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Review of Antimicrobial Textile Finishes

Venkata R. Kolli[1], Gautam K. Ginjupalli[2], Manjira Ghosh Kumar[3], Nandini D.P.K. Manne[4], Michael D. Hambuchen[5], Kevin M. Rice[2,6,7*], Eric R. Blough[2,5]

[1]Department of Toxicology /Global QC BPANS (Business Processes & Network Strategy), Shire Pharmaceuticals, Lexington, MA

[2]Department of Center for Diagnostic Nano systems, Marshall University, Huntington, WV, USA

[3]Department of Chemistry, Marshall University, Huntington, WV, USA

[4]Department of Public Heath, Marshall University, Huntington, WV, USA

[5]Department of Pharmaceutical Science and Research, School of Pharmacy, Marshall University, Huntington, WV, USA

[6]Biotechnology Graduate Program West Virginia State University, Institute, WV, USA

[7]Department of Health and Human Service, School of Kinesiology, Marshall University, Huntington, WV, USA

[*]**Corresponding author:** Kevin M. Rice, Department of Center for Diagnostic Nano systems, Marshall University, Huntington, WV, USA. Tel: +1-3046382982; Fax: +13046963766; Email: rice9@marshall.edu

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Abstract

Antimicrobial finishes have long been important in the textile market. Coated textile fabrics have a wide range of applications in both the defense and civilian sectors. In hospitals, these coated fibers are an important tool in preventing the spread of infection. There are currently several types of antimicrobial finishes commercially available. This includes oxidizing agents (e.g., aldehydes and halogens), quaternary ammonium compounds, metallic compounds (e.g., cadmium, silver), and natural antimicrobial agents (e.g., chitosan and neem). Each group of these antimicrobial finishes has different properties (e.g., durability, fabric incorporation techniques, production, etc.) and different modes of action against microbes. This review provides an overview of these differences.

Background

Antimicrobial finishes are used in clothing, medical supplies, and other products to prevent fungal, bacterial (both gram positive and negative), or algal growth which leads to odors or other offensive properties or even worse, infectious disease [1,2]. Both natural (e.g., cotton) and synthetic (e.g., polyester and polyamide) are susceptible to microbial contamination. Higher levels of moisture transport, oxygen, and nutrient transport causes the fiber to be a superior medium for microorganism growth [1]. Compared to uncoated fabrics, fabric coated with antimicrobial finishes can reduce the textile susceptibility to microbial damage. Even more importantly, these coatings have many medical and safety applications [3] in wound dressing or protective suits [4]. For example, fabrics used in a hospital setting are potential mechanisms for the spread of infectious disease, and these coatings are important in preventing this spread [5]. Indeed, nosocomial infections have both a major cost in currency and human life in the US ($4.5 billion and 88,000 deaths in 1995, respectively) [6,7]. Additionally, these finishes can be used for both health and aesthetic purposes in mass market consumer items such as towels, wash cloths, pillowcases and underwear [4].

Key considerations to designing an antimicrobial finish include antimicrobial activity, toxicity to human skin, effect of the coating on the textile, and the durability coating with use. While it is of great importance for an antimicrobial coating to inhibit microbial growth, it is also of equal importance to consider the proximity of the coated textile to human skin and to be aware of and/or minimize any potential toxicity to the human user [8]. In addition, the coating must not damage (e.g., discolor, alter structural integrity, etc.) the fabric it is applied to [8]. The durability of an antimicrobial coating to the continuous cycle of use and laundering is another major consideration when using an agent [9]. The attri-

bute of stable antimicrobial properties divides the finished textiles into two classes: durability and temporary which can and cannot (respectively) withstand laundering. Durability properties are not only due to the finish used, but also the fabric coating process. For example, wet finishing processing of a given antimicrobial agent can lead to improved durability.

Different Types of Antimicrobial finishes

There are different types of chemical compounds that can be used as antimicrobial finish on textiles. These agents have effects on both bacteria (antibacterial) and fungi (antimycotic) by inhibiting the growth of or destroying the microbes. The general actions on microbes include cell wall disruption, genome and protein degradation, and inhibition of enzyme functions [9]. Oxidizing agents (e.g., aldehydes and halogens), quaternary ammonium compounds, metallic compounds (containing e.g., cadmium, silver, etc.), and natural antimicrobial agents (e.g., chitosan and neem) are some of the antimicrobial compounds currently available [8].

