Biodeterioration has been defined as “any undesirable change in the properties of a material caused by the vital activities of organisms” (H. J. Hueck). This paper will be concerned with the deterioration of textile materials caused by micro-organisms such as fungi and bacteria, and the steps that can be taken to prevent or minimize their effects.

Under suitable conditions micro-organisms which inhabit soil, water, and air can develop and proliferate on textile materials. These organisms include species of microfungi, bacteria, actinomycetes (filamentous bacteria), and algae. Textiles made from natural fibers are generally more susceptible to biodeterioration than are the synthetic man-made fibers although textiles, in general, provide a very suitable living environment for many microorganisms. Products such as starch, protein derivatives, fats, and oils used in the finishing of textiles can also promote microbial growth. Micro-organisms may attack the entire substrate, i.e. the textile fibers, or they may attack only one component of the substrate, such as plasticizers contained therein, or grow on dirt that has accumulated on the surface of a product. Nevertheless, even mild surface growth can make a fabric look unattractive by the appearance of unwanted pigmentation. Heavy infestation which results in rotting and breakdown of the fibers and subsequent physical changes such as a loss of strength or flexibility may cause the fabric to fail in service. The material is attacked chemically by the action of extracellular enzymes produced by the micro-organism for the purpose of obtaining food\(^1\). However, microbial activity can be minimized by keeping susceptible materials dry, as surface growth will only occur when the relative humidity is high. Or by using antimicrobial treatments that are part of the fibers themselves. Therefore, some form of chemical protection is normally only required with textiles likely to be used in adverse conditions under which they remain wet or damp for long periods of time.

**Natural fibers**

Plant fibers such as cotton, flax (linen), jute and hemp are very susceptible to attack by cellulolytic (cellulose-digesting) fungi (see photo on right). Indeed, the complete degradation of cellulose can be effected by enzymes, produced by the fungi and known as cellulases. The spores of these microfungi are present in the atmosphere and when they settle on suitable substrates they can quickly grow under favorable conditions of temperature and humidity. The characteristic growth form of these “mold” fungi is known as mildew, a superficial growth which may discolor and stain the fabric, as many microfungi are capable of producing pigments. One protection against mildew is to make certain that the fabrics are dry when stored and that they do not become damp during storage. Fabrics which are to be used out of doors for awnings, beach umbrellas, military uniforms, sails, tarpaulins, tents, truck and boat covers, shoes and shoe linings, should be treated with a fungicidal finish to protect them from mildew damage and rotting. Algal greening may also occur on fabrics which remain wet for long periods and can cause particular problems in the tropics.

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\(^{1}\) This and other some other portions of this paper are from “Talking rot... and mildew” by Paul F Hamlyn. Published in the December 1998 issue of NWFG Newsletter (ISSN 1465-8054). Also, Textiles, 1990, 19, 46-50.
Above is another example of a scanning electron micrograph of historic undyed fiber with micro-organisms on the fiber surface (2,500x).

Above are scanning electron micrographs of historic undyed fiber: A, localized degradation (3,676x); B, the grooves formed by microbial degradation (10,000x).

Animal fibers are more resistant to mildew growth than plant fibers. Pure silk is less susceptible if completely degummed. Wool decays only slowly but chemical and mechanical damage during processing can increase its susceptibility to biodeterioration. When stored under very adverse conditions wool will eventually rot by the action of the proteolytic (protein-digesting) enzymes secreted by many microfungi and bacteria.\(^2\)

**Man-made fibers**

Man-made fibers derived from cellulose are susceptible to microbial deterioration. Viscose (rayon) is readily attacked by mildew and bacteria; acetate and triacetate are more resistant although discoloration can occur if the fabrics are incorrectly stored. Fibers made from synthetic polymers (e.g. acrylic, nylon, polyester, polyethylene, and polypropylene fibers) are very resistant to attack by micro-organisms. The hydrophobic nature of these polymers is probably an important factor determining their resistance. Also, these synthetic polymers contain chemical bonds which do not occur or are uncommon in nature, and so perhaps they have not been around long enough for micro-organisms to evolve the appropriate enzymes necessary to initiate their breakdown. Although the substance of a synthetic fiber by itself will not support microbial growth, contaminants of low molecular weight (e.g. residual traces of the caprolactam monomer of nylon 6) and compounds such as lubricants, spinning oils used in the finishing of textiles or skin oils may provide sufficient nutrient for mild surface growth of a micro-organism. In most cases this will not affect the strength of the fabric but can give rise to staining and discoloration which are often difficult or impossible to remove.

\(^2\)Ibid.

