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Additives in Fibers and Fabrics

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The additives and contaminants which occur in textile fibers vary widely, depending on the type of fiber and the pretreatment which it has received. Synthetic fibers such as nylon and polyester contain trace amounts of contaminants such as catalysts and catalyst deactivators which remain after the synthesis of the basic polymers. In addition, there are frequently a number of materials which are added to perform specific functions in almost all man-made fibers. Examples of these would include traces of metals or metal salts used as tracers for identification of specific lots of fiber, TiO_2 or similar materials added as delustrants, and a host of organic species added for such special purposes as antistatic agents or flame retardants. There may also be considerable quantities of residual monomer or small oligomers dissolved in the polymer matrix.

The situation becomes even more complex after the fibers are converted into fabric form. Numerous materials are applied at various stages of fabric preparation to act as lubricants, sizing agents, antistats, bleaches, and wetting agents to facilitate the processing, but these are normally removed before the fabric reaches the cutters or the ultimate consumers and therefore usually do not constitute potential hazards. However, there are many other chemical agents which are frequently added during the later stages of fabric preparation and which are not designed to be removed.

Aside from dyes and printing pigments, the most common additive for apparel fabrics is a durable press treatment. This generally involves the use of materials capable of crosslinking cellulosics by reacting through such functions as *N*-methylolated amides or related compounds such as ureas and carbamates. These materials pose some potential hazards due to both the nitrogenous bases and the formaldehyde which they usually release. There is usually also some residual catalyst in fabrics which have received such treatments.

Other types of chemical treatments which are often applied to fabrics to achieve special effects include flame retardants, soil release agents, antistatic agents, softeners, water and/or oil repellents, ultraviolet absorbers, bacteriostats, and fungistats.

All fibers, natural and synthetic, contain a variety of nonfibrous materials in their native state, but the vast majority of these are either removed prior to conversion into consumer articles or present in such small quantities that they are of little significance. Once the fibers are converted into fabric however, the situation becomes much different. Fairly large quantities of chemicals are frequently added to fabrics to produce a variety of special effects for the consumer.

Additives and Contaminants in Fibers

Commercial textile fibers include both natural fibers and those which are man-made. In the latter case, the polymer substrate may be either a natural polymer or a synthetic one. The nature and amount of contaminants and additives which are usually encountered in these fibers varies greatly from one system to the other. Consider first the natural fibers—cotton, wool, and silk. Cotton is primarily cellulose, although the surface contains small amounts of waxes, pectins, hemicelluloses, and other related materials; these are frequently removed during processing of the fiber and seldom pose any problem for either the processor or the consumer. In addition, small amounts of metal salts normally contaminate cotton fibers. These salts are usually compounds such as ferric chloride, which are also quite innocuous. There is, however, the possibility that some toxic chemical residues may occur on cotton fibers. Since cot-

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ton is vulnerable to attack by a number of insects, pesticides are frequently applied, and in most cases these do not cause significant problems because pesticides are generally applied before the cotton bolls open; thus the chemicals rarely reach the fibers. Chemical defolients, however, are routinely applied after the cotton bolls have matured and opened, and it is fairly common to find reasonably large amounts of these materials on fibers which have been processed through the ginning stage. In one recent study (*1*), arsenic, presumably in the form of arsenic acid, was reported to be present in concentrations as high as 500 ppm. Such concentrations will produce dermatitis and other toxic reactions in persons exposed to the contaminated fibers. This material, however, is generally removed during processing, so that it poses more of a hazard to workers in contact with raw fibers than it does to the ultimate consumer. Some attempts are being made to persuade cotton farmers to use other types of defolients, such as quaternary ammonium salts, but large amounts of the arsenic compounds are still being used.

Wool and silk, both protein fibers, pose less of a problem for both workers and consumers. Wool, which is primarily keratin, is contaminated by lanolin and other animal fats and oils in the raw form. The fibers also generally contain significant quantities of organic salts. These, however, are all of animal origin and are generally quite innocuous. In all areas they are removed prior to processing into fabrics. A similar situation exists with silk. This fiber, which is primarily fibroin, is coated with another protein, sericin, as a binder for the silk filaments. This is also removed prior to processing into yarn or fabric. There are cases, however, in which silk is artificially weighted by the addition of metal oxides; tin is a very common contaminator in processed silk goods.

Man-made fibers offer a different set of problems from those of the natural fibers. Since the fibers are actually formed in the manufacturing process, there is a much greater opportunity for the addition of chemical additives. These, however, are generally buried within the fiber structure and in most cases are not available to contact either workers in the processing industry or consumers. In such fibers, small traces of metal salts and oxides are almost always present as tracers. These are materials which can be easily identified by techniques such as x-ray fluorescence and thus allow fiber manufacturers to tag their fibers so that they can be distinguished from similar fibers from other producers. In addition, most man-made fibers contain titanium dioxide or some other metal oxide as a delustrant. In some cases there may also be additives for special purposes such as static reduction, increased lubricity or modification of flammability characteristics. In addition, those fibers based on synthetic polymers may also have as contaminants a variety of chemicals and reagent residues from the polymer synthesis process.

