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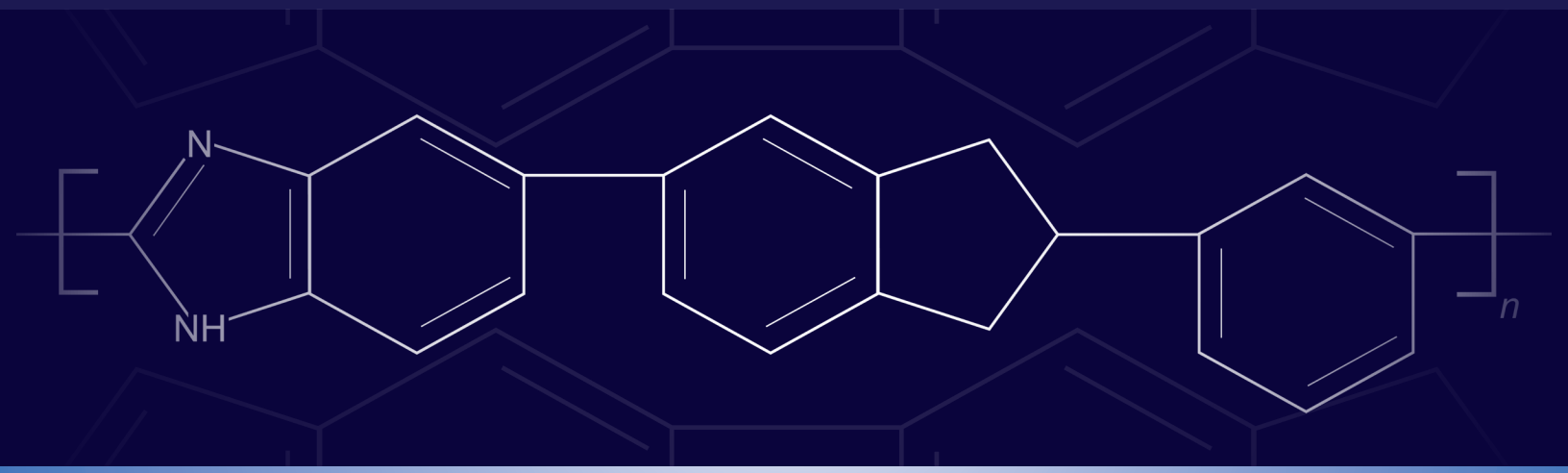
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Chemical Protective Clothing

3rd edition



A comprehensive overview of the considerations necessary for the implementation of a successful protective clothing and equipment program.

Edited by
Derek A. Newcomer, DrPH, CIH, CHMM, CSP, REHS
Robert N. Phalen, PhD, CIH, CSP, FAIHA®

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Chemical Protective Clothing

3rd edition

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Robert N. Phalen, PhD, CIH, CSP, FAIHA®



Published by AIHA®

Falls Church, VA

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Stock Number: SPCM25-618
ISBN: 978-1-950286-70-6

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Acknowledgments

The AIHA® Protective Clothing and Equipment Technical Committee is grateful to the many people who were involved with the production of this third edition.

First, special thanks go to the authors for volunteering their valuable time and expertise. They have done an outstanding job in creating a detailed and informative resource for OEHS professionals. Thanks also go to the committee members and members of the OEHS community who supported the project and reviewed the technical content.

The editors also acknowledge the following reviewers for providing their expertise: John Baker, MS, MBA, CIH, FAIHA of Baker EHS Solutions for his technical review of Chapter 11 and Mark Saner, FR Technical Expert at Bulwark Protection for this technical review of Chapter 12. Their insights were helpful in ensuring that the complexities of the subject accurately reflect current technology and research.

Additionally, Lisa Lyubomirsky, AIHA Senior Publications Editor, kept this project on track as project manager and provided cohesiveness and polish to this multi-authored publication as copy editor.

Finally, special thanks go to the editors and authors of the first and second editions. Their early contributions provided a solid foundation for this updated publication that addresses the evolving changes in chemical protective clothing.

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Preface

The history of protective clothing and improvements in material technology and construction methods is well documented. From the early use of animal hides to the use of natural materials and the increasing number of synthetic materials available today, all protective clothing provides some level of protection. Matching the proper protective clothing to the hazard to take advantage of the protection offered is the goal for proper and effective use. The concept of using protective clothing as the "last line of defense" implemented when engineering and administrative controls are not feasible, or as an additional level of protection, continues to be the ideal standard of use. In jobs where personal protective clothing and equipment are the only available control option, the purpose of the clothing and equipment is to shield or isolate individuals from chemical, physical, and biological hazards.