**Plastics**

Several types of plastic materials have become important as components of textile products, for example, to provide waterproof coatings for rainwear. Plastics which are made mainly or entirely from polymers such as polyethylene are usually highly resistant to microbial growth. However, two types of plastic used extensively as coatings for textile materials, plasticized polyvinyl chloride (PVC) and polyurethanes, are susceptible to biodeterioration (see photo on left). In the case of PVC, the polymer itself does not readily provide a source of nutrients for bacteria and fungi. The susceptibility of PVC formulations to microbial attack is related to the amount and types of plasticizers, fillers, pigments, and stabilizers, etc., added during processing. Many of these additives are organic compounds of relatively low molecular weight. For example, plasticizers (predominantly esters of organic acids, polyesters, and chlorinated hydrocarbons), which are added to increase the flexibility of an otherwise brittle polymer, will in most cases support microbial growth and their degree of susceptibility exercises a profound influence on the propensity of the textile coating...
to biodeterioration; such microbial utilization of the plasticizers may cause the PVC coating to crack during use. With polyurethanes on the other hand the actual polymer is capable of supporting microbial growth, both bacterial and fungal, because of the similarity of some of the chemical linkages in polyurethanes to those found in nature. Some urethanes are moderately to highly hydrophilic, swell and absorb water which can accelerate the growth of organisms both inside the coating or films and on the surface. As a practical measure, therefore, biocides are often added to both plasticized PVC and polyurethanes.

Use of biocides
Antimicrobial treatment for textile materials is necessary to fulfill the following objectives:

1. To avoid cross infection by pathogenic micro-organisms,
2. To control the infestation by microbes,
3. To arrest metabolism in microbes in order to reduce the formation odor, and
4. To safeguard the textile products from staining, discoloration and quality deterioration.

The best method of avoiding microbial deterioration is to use synthetic materials which are inherently resistant to attack and to apply antimicrobial chemicals known as “biocides” which are normally incorporated into the finished textile product. The requirements for an “ideal” biocide include:

1. Effective against a wide range of micro-organisms, particularly bacteria and fungi.
2. Active during the life of the product.
3. Of low mammalian toxicity and non-toxic to humans at the concentrations used.
5. Effective at low concentrations.
6. Inexpensive and easy to apply.
7. Resistant to sunlight and leaching from the fabric.
8. Not affecting fabric handle or strength.
10. Does not sensitize the fabric to damage by light or other influences.

Needless to say, there are commercial biocides available and a thoughtful “compromise” selection of a suitable product is not always easy. Some chemicals, for example organo-mercury, some tin and copper compounds, have fallen out of favor because of their persistent and cumulative toxic effects in the environment. Textile materials which are to be used outdoors require a stable fungicide that is resistant to being washed out by rainwater and to breakdown by light. If the environment is extremely wet, control of algae and bacteria becomes more important. However, many compounds which are effective against fungi are not necessarily good bactericides and vice versa.

Traditionally, biocides in the textile industry include organo-copper compounds, organo-tin compounds, and chlorinated phenols. These act by interfering with the energy-producing processes of microbial cells. Copper naphthenate and copper-8-hydroxyquinolinate are extremely versatile biocides, very effective against fungi, bacteria, and algae. They are applied in particular to protect textiles likely to be exposed to soil and to severe weathering conditions, e.g. cotton and flax canvases, awnings, tarpaulins, cordage, ropes, sacks, tents, military uniforms and military equipment. The main disadvantage is that they impart a yellow-green color to treated materials. Pentachlorophenol esters, typically pentachlorophenyl laurate (LPCP), are resistant to leaching by rainwater and so are used as fungicides for the rot-proofing of a wide range of textiles including cotton, flax, and jute fabrics used as covers, tarpaulins, shop blinds, tents, etc.; also carpet backings, coated fabrics, hospital materials, mattress covers, pressed felts and woolen textiles. Some biocides can serve more than one purpose; thus organo-tin compounds can serve as stabilizers for plastic formulations as well as fungicides.

More recently, silver has become popular and is used in many medical and consumer textile and plastic products. The effectiveness of silver as an antimicrobial relies on
the ability to release silver ions (Ag+) at a steady state when needed to counteract a microbial challenge. This is difficult as silver naturally photo oxidizes and presents a color that is generally not acceptable. Additionally, silver can be prematurely depleted by salts and halogens (chlorine) if not placed into a stabilized format or delivery system.

Despite the long list of prior solutions or partial solutions, silver in a controlled release ionic format has gained acceptance as the “technology of preference”. There are complications however. Silver exists in many forms from elemental to nano, compounds, complexes, colloidal, etc. Metallic silver is marginally useful as it must be presented in an ionic format to become effective and a dosing system or delivery system must be present. Color change or even skin staining can occur with many systems. It is a challenge to develop and select an optimized formulation or blend of formulations. It is even more challenging to optimize the performance vs. price vs. manufacturing complexity curve. Biovation specializes in exactly this.

