitrogen stabilizes the N – X bond, unlike the imide group which has two electron withdrawing carbonyl groups beside the N – X bond. The halogen in an amine should be most stable among them, which means the "free chlorine" released from the *N*-halamine is limited and held tightly. Thus, the N – X in amines may have biocidal activity for an extended time.

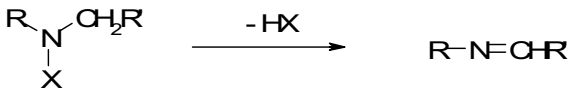
In the imide case, due to destabilization of two carbonyl groups, the N – X bond tends to release halogen rapidly. In other words, instead of the N – X bond, N – is preferred for the stability. This can provide rapid biocidal activity.

In the amide case, it has both electron withdrawing group and electron donating group at the same time. In consequence, the stability and the releasing rate of halogen are intermediate between amine and imide. Consequently, the amine has the lowest dissociation constant and is the most stable. Conversely the imide has the highest dissociation constant and is least stable[38].

One other factor for the stability of the bonding force between halogen and nitrogen is the type of halogen. The greater the bond overlap between halogen and nitrogen, the stronger the *N*-halamine bond. Among halogens except fluorine, chlorine is the smallest one. Hence, chlorine bonds with nitrogen with greatest overlap.

The order of the stability in terms of the identity of halogen is N – Cl > N – Br > N – I. In the same formulae in an *N*-halamine, N – Br has been shown to have a faster biocidal activity than N – Cl.

If there is an α-hydrogen in an amine or amide, the halogen in the N – X bond can undergo dehydrohalogenation with the adjacent α-hydrogen to form C=N bonds.



In general, UV light and heat can promote this kind of reaction. After losing the halogen through dehydrohalogenation, it would not be an *N*-halamine biocide anymore.

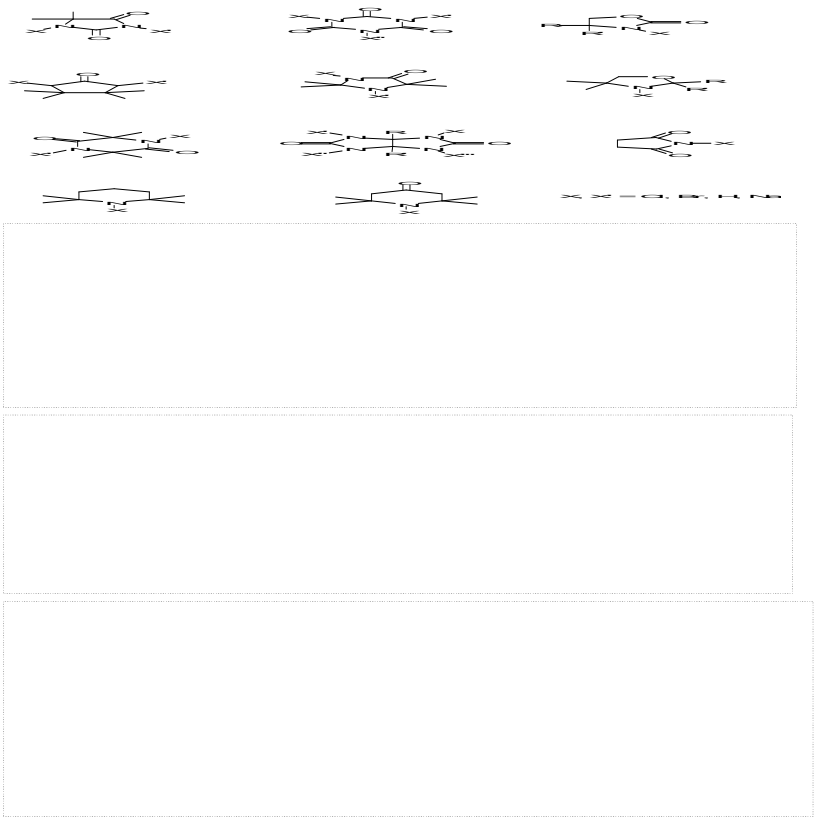
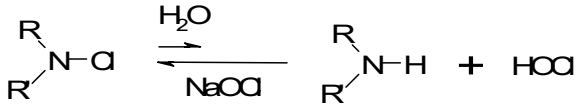


Fig. 8. Structures of Cyclic Organic N-halamines.