Exposure concerns have expanded throughout the years. In the 1970s and 1980s, emphasis was placed on reducing exposure to carcinogenic materials. In the 1980s and 1990s, considerations for the prevention of exposure to bloodborne pathogens and the spread of diseases through contact with bodily fluids were added. In the 2000s, the increasing prevalence of nanoparticles in the work environment has raised numerous questions about the potential impact on worker health and the methods needed to control those exposures. The perception, significance, and use of protective clothing continues to evolve. The introduction of terrorism, along with chemical and biological threats to standard business risks, has elevated the significance of planning for non-standard conditions, where protective clothing and equipment play a key role in preventing exposures. The ever-changing work environment in chemical, pharmaceutical, and other high-tech industries often limits or prevents the effective implementation of engineering controls. As a result, the number of workers that rely on protective clothing to reduce their exposures has increased.

Standards, Test Methods, and Performance Data

An increasing number of standards and practices emphasize the need for protective clothing to be part of an overall safety and health plan. OSHA's requirement to complete and revise personal protective equipment (PPE) assessments for all workplace hazards remains a significant challenge for many companies and workplaces. Even after hazard assessments are completed, the selection of appropriate protective clothing is complicated by the variety of available materials and models. Performance data for protective clothing has become widely available, but guidelines for the use and interpretation of the data continue to be developed. Test methods were developed to provide a basis for evaluating clothing and material effectiveness for protection against a specific hazard. Although methods are designed to allow comparisons between the relative performances of various products, the influence of other factors, such as size and fit, must be incorporated into the selection process. Without adequate interpretation guidelines, the selection process can be confusing for many safety and health professionals, particularly when the test method does not simulate the conditions of the actual exposure.

Product Development and the End User

The development of new clothing materials and sophisticated advances in polymer technology and laminate methods have broadened the capabilities of available products. At the same time, there are additional variables to consider, which make selection more difficult.

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In addition to the development of new materials, the focus has shifted to the factors that affect the end user. Protective clothing must not only be effective but also practical for use in the workplace. Improvements in manufacturing have increased the selection of garment sizes and models. As more attention is focused on understanding ergonomic issues, heat stress implications, and the relationship between the task and the clothing, improved fit and comfort will be necessary to help ensure proper and consistent use at all times. New materials, garments, and standards and test methods will need to be developed in a manner that will encourage the end user to wear the protective clothing as intended. Easy methods of identification, such as color-coding, will need to be incorporated to simplify the selection process. The development of field-based end-of-service indicators will help improve the usefulness and protection afforded by the clothing and minimize risks associated with the reuse of previously exposed clothing materials.

Risk Analysis

The combination of suits and other clothing and protective equipment, including respiratory protection, form ensembles for true full-body protective clothing. The increased reliance on protective clothing in emergency and disaster situations increases the need to determine the effective protection offered by the collective ensemble. As information about combinations of protective clothing components are developed, questions about the "overprotection" of workers emerge. The realization of chemical and biological threats has shifted the emphasis onto preplanning so that quick and timely selection decisions can be made. Risk-based decisions about the appropriate level of protection may result in accepting some level of exposure.

With occupational skin disease being recognized as one of the leading work-related illnesses, the interest in preventing dermal exposures has risen considerably. Dermal contact with hazardous materials can contribute significantly to a worker's overall exposure. Therefore, knowledge of basic information about the skin and the impact of protective clothing on the behavior of the skin as a protective mechanism is essential to ensure proper selection of protective clothing materials. As future considerations are made regarding protective clothing, the issue of dermal exposures will need to be readdressed. It will be necessary to develop more sophisticated quantitative evaluation techniques that are more field-adaptable than those that currently exist. In addition, simple indicators of acceptable dermal exposures will need to be developed. Overall, this will mean an increased emphasis on examining multiple exposure routes, including the sources of dermal exposures from surface contamination as well as those from direct contact. Eventually, this may necessitate developing dermal exposure limits and broadening the available biological exposure indices.

As information about the selection, use, and evaluation of protective clothing and equipment continue to evolve, the development of a comprehensive program covering these aspects of protective clothing can enhance the level of protection afforded to the workers.