N-halamines (oxidizing agent)

Halogens, isothiazones and peroxo compounds form free radicals which react with amino acids causing mutations and dimerization [10]. One type of oxidizing halogen-based compound are the N-halamines. These compounds stably form covalent bonds between nitrogen and a halogen and can transfer the halogens to a microbe producing oxidative damage; this mechanism leads to broad spectrum antibacterial activity and also activity against fungi and viruses [11]. While this mechanism eventually depletes the oxidative halogen, the N-halamine can be reactivated by re-exposure to halogens (e.g., washing the coated fiber in bleach) [11] (Figure 1). The N-halamine antimicrobial fabrics can be produced by physically/chemically bonding N-halamine precursors to polymers or fibers, mixing the N-halamine precursor with a fiber forming polymer, or ideally by using a polymer that is both fiber-forming and an N-halamine precursor as this method requires no additional finishing and is very durable [12].

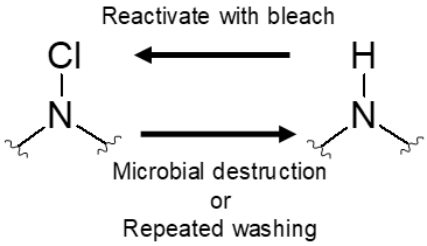

Figure 1: Use, inactivation, and reactivation of N-halamines.

For example, fibers produced with meta-aramid (m-aramid; an N-halamine)/cellulose combinations can be highly chlorinated compared to m-aramid alone; additionally, the m-aramid does not leave the cellulose matrix during washing [12]. Both gram-positive and negative bacteria are inactivated within 30 minutes of contact time with this fiber, but the hydrophobic nature of m-aramid after chlorination makes it slightly less effective against gram-negative bacteria due to the outer membrane permeability layer [12,13].

Another N-halamine example involves 2, 2, 5, 5-TeTramethyl-Imidozalidin-4-One (TMIO) first being grafted onto a Poly Urethane (PU) surface and then being activated with chlorine [14]. Such treatment results in ~8 x higher chlorine content which effects overall antimicrobial capability and increased hydrophilicity which improves contact with the bacteria. Indeed, the TMIO modified membrane improved the action against both gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria. Like the previous example, this finish has less effects on gram-negative material due to the properties of the cell membrane [13,14] Imide and amide halamine structures created by treatment of cellulose with 1,3-dimethylol-5,5-dimethyhydantoin (DMDMH) and activation with bleach; these N-halamines amide have low durability during washing, especially with the imide structure [15]. A durable, longer lasting amine structure can be created on cellulose by using 3-Methylol-2,2,5,5-TetrMethylImidazolidig-4-One (MTMIO) [15]. While the imide halamines react faster, the amine halamines have more stability [15]. The combinations of DMDMH and MTMIO have higher washing durability and storage stability [16].

As all the commercial cloth materials are laundered and possibly ironed, understanding the thermal stability of these fabrics is essential. To test this property, fabric samples containing amine, amide and imide halamines were treated at different temperatures (125^0C, 165^0C and 185^0C) over different durations [1]. While below 125^0C, all the three halamines structures are intact higher temperatures can damage the halamine structure attenuating the biocidal properties [1]. At higher temperatures, the amine halamines was the most stable and imide halamines was least stable; this mirrors to the previous washing durability properties amongst the N-halamine types [1]. For the fabric to retain the biocidal functions obtained due to DMDMH and MTMIO, the ironing temperature should not exceed 125^0C [1].

Quaternary ammonium compounds

Quaternary Ammonium Compounds (QAC) are widely used as disinfectants. They are also used in preserving ophthalmic solutions and pharmaceutical preparations such as creams, lotions, and injections for treating skin. There are different QACs that are commercially available in market with different names which include Bioguard from Aegis and Reputex-20 from Arch chemicals. The antibacterial properties of QACs were first found in 1916 by Jacobs and associates [17]. These compounds contain 12-18 carbon atoms and carry a positive charge on the nitrogen that is responsible for

antimicrobial properties of QACs. The lipopolysaccharide structure of microorganism's cell membrane gets disrupted by QACs like biguanides, amines and glucoprotamine [18]. The surfactant properties of QACs denature proteins (see Figure 2), inhibit DNA production, and cause loss of membrane integrity; one or more of these mechanisms cab produce biocidal effects against gram positive and gram-negative bacteria, fungi, and some virus types [19].

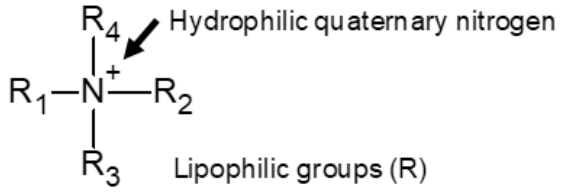

Figure 2: The base QAC structure produces surfactant properties.