Condensation polymers such as nylon 6, nylon 66, and polyester are melt-spun at high temperatures and thus must be fairly free from large quantities of unwanted contaminants. There will, however, be traces of catalyst systems present in the polyesters. The polyester synthesis is a two-step process in which both steps require separate catalysts: the first catalyst must be deactivated by the addition of a phosphorus compound or other similar materials and then a second catalyst added. Thus, two catalysts and a deactivator are always present in the final polymer. In addition, the process is such that small amounts of cyclic dimers and trimers are generally produced. These materials are small enough to migrate from site to site within the fiber and at times may be extractable from the fiber.

Unlike the polyesters, nylons are usually catalyst-free because of their method of preparation. Nylon 6 may contain considerable quantities of caprolactam, the monomer from which it is prepared; both systems may also have small amounts of cyclic oligomers.

Both nylon and polyesters may be modified for a variety of special purposes. Comonomers such as 5-sulfoisophthalic acid may be included in the polymer backbone in order to produce special dyeing characteristics. Also, since both of these materials are essentially hydrophobic, static can be a considerable problem both in production and to the ultimate consumer. For this reason, antistatic agents (antistats) are frequently added. These are usually amine derivatives or polyethers. In the case of polyester there is also the possibility that some phosphorus and/or bromine compounds may be added as flame retardants. At present no flame retardant systems are available for the nylons.

Addition polymers such as the polyolefins, acrylics, modacrylics, and specialty fibers made from copolymers of acrylonitrile, vinyl chloride, and/or vinylidene chloride are usually somewhat cleaner. These systems are generally prepared in such a manner that little or no catalyst residue is present. The polymers are usually solution-spun without the necessity for the high temperatures of melt spinning. This reduces the number of contaminants arising from degradation and/or side reactions of the polymer. There are cases in which these materials are modified for better dyeing and for such purposes as modification of the polymers or flammability. In most of these, modification relies on the utilization of halogen compounds as vapor phase inhibitors. If the material does not contain halogen in the backbone of the polymer, organohalogen compounds are frequently added. Antimony oxide is also frequently added as synergists to the flame retardant systems in order to promote the activity of the halogen.

Man-made fibers based on natural polymers pose quite a different set of problems. Although numerous fibers of this type have been tried in the past, only those based on cellulose or cellulose acetate are currently commercial. Rayon, the most common of these fibers, is primarily pure regenerated cellulose. All rayon manufactured in this country is now prepared by the viscose process. In this process crude wood pulp in the form of heavy paper is soaked in a solution of sodium hydroxide to remove residual lignin and to convert portions of the cellulose into sodium cellulosate. After allowing the sodium cellulosate to undergo controlled oxidative degradation, carbon disulfide is added to convert the material to cellulose xanthate. The xanthate is then dissolved in aqueous sodium hydroxide, allowed to stand, and then spun into an aqueous solution containing zinc sulfide, sulfuric acid, and a variety of other constitutents. Thus, rayon is usually contaminated with small amounts of zinc salts as well as other metallic species. As in the case of the fibers based on synthetic polymers, a variety of special purpose additives may also be included in the fiber structure. Flame retardants generally are of the substituted phosphazene type; basic dyeing capability may be imparted to the rayon by inclusion of polyvinylpyridine, polyvinylpyrrolidone, or other basic polymers. There are also modifications of the rayon structure including polymeric acid systems such as poly(acrylic acid) for increased absorbancy.

The cellulose acetates, both primary and secondary, are generally somewhat cleaner. They are spun from halogenated organic solvents into warm air and are precipitated by evaporation of the solvent. For this reason, they are generally not contaminated by any type of spin additive. They may have special purpose chemicals such as flame retardants added to meet special consumer demands. Flame retardants for the acetates are generally those related to tris(dibromopropyl) phosphate.

Additives and Chemical Treatments for Textile Fabrics

Textile fabrics in the greige state, prior to dyeing and finishing, generally contain significant amounts of special chemicals added to aid mechanical processing of the fibers. In many cases hydrophobic fibers must be treated with antistatic agents in order to facilitate the conversion of the fibers into yarn. In most cases, lubricants must also be added. These are usually added as topical treatments which are later removed by washing. If the yarns are to be woven rather than knitted, warp yarns must usually also be stiffened by the addition of some type of sizing material. For the cellulosics and related hydrophylic fibers this sizing is generally starch or some starch derivative; for the hydrophobic fibers the sizing is generally poly(vinyl alcohol) or some related polymer system.