Here are some of the attributes of a modern silver antimicrobial:

- Silver is recognized as safe and effective by both EPA and FDA when used as an infection-control and odor-control “active”. It is used in many FDA medical devices including dressings.
- Silver is a broad-spectrum biocide as it functions well against gram-negative and gram-positive bacteria plus fungi. Note that fungal performance may require a higher concentration.
- Silver is effective at low levels, often 20-50 ppm of available silver imparts robust end-use performance. The MIC or minimum inhibitory concentration can be in the 1-3 µg/l or ppm range with most bacteria.
- Silver is generally thought to enter the bacterial cell-wall prevent from reproduction, thus preventing the “mildew” smell on wet fibers and the toxins and odors often generated by bacteria. Fungi simply do not thrive in the presence of silver ions.
- Silver, when properly formulated, is durable and is effective for years, generally good for the life of the article.

- When placed in a “controlled release” structure, silver ions are released in response to local conditions and provide a reactive or demand-release situation in which concentration equilibrium is maintained and protection is constant.
- Silver does not degrade into harmful byproducts like some other agents.
- Silver is completely non-toxic to mammals and has not been shown to promote bacterial resistance like antibiotics do.
- Silver is not highly acidic or basic and does not contain salts like some other antimicrobial agents. It is safe for extended skin contact and if eaten is harmless. The hand or feel is not affected.

For a silver technology to be appropriately structured for a target application in textile, the below aspects need to be considered:

- The silver must be delivered in an ionic format for greatest effectiveness. Compounds, salts, complexes, and the many, many formats silver can be found in are far from ideal antimicrobial solutions.
- Silver discolors as it photo oxidizes to the traditional sepia/brown color from old black & white photos, the silver halide color and hence creative solutions need to be employed to negate this effect.
- Silver can be delivered in a nano format and as such, is of great concern from a safety perspective as nano particles can too easily cross cell-walls or bodily protective membrane.
- Silver is non-migratory and remains in-place. It therefore must be utilized effectively.
- Silver can be incorporated into polymers, fibers and films however if not exposed to a surface, can be effectively trapped and wasted, a costly problem.
- Silver readily complexes with sulfur groups and chlorides and rapidly forms insoluble compounds although still technically antimicrobial; so a careful analysis of the end application needs to be considered.
To design an optimized solution, with a good cost/ performance ratio, one must analyze many factors including:

- The end-use, conditions of use and the performance objectives.
- The manufacturing process and how it can be adapted or modified, if required.
- Claims language as allowed by regulatory constrains.
- Advertizing and documentation within regulatory boundaries.
- EPA and/or FDA oversight and compliance issues.

Each application is studied to ascertain the requirements and options. Important solution design parameters that Biovation employs are:

- Optimizing a formulation that is low-cost yet performs well.
- Deploying silver technology that is delivered from an ionic-release system.
- A unique optically clear formulation has been selected to prevent a color shift.
- Additional features can be added and generally include:
  - Enhanced Fungal performance.
  - Oxidizer functionality.
  - Odor scavenging technology (although the effective life of these systems is limited).
- The concentration determines the speed of kill with versions ranging from consumer odor control to FDA medical-grade pathogen control.

Mechanism of anti-microbial activity

Negative effect on the vitality of the microorganisms is generally referred to as antimicrobial. The degree of activity is differentiated by the term “cidal” which indicates significant destruction of microbes and the term “static” represents inhibition of microbial growth without much destruction.

The activity which affects the bacteria is known as antibacterial and that of fungi is antymycotic. The antimicrobial substances function in different ways. In the conventional leaching type of finish, the species diffuse and poison the microbes to kill. This type of finish shows poor durability and may cause health problems. The non-leaching type or bio-static finish shows good durability and may not provoke any health problems. A large number of textiles with antimicrobial finish function by diffusion type. The rate of diffusion has a direct effect on the effectiveness of the finish. For example, in the ion exchange process, the release of the active substances is at a slower rate compared to direct diffusion ad hence, has a weaker effect. Similarly, in the case of antimicrobial modifications where the active substances are not released from the fiber surface and hence rendering them less effective. They are active only when they come in contact with microorganisms. These so called new technologies have been developed by considering the medical, toxicological and ecological principles.

The antimicrobial textiles can be classified into two categories, namely, passive and active based on their activity against microorganisms. Passive materials do not contain any active substances but their surface structure (Lotus effect) produces negative effect on the living conditions of microorganisms (anti-adhesive effect). Materials containing active antimicrobial substances act upon either in or on the cell[4].