To avoid the defect of dehydrohalogenation, nitrogen in a heterocyclic structure is preferred hence, a cyclic organic *N*-halamine biocide without α-hydrogen could be the best choice. To date Worley's group at Auburn University have synthesized various cyclic *N*-halamine precursors which are depicted in Fig. 8.

As a biocide, refreshability is one of the most outstanding features of *N*-halamines. Even if it loses the halogen after repeated application, halogen can be recharged through simple halogenation with sodium hypochlorite solution or household bleach to recover its biocidal efficacy, as depicted in the following scheme:



As discussed, cationic biocides, alcohols, phenols, chlorinated phenols, and metal ions have biocidal efficacy for most Gram-positive and some Gram-negative bacteria, whereas *N*-halamines, aldehydes and peroxygens are broad spectrum bactericides and sporicides. The refreshability and broad spectrum and sporicidal activity to microorganisms make cyclic *N*-halamines versatile biocides. To date, most works for cyclic *N*-halamine biocides have been devoted to water purification[39-41]. The applications of cyclic *N*-halamine for polymers and fibers have tremendous potential which has not been completely exploited.

5. Antimicrobial Textiles

Antimicrobial textiles are one of important and growing sectors in the textile world. Compared with conventional textiles, their antimicrobial properties broaden the application area, enhance the product value, and upgrade the service quality of textile products. Applications can be found in apparel, medical and healthcare, housing and decorative, automotive, construction, marine, and military and space, etc.

A discussion of how antimicrobial compounds function can be found in references[42-44].

Selective toxicity is the desirable mode of action, and selectivity is often the deciding factor in choice of antimicrobial agent (which agent does the least harm to the life forms other than the target of the antimicrobial). The term ecotoxicity is sometimes used to describe the effect of a discarded agent on the environment. Particular concerns are the beneficial insects, birds, and organisms at the lower end of the aquatic food chain. There is also concern about the depletion of beneficial microorganisms, in specific local environments.

Selectivity is often a two edged sword. An antimicrobial that is very selective usually acts by blocking a specific metabolic pathway. Microorganisms can often find a way around a specific metabolic bottleneck. Indeed, the natural population of a microorganism may naturally contain strains which conduct specific metabolic reactions by different mechanisms. The antimicrobial in these cases simply provides a selection mechanism which increases the population of the unaffected (resistant) microbe.

Even though many antimicrobial chemicals can be selected, the number of antimicrobials used on textiles is very limited because of the challenges in making a textile product which is antimicrobial include the following:

Selecting an agent that will kill the undesirable microbe;

Attaching the antimicrobial agent to the textile in at least a semipermanent manner;

Insuring that the attachment to the textile does not inhibit the antimicrobial activity;

Insuring a durable effect or easy regeneration (excessive persistence is not desirable);

Insuring that the product is not excessively toxic to humans or the environment (EPA);

Insuring that microbial life does not develop immunity to the agent;

Demonstrating the antimicrobial effect to regulators and institutional legal advisors; and

Retention of other desirable fabric properties, depending on the use.

Initially the industry largely ignored the toxicity problems and did not mind using agents which were toxic to most life forms. The result was (for example) a rot resistant cotton tentage product used by the military. The cotton fabric was treated with

a mixture of chlorinated waxes, antimony and copper salts, and the fabric became resistant to water, fire and microorganisms. Among the early treatments used to impart microbial resistance in cellulosic fabrics are[45,46]:

Cadmium, copper, chromium, mercury, tin, and zinc salts or organometallic compounds;

Phenols and various phenol derivatives;

Ammonium and phosphonium compounds;

Amino-formaldehyde resins;

Various tars and creosote compounds; and Chemical modification of cellulose (makes cellulose indigestible to microorganisms).