An understanding of the performance data in conjunction with the integration of risk assessment into the selection process can lead to better selections and, therefore, better protection for workers who rely on protective clothing to minimize or prevent exposure.

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Introduction

Chemical Protective Clothing, 3rd edition: The Book

This updated book provides a comprehensive overview of the considerations necessary for the implementation of a successful protective clothing and equipment program. The content is organized into three areas: Background, Fundamentals, and Theory; Manufacture, Design, and Testing; and Considerations for Proper Selection and Comprehensive Program Development. In addition, a new chapter on Flame-Retardant Chemical Protective Clothing has been added to highlight the emerging issues and advancements in this crucial field of protective clothing. Throughout the book, the discussion focuses primarily on the prevention or reduction of chemical exposures, but often, the information can be applied more broadly to reduce exposures to biological and physical hazards.

Background, Fundamentals, and Theory (Chapters 1–3)

As an introduction to protective clothing, the first chapters address the effects of chemical exposures on the skin, the theory behind the protective mechanisms of the clothing, and the interaction between the performance of protective clothing and the skin. The basics of polymer chemistry related to the manufacture of different protective clothing materials are presented. A review of permeation theory helps to explain the differences in protection levels and sets the stage for later discussion of the interpretation of testing data.

Manufacture, Design, and Testing (Chapters 4–6)

The second segment of this book covers the different types of available protective clothing and the basics of the manufacturing processes. Differences in performance that are results from the manufacturing methods and styles are discussed. A thorough review of the applicable test methods and standards and a discussion of the test data and interpretation are provided.

Considerations for Proper Selection and Program Development (Chapters 7–12)

This segment of the book comprises recommendations for developing an appropriate risk-based selection strategy and additional considerations related to the proper use and handling of protective clothing. Issues related to the proper decontamination of protective clothing and the prevention of heat-related illnesses are all discussed. Guidelines for selecting the appropriate protective clothing to control nanoparticle exposures are discussed in detail. This section also includes a chapter that covers the development of a comprehensive protective clothing and equipment program.

An updated chapter on Considerations for Selection of Personal Protective Equipment to Protect Against Engineered Nanomaterial Dermal Exposure provides an overview of the different types of engineered nanomaterials, how they are formed in workplaces, and the important factors to consider when selecting protective clothing. Various test methods for determining particle penetration through protective clothing are provided, along with guidelines and regulations to help OEHS professionals select appropriate PPE.

A new chapter on Flame-Retardant Chemical Protective Clothing has been added to highlight the emerging issues and advancements in this crucial field of protective clothing. This specialized clothing is used by military personnel, firefighters, first responders, oil-field workers, and those in various industrial sectors to shield users from flames, hazardous chemicals, splashes, electric arcs, and molten materials.

Without the inclusion of all the elements of an effective protective clothing program, the exposure risk to workers increases. The proper selection, use, and maintenance of protective clothing help to ensure that the expected and actual protection levels are the same.

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Chemical Protective Clothing and the Skin: Practical Considerations

1

By Robert N. Phalen, PhD, CIH, CSP, FAIHA®

Many occupational safety and health professionals consider chemical protective clothing (CPC) the "last line of defense" for protecting the skin from chemical and physical hazards. In several respects, CPC is justly regarded this way. First, it is physically very close to the skin. Because of CPC's intimate contact with the skin, its purpose is to form a physical barrier that separates the skin from the outside environment. Second, CPC provides an additional level of protection if other control measures fail to provide adequate protection against hazards (e.g., splash guards or ventilation).

Aside from this rather obvious physical description of its proximity to the skin, CPC as a last line of defense can also be considered from a pragmatic viewpoint. In industrial hygiene practice, there is a hierarchy of controls (Figure 1.1) that has evolved from the effectiveness, reliability, user comfort, and operating costs of each intervention. Generally, personal protective equipment (PPE) is considered a last resort for protecting workers, to be issued only when all other options for control are considered inadequate (refer to https://www.osha.gov/sites/default/files/Hierarchy_of_Controls_02.01.23_form_508_2.pdf). This is accepted as true for inhalation hazards, where respirator use has practical limitations. However, with regard to protecting the skin, CPC is often considered first without giving much consideration to possible alternative approaches. Using CPC should not be preferred over other options because there may be adverse consequences and costs associated with this choice. The hierarchy of controls does not infer that choosing only a single control strategy is recommended. Adequate worker protection may require a combination of controls, including CPC as that last line of defense. This chapter will provide some basic information about the skin and focus on the direct consequences of wearing CPC on the skin and the effectiveness of exposure reduction.