Once the mechanical process of fabricating the textile structure is completed, the fabrics are subjected to a series of wet processing steps to prepare them for conversion into consumer items. The first step in this wet processing almost always involves the desizing, scouring, and bleaching to remove colored materials as well as the natural contaminants and added antistats, lubricants, and sizes. This process frequently also enhances the absorbancy of the fabrics to aid in dyeing, printing, and chemical finishing.

Following the clean-up operation, most fabrics are subjected to either dyeing or printing processes. In both operations the quantity of material applied to the fabric is usually quite small and normally presents no hazard to either workers or consumers. The dyes are

organic compounds which are usually added with a combination of salts, accelerators and wetting agents. In some cases silicone antifoam agents may also be necessary to facilitate processing. Certain classes of dyes require additional chemical auxiliaries, e.g., vat dyes require chemical reduction prior to application to the fabric, mordant dyes and related premetallized dyes contain significant quantities of chromium or other heavy metals. Perhaps the most significant auxiliary from an environmental standpoint is the carrier, which is necessary for the dyeing of most polyester fabrics by dispersed dyes. These carriers are frequently aromatic hydrocarbons or halogenated aromatic hydrocarbons. In some cases, the material remains in the fiber after dyeing and process washing, and in such cases it is entirely likely that small amounts of the carrier may come in contact with the ultimate consumers.

The situation with printed fabrics is quite similar, except that printing is a surface treatment and therefore requires chemical binders to retain it on the surface. It generally does not require the addition of chemicals such as wetting agents and accelerators. Since the printing process is not carried out in solution, antifoam agents are not used.

A much more significant potential hazard is encountered in chemical finishing. In these operations large amounts of compounds are frequently added to the fabric, e.g., durable-press characteristics are imparted to cotton and cotton/polyester blends by treatment with a variety of nitrogen-containing resins: urea/formaldehyde (UF), dimethylol ethyleneurea (DMEU), dimethylol dihydroxyethyleneurea (DMDHEU), dimethylol alkyl carbamates, dimethylol propyleneurea (TMU) methylolated triazones, methylolated melamines (TMM), or methylolated urones. It is not infrequent for these materials to be present in quantities approaching 15–20% the weight of the finished fabric. Although these materials are polymerized on the fabric and therefore relatively inaccessible to skin, they are somewhat labile toward hydrolysis. The hydrolysis products from the resins may be species such as ammonia and formaldehyde which can diffuse out of the fibers and contact the skin or be liberated into the air. In some cases these problems can be so severe that areas where large quantities of fabric are stored become almost uninhabitable.

A somewhat similar situation exists with fabrics which have been treated for flame resistance. In some cases the chemical flame retardants are added along with nitrogenous resins similar to those used for durable press. In other cases the flame retardants are of a type that can undergo self-condensation and polymerization on the fabric. In almost all cases the retardants contain phosphorus in the form of phosphonate esters or phosphine derivatives. Such structures usually have biological or toxicological activity.

Although the durable-press treatments are the most common, a wide variety of other chemical finishes may be encountered by the consumer. Fabrics which are hydrophobic, either because of the nature of the fiber or because they have been treated with durable press resins, frequently require the addition of chemical agents to aid in soil release during laundering. Although a variety of soil release chemicals are currently available, they all can be classified as hydrophilic polymers. They are deposited and bound to the surface of the fabric in order to provide easier wetting of soil particles during cleaning. These materials, which are usually polymeric carboxylic acids, fatty acid amides or quaternary ammonium salts, are generally quite innocuous physiologically.

In a different approach to the problem of soiling and soil release, some fabrics may be treated with fluorocarbons or other materials to make them repel water and/or oil. In addition to fluorocarbons, water repellents may be compounded from a variety of fatty acid derivatives. Most commonly, metal salts of the fatty acids are encountered.

Summary and Conclusions

In summary, it can be assumed that all fibers and fabrics contain measurable amounts of contaminants and additives. Natural fibers contain primarily contaminants of biological origin unless they have been treated with species such as arsenic for defoliation purposes. Man-made fibers, whether based on natural or synthetic polymers may contain a wide variety of heavy metals, titanium dioxide, antistatic agents and flame retardants, and residues from polymerization and spinning processes. In all cases, however, the level of contamination of the fibers is usually quite low.

Textile fabrics may contain much larger quantities of added chemical material. Particular offenders may be those treated for durable-press characteristics. In these materials, large quantities of nitrogenous resins are used to stabilize cellulose and cellulose blend fabrics. Significant levels of added chemicals may also be encountered in fabrics treated for flame resistance, soil release, oil and water repellency, or a variety of special purposes.

REFERENCE

1. Perkins, H. H., Jr. Quick check for arsenic on cotton. Textile Inds. 132: 151 (1968).