Resistance to attack from microorganisms is not always the result of antimicrobial activity, and lack of microbial growth does not always indicate good biocidal activity. In particular, most synthetic textiles inherently resist attack by microorganisms, but are generally not inherently biocidal. Further, ability to inhibit growth of microorganisms does not reveal how fast, or even whether the microorganism is destroyed. (Those products that do not allow bacterial growth, but do not kill the organisms are called bacteriostatic.) With natural fibers, however, there is a significant overlap of treatments which both protect the textile and attack the microorganisms. All of the treatments which have broad-spectrum antimicrobial activity also provide some measure of protection for the textile itself. Antimicrobial compounds, some of which have been proposed for antimicrobial textiles, include:

Quaternary ammonium compounds

Chitosan

Metals and cations of heavy metals; Copper, silver, mercury, zinc, etc

Oxidizing agents; Compounds which release atomic oxygen or OH radicals

Compounds which release halogen atoms or cations

5.1 Quaternary Ammonium Compounds

Most of quaternary ammonium compounds for antimicrobial textiles are quaternary ammonium salts (QAS), and they, especially containing 12-18 carbons, have the best antimicrobial activity. For cellulose application, in general, the hydroxyl group of cellulose has been modified to prepare strong ionic interaction with QAS. A dichloro-*s*-triazinyl reactive group, which has a reactive sulfonate, was applied on cotton fabric. A natural quaternary ammonium cationic colorant, Berberine, was reacted with this sulfonate, the solubilizing group. The treated cotton fabrics showed an antibacterial property against *S. aureus*[47,48].

Cationic dyes, which include QAS, were prepared. Specifically, anthraquinone derivatives were connected to QAS to make antimicrobial cationic dyes. *N,N*-dimethylbutylamine, *N,N*-dimethyloctylamine, or *N,N*-dimethyldodecylamine was applied as QAS parts. Those antimicrobial cationic dyes were used for dyeing acrylic fabrics, and the cationic dyed fabrics exhibited antibacterial efficacy against *E. coli* and *S. aureus*[49,50]. Conversely, acid dyes were employed to combine QAS onto nylon fabrics. Most acid azo dyes also have sulfonate groups; thus, acid dyed nylon 66 and nylon 6 fabrics were readily treated with QAS and durable antimicrobial nylon fabrics were prepared[51,52].

Carboxylic acid end groups of nylon were converted to carboxylate anions with base to allow ionic interaction with cationic antimicrobial QAS. This interaction provided durable antimicrobial functions. Bulky QAS showed low exhaustion ratio and poor durability[53]. Antimicrobial wool fabrics were prepared through ionic interactions between carboxylate groups in wool protein and, QAS or cetylpyridium chloride (CPC). The antimicrobial functions of CPC survived repeated washing with better durability[54]. A quaternary ammonium surfactant, *N*-dodecyl-*N,N*-dimethylglycine cysteamine hydrochloride (DABM), was used for wool fabrics. The DABM treated wool fabrics showed antimicrobial activity against *B. pumilus*[55].

5.2 Chitosan

Because of non-toxicity to humans, ready degradation into the environment, and abundance next to cellulose, chitosan is a wide-researched material for textile finishing. Chitosan is the derivative of chitin

and is prepared through the deacetylation of chitin. It is assumed that positively charged chitosan interacts with the negatively charged components of microorganisms. This may cause inactivation of microorganisms. Considerable research of chitosan applications is ongoing for antimicrobial textiles.

The antimicrobial activities dependent on different molecular weight were studied. Similar degrees of deacetylation of chitosan were used, and the treated cotton fabrics were prepared by a pad-dry-cure method[56]. Immobilizing chitosan or chitosan derivatives onto fabrics is the key to enhance durability. For this reason, corsslinking agents were employed.