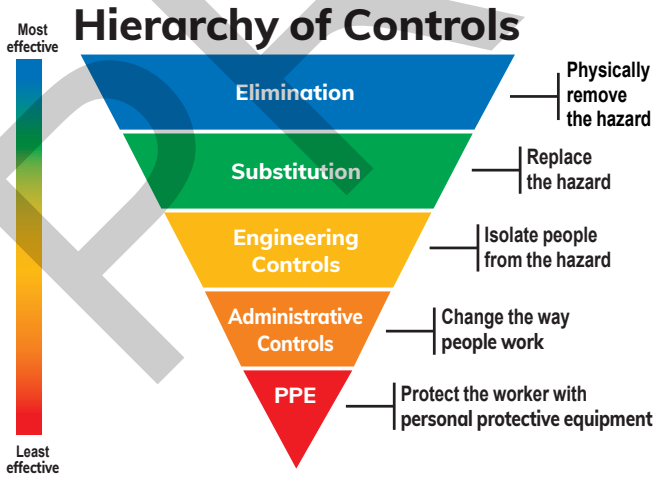


Figure 1.1: The hierarchy of controls from least effective to most effective. [Source: National Institute for Occupational Safety and Health (NIOSH). In public domain].

Skin Anatomy and Physiology

The skin is the largest organ of the body, constituting 10–15% of the normal body weight, with a surface area of approximately 1.8 m^2. After more than a century of scientific study, much is now known about the seemingly amazingly effective function of the skin as a barrier to the outside environment and its ability to help maintain homeostasis within. However, research is still intensely attempting to understand all the physicochemical aspects of the skin. This is especially the case among cosmetic and pharmaceutical industries, which venture to profit from improving the skin's condition and delivering drugs through the skin, respectively.

There are several excellent, comprehensive books available that should be referred to if more information is needed on skin anatomy and function (Freinkel and Woodley, 2001; Harris, 2000; Lodén and Maibach, 2006; Phalen and Maibach, 2023; Swen et al., 2020; Wilhelm et al., 2013). The purpose of this chapter is to provide a basic broad background about the skin as it relates to occupational exposures. More specifically, this overview will provide readers who are involved with CPC use with information relevant to the impact of wearing CPC on the skin. The proximity of CPC to the skin (especially for gloves) and its potential health importance make this discussion essential.

For review, the skin constitutes three structurally and functionally distinct important regions: the stratum corneum (outer layer), the viable epidermis (second layer), and the dermis (the thicker layer, which includes hair follicles, sebaceous "sweat" glands, tactile corpuscles, nerve fibers, etc.). The stratum corneum (Latin for "horny layer") is the uppermost and thinnest layer of flattened squamous cells exposed to the outside world (Figure 1.2). It is composed of flattened denucleated cells called corneocytes, which contain mainly highly cross-linked fibrous keratin proteins. Keratin is a waxy, lipophilic material that is insoluble in

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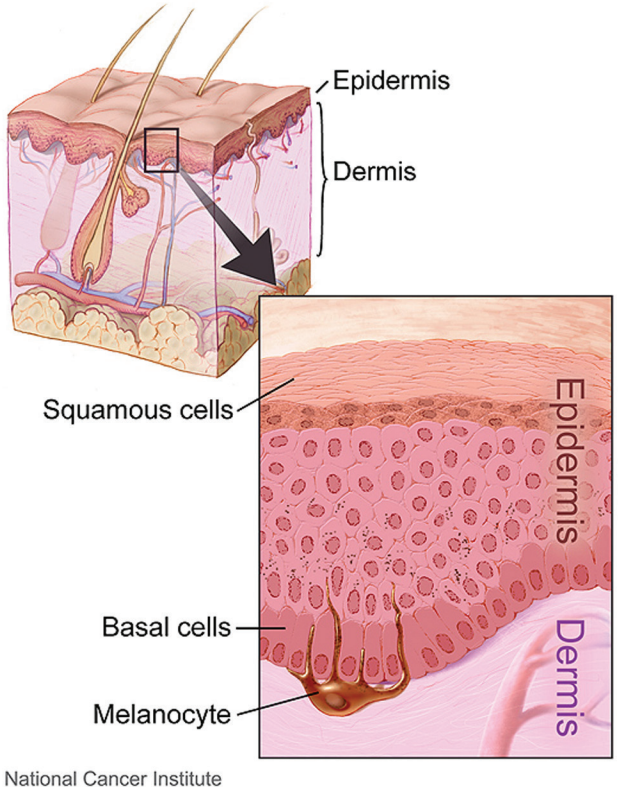