The attachment of QACs is primary due to the ionic interaction action of the anionic surface of fiber with cationic portion of QAC [20]. QACs can be divided into hard and soft drugs based on the fate of the drug after interaction with microbes [21]. Hard drugs are either non-metabolizable drugs or metabolized to biologically active metabolites e.g. benzalkonium chloride; this limits their use as antibacterial agents [21]. Soft drugs are *in vivo* inactivated to non-toxic substances after they have produced their effect; unfortunately, they are unstable *in vivo* which makes them less suitable as antibacterial agents [21]. Considering that resistance is an issue with QACs, N, N-dichloroamines, in which the back bone structural modification is done using sulfonic acid replacements, were designed to overcome the resistance developed by microbes [22].

Metals and metal salts

There are many metals and metal salts like silver, copper, zinc oxide and titanium dioxide that have antimicrobial properties. The use of silver as an antimicrobial agent dates back to over 2000 years ago; for example, the Roman and the Arabian people added silver coins to drinking water to maintain its freshness [23,24]. Silver-based compounds can be effective antimicrobial finishes as these compounds are insoluble in water and do not leach with washing or autoclaving. These compounds have long lasting microbial properties, are stable at high temperatures, and have low volatility [24]. Additionally, these silver based compounds are considered non-toxic to humans [25-26]. Generally, 0.5% silver nitrate in a solution offers antimicrobial activity without causing tissue toxicity [23]. The metallic silver reacts with water molecules and oxidizes to active species of Ag+ cation which are responsible for the antimicrobial activity of silver; the concentration of 0.1 ppb Ag has been shown to have the antimicrobial effect [27]. In addition, it is very difficult for most bacteria to develop resistance to silver ions [28]. Silver nitrate inhibits the growth of most bacterial strains and is effective against *Staphylococcus aureus* and *Klebsiella pneumoniae* [23]. Because silver is stable, silver that accumulates in a dead microbe will target other living microbes (Figure 3) [29]. There are different methods of incorporating silver in various polymeric substances which include direct deposition of metallic silver on to the substances and incorporation of silver into molten polymers [24]. Poly Amides (PA) are group of compounds that contain repeated amide groups, as seen in various kinds of nylon; Poly Amide/silver (PA/Ag) systems release silver ions to produce silver concentration dependent antimicrobial effects [24]. Another incorporation technique involves dipping fabric in a water solution consisting of silver salt and surfactant-stabilizer silver salt suspension; Silver salts form nano-sized crystals and get deposited uniformly on the surface of the fabric [4]. Indeed, fabric coated with this finish inhibits the growth of both grams positive (*Staphylococcus Aureus*) and the gram negative (*Escherichia Coli*) bacteria, and the zone of growth inhibition was found to be 2-3 mm [4].

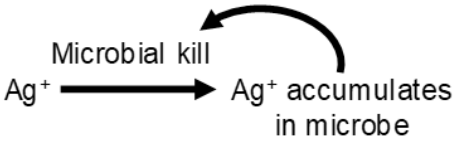

Figure 3: The stability of silver allows killed microbes to act as a drug delivery mechanism.

Biological syntheses may help in attain better size distribution than colloidal metal particles over the fabric surface. Intracellular production of silver nanoparticles can be obtained by *Verticillium* fungal stains [30]. Silver alginates are often prepared in a two-step process [23]. In the first step, each of the aliginated dressings is treated with 1-2 % of acetic acid and in the second step; they are treated with silver nitrate. Silver nitrate treatment causes hydrogen ions to be replaced with silver cations [23]. The produced antimicrobial Ag-CM (Alignate-Carboxymethylated) print cloth has been found to be effective against both gram-positive (*S. aureus)* and gram-negative (*K. pneumoniae*) bacterial infection. The silver-treated alginate dressing hydrofiber (AQAg) has been found to reduce the depth of diabetic foot ulcers when compared to calcium alginate with the AQAg requiring less antibiotic treatment for the infection [23]. The nanoparticles can be stabilized by proteins in biological synthesis [31]. The nanoparticles incorporated using the biological synthesis exhibited antimicrobial activity against *S. aureus,* and most of the silver nanoparticles are eliminated from the effluents through the process of biosorption [31]. In general, healing is more efficient in moist conditions, indeed, occlusive dressings facilitate healing by controlling the moisture in the vicinity of wound [23]. Aliginate fiber is an important fiber for wound dressing. It is a naturally occurring polysaccharide which has 1,4-linked-β-D-manuronic acid and α-L-guluronic acid that is widely used in pharmaceutical industry for the drug delivery

[23]. There are a number of commercially available moist-wound Ca/Na-alginated dressings like Kaltostat (Conva Tec), Sorbasan (Maersk Medical) and Curasobr (Kendall) [23].