Butanetetracarboxylic acid (BTCA) and Arcofix NEC (low formaldehyde content) were used with chitosan to prepare a durable press finishing and antimicrobial properties at the same time. Both treated fabrics had antimicrobial activity against Gram-positive and Gram-negative bacteria[57].

Chito-oligosaccharides were applied on cotton fabrics with dimethylol dihydroxyethyleneurea (DMDHEU) as a crosslinking agent. The treated cotton fabrics showed good durability and antimicrobial activity after twenty washing cycles[58]. Citric acid (CA) and chitosan were also used for durable press and antimicrobial finishing for cotton fabrics[59].

N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTCC), a water-soluble chitosan quaternary ammonium derivative, was applied onto cotton fabrics with DMDHEU, BTCA and CA[60].

Methyltrimethoxysilane and ɣ-glycidoxypropyltrimethoxysilane were used with chitosan as flexible couplers for cotton fabrics. A pad-dry-cure process was used and chitosan-silane mixed solution showed improved antimicrobial activity and durability without significant loss of tensile strength[61].

Another method to apply chitosan or chitosan derivatives onto fabrics is by the modification of chitosan and chitosan derivatives. Thus, fiber-reactive chitosan derivatives can be readily applied to fabrics. A fiber-reactive chitosan derivative, *O*-acrylamidomethyl-*N*-[(2-hydroxy-3-trimethylamm onium)propyl] chitosan chloride (NMA-HTCC), was applied to cotton fabrics, and the antimicrobial activity against *S. aureus* remained after 50 washings[62].

A fiber-reactive chitosan-cyanuric chloride (CHI-CNC) was used to enhance the durability of antimicrobial activity on cotton fabrics[63].

Blending of chitosan with other fiber forming material can produce antimicrobial fibers.

Specifically, chitosan antimicrobial fibers were prepared through chitosan/cellulose blending system. Chitosan, which was dispersed (not dissolved) in cellulose solution in dimethylacetamide (DMAc) with LiCl, was spun by wet-spinning[64].

5.3 Metal and Metal Salts

Except for silver and copper, others of the less toxic heavy metals exert a weak antimicrobial activity or toxicity to the environment. Thus, the major concern of metal or metal salts for antimicrobial textiles is silver and copper. The mechanism of metal or metal salts to inactivate microorganisms is due to the fact that most metal ions can combine with electron donor groups such as sulfur, oxygen, or nitrogen. Hence, in biological systems, thiols, carboxylates, phosphates, hydroxyl, amines, imidazoles and indoles can combine with the metal ions[65]. As a result, metal ions can inhibit the metabolism of microorganisms.

Layers of silver, copper, gold, platinum and platinum/rhodium (90/10) were deposited on SiO_2 fabrics using magnetron sputtering. Antimicrobial activity of copper was most effective against bacteria and fungi. Silver was also effective against bacteria, but the effectiveness was limited against fungi[66]. A protein fiber, Bombyx mori silk was modified by tannic acid (TA) or ethylenediaminetetraacetic acid (EDTA) dianhydride followed by the absorption of Cu^{2+} and Ag^{+}. The reaction of silk with EDTA - dianhydride enhanced the capacity of the fiber to absorb and bind metal cations. All metal containing silk exerted significant antimicrobial activity[67]. Cotton fabrics were modified with succinic anhydride to attach metal salt ions such as Cu^{2+}, Fe^{2+}, Fe^{3+} and Zn^{2+}. The antimicrobial activity of Cu^{2+}treated fabric against *Escherichia coli* was the most effective[68]. After functionalizing the polyester-polyamide fabric surfaces by RF-plasma or vacuum-UV, the fabrics are immersed in sol-