Application of biocides

Application of biocides to textile fabrics for rot-and mildew-proofing is usually carried out as a final finishing process. The fabric is impregnated with either a solvent solution or, more usually, an emulsion of the biocide; it is then pad roll extracted and dried using a tenter frame, or other suitable equipment. The fabric may be scoured first but more usually, and especially with heavyweight materials, the biocides are applied to greige goods material without scouring. Often they are co-applied with water-repellents, fire-retardants, and pigments. In vinyl polymers such as PVC the biocide is normally dispersed in the plasticizer which is usually the most biodegradable component. As the surface film is removed, fresh

plasticizer will migrate to the surface, carrying with it a constant source of biocide. It is important to note that some products can lose their protective qualities through weathering even though 70%-80% of the biocide remains chemically unchanged in the formulation. One possible reason for this is that, under the effects of heat and ultraviolet radiation, depolymerization of the vinyl resin and subsequent cross-linkage may encapsulate the biocide, preventing its migration to the surface where biodeterioration takes place.

Various other methods, depending on the particular active agent and fiber type, have been developed or are under development to confer antimicrobial activity to textiles.

- For synthetic fibers, the antimicrobial active agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their formation. Such processing provides the best durability as the active agent is physically embedded in the structure of the fiber and released slowly during use.
- The conventional exhaust and pad-dry-cure processes have been used for antimicrobial finishing on natural as well as synthetic fibers for some biocides.
- Padding, spraying and foam finishing have been used for the silicone-based quaternary agents.
- Many other methods have been reported, such as the use of nanosized colloidal solutions, nanoscale shell-core particles, chemical modification of the biocide for covalent bond formation with the fiber, crosslinking of the active agent onto the fiber using a crosslinker and polymerization grafting. When considering "nano" particles, one should consider there is some scientific concern about nano-metals and the possibility of these small particles to travel thru cell membranes and lodge in areas of the body (organs and the brain) where they are not desired. There is active research in this area to determine in this is a valid reason to be concerned.

The net desire is to implement a clear, flexible and durable surface coating on each textile fiber. Coatings developed by Biovation emit a low-level of silver ions to maintain equilibrium on the fiber surface. There is a deep reservoir of silver-ions for years of protection. Biocides are also used to provide hygienic finishes for fabrics that are used in health-care products. These finishes are classified as either renewable or durable, although even durable finishes are removed gradually during laundering. Renewable finishes can be replaced during laundering, for example using quaternary ammonium compounds although this is strictly for a commercial laundry and is not common. N-Halamines can also be utilized to provide bonding sites for halogens, generally chlorine. N-Halamine chemistry is not particularly durable however, when fabrics are washed, in the presence of bleach (chlorine) they can effectively be recharged and brought back to full-power.

Within the healthcare industry, nonwoven fabrics have taken a dominant position in drapes, owns and protective-apparel in general. It has generally been assumed that modern high-performance antimicrobials that are safe and fast would be too expensive to incorporate into the polymers or applied via a finish. In the next few years we may see the start of very cost-effective and robust antimicrobials that effectively provide infection-control to medical nonwoven fabrics.

It is important to note that the biocides are also effective against micro-organism that cause odor and hence, their action acts as a deterrent against release of foul odors from textiles. Antimicrobial treatments control the growth of odor-causing bacteria arising in everyday use of apparel & home textiles. Normally these bacteria would generate unpleasant odor molecules, but by controlling their growth, treatments suitable chemicals, prevents the formation of these odors and keeps fabrics fresher longer. More specifically, these chemicals are applied at the manufacturing level and binds onto fabric. Once the bacteria are dead they can no longer produce smelly waste metabolites, and fabrics maintain their freshness.

\[\text{Ibid, Hamlyn.}\]
Biovation Expertise

Biovation is chemical technology agnostic; meaning, Biovation does not limit itself to any particular set of antimicrobial platforms available in the commercial market. Rather, based on decades of research and development of formulations, it compounds and formulates customized and unique solutions for targeted specific applications. Hence, as part of chemical platforms available to Biovation, we can consider metals (for example, there are commercially available silver releasing powders that have obtained FDA and EPA approvals), metal compounds, surface active agents, surfactants, quaternary ammonium compounds, organic acids, inorganic acids, biopolymers, antioxidants, oxygen scavengers, carbon dioxide emitters and others provided in any combination and concentration. The combination and concentration of the various elements depends on the several factors such as the specific textile type, type of targeted end-use, the nature of the microbes to be controlled and hindered and other synergistic affects with the conditions present in the application environment.

Contact Us

Biovation’s expertise is in infection control formulations and we look forward to partnering up with you. We invite you to contact us solutions@biovation.com to discuss how Biovation can help you with our portfolio of technologies and solutions.

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