Titanium dioxide (TiO_2) is another metal containing chemical that is used for its bactericidal properties. Sol-gel, spray pyrolysis, and chemical vapor deposition are some of the techniques that can be used for preparing thin films of titanium dioxide [32]. There are, however, obstacles for these processes. One is the need for UV radiation; titania acts as a photocatalyst in its antibacterial applications [32]. Titanium dioxide coatings inhibit the growth of bacteria through free radical formation but may not kill the microbes [32]. Zinc oxide (ZnO) is also used in fabrics as an antimicrobial agent. While silver nitrate is commonly used as antibacterial agent, ZnO usage is very cost effective. Additionally, ZnO more effectively whitens and contains UV-blocking properties on textiles than silver nitrate [33]. The pad-dry-cure method can be used for applying nano-ZnO onto the cotton fabrics. ZnO nanoparticles impregnated onto cotton have antimicrobial activity against *Staphylococcus aureus* and *Klebsiella pneumonia* and also against UV radiation [33].

Natural substances

Even though metals and their salts, organometalllics, phenols, quaternary ammonium compounds, and organsilicons are the most common antimicrobial compounds, natural substances like chitosan and neem play important roles as naturally occurring antimicrobial compounds. One of the main advantages of natural occurring antimicrobial compound is that they are less toxic to humans and easily biodegradable [34].

Chitosan is a natural substance with antimicrobial properties; it is thought to shrink and deform the cell membrane of bacteria and yeast leading to the death of microbes. Chitosan is formed from chitin upon deacetylation. In addition, the hydroxyl group on the number two carbon is replaced by amino groups [poly (1,4)-2-amido-2-deoxy-β-D-glucose]. Among the natural polymers, chitin is the second most abundant [34]. Chitosan is an excellent agent due to its biodegradation, lack of toxicity, and wound healing promotion properties, in addition to its antimicrobial activities (Figure 4). While increasing concentrations of chitosan eventually decreases the integrity of the coated fabric, the peak anti-*Staphylococcus aureus, Escherichia coli*, and other microbe activity occurs at concentrations as low 0.5 - 0.75% [34].

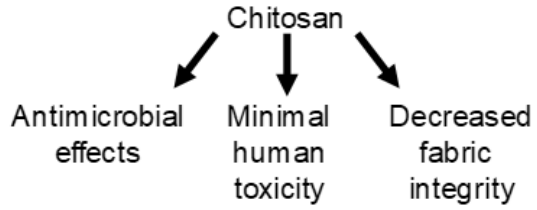

Figure 4: Advantages and the challenge of using chitosan as a finish.

The cross-linking agents used in binding chitosan with cotton also play an important role in imparting different levels of antimicrobial properties to cotton. Cotton fabrics are treated with two different cross linking agents namely ButaneteTraCarboxylic Acid (BTCA) and Arco fix NEC (low formaldehyde content) along with chitosan [34]. In testing the antimicrobial properties against the gram-negative *(Bacillus subtilis, Bacillus cereus, Escherichia coli, Pseudomonas aeruginosa*) and gram-positive bacteria (*Staphylococcus aureus*) and fungi (*Candida albicans*), it was found that cotton fabrics treated with chitosan and cross linking agent BTCA had increased antimicrobial properties compared to the one treated with cross linking agent Arcofix [34].

Compounds from neem trees (*Azadirachta indica*) have been used by humans since the times before recorded history [35]. Currently, compounds extracted from neem used in toothpastes, cosmetics and pharmaceuticals; neem tree belongs to the family of Meliaceae and is found in Indian subcontinent [36]. Neem extracts like azairachtin, salnnin and meliantriol regulate growth of insects and antifeedants [37]. The neem extracts, when applied to blend fabrics along with the cross linking agents like glyoxal/glycol, aluminum sulfate and tartaric acid, showed antimicrobial properties. Neem extract textile coating has been shown to effect both on gram-positive bacteria *(Bacillus subtilis)* and gram negative bacteria *(Proteus vulgaris)* without disrupting the tensile strength and flexibility of the fabric [38]. Cross linking agents plays an important role in the attachment of neem extract to fiber and imparting antimicrobial properties [38].

Conclusion

Textile coating and the associated potential for antimicrobial properties can provide great benefit to society. As coating research introduces more effective antimicrobial treatments the potential

applications will explained. In the westernized countries and in third world countries the introduction of antimicrobial-coated fabrics will have a direct effect on public health and welfare of the population. With the burgeoning field of nanomaterials, the textile industry is strategically positioned to experience a myriad of potential coating options.

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