utions with different concentrations of $AgNO_3$ solution. The Ag clusters were deposited on the two polymer components of the fabric but having widely different sizes. The antimicrobial activity of the fabric was effective against *E. coli*[69]. Nano-emulsion of chitosan/ silver oxide composite was prepared using ultrasound. The antimicrobial activity of the treated cotton fabric was durable and effective[70]. Nano-sized Ag colloids were used for antimicrobial activity on polyethylene/polypropylene (PE/PP) nonwovens. A dip-pad-dry method was employed, and the 10 ppm of Ag colloids treated nonwovens showed a complete inactivation against Gram- positive and Gram-negative bacteria[71]. Nano-sized silver (Ag) powder was mixed with polypropylene (PP) chip for conjugate spinning with PP. The PP/Ag nanocomposite fibers were melt-spun by co-extrusion, and the antimicrobial activity against Gram-positive and Gram-negative bacteria was effective when PP/Ag master-batches were used as the sheath[72].

5.4 Photocatalyst

The photocatalytic activity of titanium dioxide (titania) allows a thin layer coating of the material to exert self-cleaning and antimicrobial properties. Exposure to UV radiation results in the production of the (· OH) radical which is a strong oxidizing agent. Due to its abundance in the world, low cost, and outstanding stability, titanium dioxide could be the representative of photocatalysts. To date most of photocatalyst applications are devoted to wall paper, or other furniture, plastic, or interior surfaces. Photocatalysts have recently been tried for antimicrobial textiles.

Thin film coating of TiO_2 was prepared on polyacrylonitrile (PAN) fibers through a dip-coating method[73]. Nanoparticles of TiO_2 added into polyester gave antimicrobial polyester fibers when extruded through melt spinning. Dipping fabric into a TiO_2 nanoparticle solution also provided a photocatalytic antibacterial textile[74]. A TiO_2-SiO_2 complex of two different sizes (90 and 30 nm) was added to the spinning solution of rayon fiber. The antimicrobial activity showed that 30 nm TiO_2-SiO_2 complex fibers had better effectiveness than 90 nm fibers[75].

5.5 N-Halamine Based Antimicrobial Textiles

N-halamines are compounds which have at least one nitrogen and halogen covalent bond within the structure. After repeated exposure to microorganisms or releasing antimicrobial functions, *N*-halamines can be recharged through simple exposure to diluted household bleach or halogen releasing agents; thus the biocidal properties of *N*-halamines could be retained indefinitely[76]. The antimicrobial mechanism of *N*-halamines against microorganisms is that the positive charged halogen transfers from the *N*-halamines to the proper reacting site of microorganisms. The reaction directly inhibits and inactivates the metabolism, and destruction of microorganisms is promoted[77,78].

Thus, *N*-halamines are regenerable and are strong biocides against microorganisms. Various *N*-halamine compounds have been used as an effective antimicrobial compounds for treating cotton, polyester, nylon, etc.

The antimicrobial activity of cellulose with incorporation of *N*-halamine has been studied. An *N*-halamine precursor, 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH) was used for the chemical finishing process with cotton fabrics. Theoretically, DMDMH is a crosslinking agent for cellulose, and DMDMH treated cotton fabric should have no available site for chlorination. In practice, however, after some loss of formaldehyde during the treatment process, the DMDMH treated cotton fabric was exposed to chlorine bleach and was turned into antimicrobial textiles[79]. A similar finishing process was employed for 3-methylol-2,2,5,5-tetramethylimidazolidin-4-one (MTMIO) and monomethylol-5, 5-dimethylhydantoin (MDMH), which have one methylol group to connect to cellulose. The MTMIO and MDMH treated cotton fabrics had durable and rechargeable antimicrobial activity[80,81].

Siloxanes have been used as an *N*-halamine precursor coupler due to versatile bonding properties on most of surfaces. For instance, an antimicrobial cotton fabric was produced using 3-trihyroxysilylpropyl -5,5-dimethylhydantoin (SPH), and the chlorinated fabrics showed a complete 5.7 log reduction against

S. aureus and *E. coli* in 30-120 min contact-time. Other *N*-halamine siloxane monomer precursors, which are 5,5'-ethylenebis[5-methyl-3-(3-triethoxysilyl-propyl)hydantoin] and 3-[3-triethoxysilylpropyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (TS), and a polymer precursor, poly[3-(7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dion-3-yl)propylhydroxy siloxane] (PTS) were applied onto cotton fabrics[82,83]. Grafting is another method to incorporate *N*-halamine precursors on textiles. An *N*-halamine precursor, 3-allyl-5,5-dimethylhydantoin (ADMH) was grafted on cotton fabrics[84].

Acrylamide (AM), methacrylamide (MAM) and tert-Bu acrylamide (TBAM) were also grafted onto cotton fabrics followed by chlorination[85]. A dyeing process was used for application of an *N*-halamine precursor on cotton fabrics. An *s*-triazine based *N*-heterocycle, dichloro-*m*-aminophenyl hydantoinyl-*s*-triazine (DAPHT), which could be rendered antimicrobial through exposure to diluted chlorine bleach, was synthesized. Dyeing technology, particularly reactive dyeing, was used to apply the *N*-halamine precursor onto cotton fabric.

The DAPHT treated cotton fabric resulted in durable and rechargeable antimicrobial properties for up to 50 standard washing cycles[86].

Synthetic fibers have been also challenged to apply *N*-halamine precursors. Polyester fabrics were modified with ammonium hydroxide solution to impart *N*-halamine moieties, and then the treated polyester fabrics were chlorinated[87]. A cyclic-amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) was grafted on polyethylene (PE), polypropylene (PP), acrylic, polyester/polyamide (PET/PA) and polyamide 66 fabrics with triallyl-1,3,5-triazine- 2,4,6(1H,3H,5H)-trione (TATAT). The treated fabrics exerted antimicrobial activity against *E. coli*[88].

Antimicrobial Nylon fabrics were prepared. After attaching a hydroxymethyl functional group on Nylon 66, *N*-halamine precursors were imparted. The chlorinated fabrics showed 7 log reductions against Gram-positive and Gram-negative bacteria in 30 min contact-time[89].

A wet-spinning method was used to prepare *N*-halamine antimicrobial fibers. Polystyrene hydantoin (PSH), which was an *N*-halamine precursor, and polyacrylonitrile (PAN) were blended in dimethyl acetamide (DMAc). The PSH/PAN blended fibers were spun through a dry-jet wet spinning process.

The *N*-halamine fibers showed durable and regenerable antimicrobial activity after recharging up to 50 standard washing cycles[90]. A copolymer, polyacrylonitrile-co-3-allyl-5,5-dimethylhydantoin was blended with PAN in a NaSCN aqueous solution. A wet spinning process was used, and the chlorinated blended fibers had antimicrobial ability[91].

Fiber forming polymers, which are also *N*-halamine precursors, were introduced[92]. They have advantages such as higher durability and no additional finishing.

5.6 Commercial Products

The considerable commercial products for antimicrobial textiles are growing. In spite of the risk that claims of antimicrobial activity might invite litigation, the number of antibacterial products has grown dramatically over the last couple of years. Sometimes the products are offered under the guise of freshness or odor control, but successful EPA/FDA registration of several products has allowed the antimicrobial claims to be advertised, and most large fiber producers now have these specialty products in their inventory.

The antimicrobial products currently available in the textile/fiber market (or known by the author to be in commercial development) include the following: Interface Inc. developed an organic substituted ammonium phosphate sold under the name Intersept®, and used by Interface in its carpet products[93,94].

Dow-Corning produced a series of quaternary amines which could be fixed to a surface via silane chemistry[95-97].

Aegis Environments (Midland Michigan), a spin-off company, has developed the technology under the trade name Microprobe Shield®. The product is used in a wide cross-section of the textile industry – nonwovens, wipes, medical wear, socks, athletic apparel, uniforms, floor mats, ceiling tiles etc.

Familiar companies using this technology include: Dr. Scholls®, Brillo®, Odor Eaters®, Franklin Sports, Burlington, Kaiser Roth, BBA, Precision Fabrics, Russell, US Gypsum (ceiling tiles), and others.

Bioshield, has modified the Dow chemistry in their laboratories[98-100] and has a number of companies using their technology. They claim control of dust mites via control of the fungus dust mites eat. With three recent patents and EPA registrations, Bioshield is beginning to capture some textile/ nonwovens applications (Burlington House, Milyon, and others). They also offer cleaning and fabric freshening products for home use.

Triclosan appears in the patent literature as early as 1976. It is produced by Ciba and most promoted under the name Microban® (Microban Products Co., Huntersville, NC, U.S.A.). It is available in a variety of fiber and textile products[101].

It is easily the most widely known of the antimicrobial products. Most often it is incorporated into the fiber. Fibers using triclosan are available from Synthetic Industries (olefin), Sterling Fibers (acrylic), and Cydsa (acrylic) as well as from several other suppliers of acetate, olefin, and acrylic fibers.

Healthshield® Agion® appears to be a rapidly developing technology which has significant development momentum. The technology is a silver based inorganic ion exchange material and has signed on Foss, DuPont (tooth brushes), Smith and Nephew, Taconic (conveyor belting), and a variety of shoe companies, medical fabricators, metal fabricators, surface coating, and film producers. While one might question the safety of releasing silver ions, apparently the concentration is small, and the product has FDA (food contact) and NSF (National Sanitation Foundation) approval (food and beverage contact)[102,103].

Biguanides[104,105] were developed for textile applications by Zeneca, (now Avecia®) and are available under the trade name Reputex®. The textile treatment works well on cellulosic fibers and is available in fiber form from Acordis® and in cotton fabric from Kendall Health Care®. A number of other manufacturers are developing products with Reputex as a fabric finishing agent. Thomson Research Associates (Toronto, Canada) sells a variety of antimicrobials under the name Ultra- fresh®. Their formulated products include iodine releasers (eg. diiodomethyl-p-tolyl sulfone), organotin compounds, isothiazalonones, quaternary ammonium compounds, and triclosan. Textile products using the Ultra-fresh® technology are available from Avondale, Charlescraft, American Textile, Spenco, Rockland and others.

Chitosan is derived from chitin, a major component in crustacean shells. Chitosan has some level of antimicrobial activity, and fibers made from chitosan are available in the marketplace. Coatings of chitosan on conventional fibers or films appear to be a more realistic prospect for development of this material. Because it does not provoke an immunological response, chitosan has been suggested for bandages, sutures and other items placed in the human body[106]. Purity will certainly be an issue in these applications.

Most *N*-halamine based antimicrobial textile applications are household articles such as socks, shirts and towels. In addition to household products, interests from military applications such as tents and army uniforms have been developing because of powerful biodcidal effects. Sheets and pillowcases containing HaloShield® (*N*-halamine compounds made by Vanson HaloSource (Seattle, WA)) treated bed-linen products are now available from Medline Industries for use in hospitals, nursing homes and managed care facilities in the U.S., and more companies are joining to develop *N*-halamine based antimicrobial textiles; Miliken & Company (Spartanburg, SC, U. S. A.), and Ecolab Inc. (St. Paul, MN, U. S. A.) etc.

It is recommended that some comments about testing are probably made. Most published data for textiles andfibers are still generated by placing a fabric on an inoculated nutrient agar plate and measuring the inhibition zone[107]. This procedure depends on antimicrobial diffusion in the agar and reveals little about the speed nor whether the action is bacteriocidal or bacteriostatic. Therefore, it is much preferred the process of soaking the textile

with inoculum for varying time periods and washing out and growing the residual microorganisms[108].

6. Conclusions

In terms of disinfection, numerous biocides have been developed, and research which is related to biocides has been carried out to show the prominent properties against bacteria. For antibacterial textiles, diverse materials including quaternary ammonium compounds, chitosan, metals and cations of heavy metals, and oxidizing agents have been employed. In commercial area, various products for antimicrobial are available and the market for antimicrobial textiles has been grown rapidly and will expand with potentiality.

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