Figure 1.2: Illustration of the skin anatomy and layers, including the outer squamous cells of the epidermis, basal cell layer, and dermis. The melanocytes produce melanin, a brown pigment associated with skin color. [Source: Layers of the Skin. Illustrated by Don Bliss, 2005. National Cancer Institute. In public domain].

water, but its complex protein structure does interact with water, which is necessary for it to remain flexible. If dried from contact with organic solvents and/or low amounts of associated water, the stratum corneum can become brittle and crack (Blank, 1953). The corneocytes are non-respiring cells that are tightly connected, forming a surprisingly rugged membrane. Each corneocyte is typically 25–40 µm (micrometers) in diameter and only 0.2–0.5 µm thick. These are randomly stacked some 15–25 layers thick over most human skin surfaces, which have an approximate total thickness of about 15 µm (Flynn and Steward, 1988). This varies somewhat by anatomical location, being thickest on the palmar skin and soles of the feet with a thickness of 400–600 µm. Figure 1.3 is a histological cross-section of the outer skin showing the epidermis and dermis.

The intercellular space between the corneocytes has a diameter of between 0.01 and 0.1 µm and has been estimated to occupy approximately 20% of the total stratum corneum volume (Elias and Friend, 1975; Elias et al., 1983; Jackson and Elias, 1993). Within this space are well-organized lipophilic and hydrophilic domains that represent parallel channels (lamellar bilayers) of least resistance to diffusion of either nonpolar (lipophilic) or polar (hydrophilic) compounds, respectively (Elias et al., 1977; Forslind, 1994; Swartzendruber et al., 1989).

These structured layers in turn occupy a space of only 0.5–1.0 µm (Hou et al., 1991). These domains constitute an

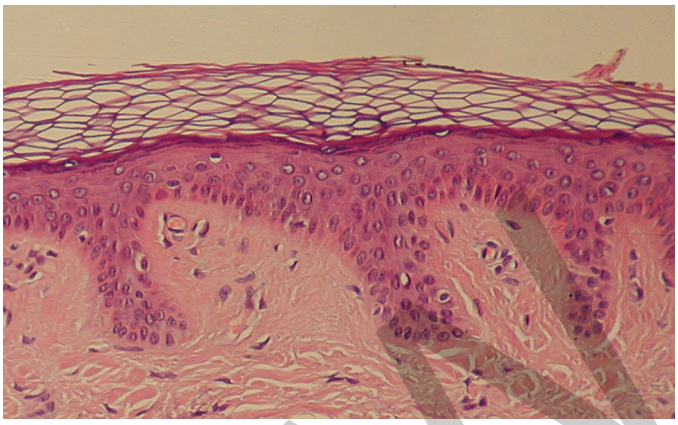


Figure 1.3: Histological cross-section (10× magnification) of the outer skin showing the epidermis and dermis. [Source: Kilbad, 2008. Wikimedia Commons (https://en.m.wikipedia.org/wiki/File:Normal_Epidermis_and_Dermis_with_Intradermal_Nevus_10x.JPG). In public domain].

important, tortuous pathway for molecular transport through the stratum corneum. This phenomenon is later discussed and illustrated in Figures 1.4 and 1.5. Normally the intercellular fluid is predominantly lipid, consisting mainly of lipid classes called ceramides (~45%), cholesterol (~25%), and free fatty acids (~15%), which spontaneously form multilayer bilayers (Yardley, 1991). Lipids comprise approximately 8% of the total stratum corneum dry weight (Gray and Yardley, 1975). It has been found that long-chain ceramides covalently bind to the surface proteins on the corneocytes, acting as anchors to which the other lipids adhere and also participate in intercellular adhesion (Wertz et al., 1989).

Because the normal intercellular space consists predominantly of lipids, chemical solubility and diffusion of lipophilic (fat-soluble) compounds through the skin occur more readily than for hydrophilic (water-soluble) compounds. This will be discussed in more detail in the following passages.

A simplified schematic of the stratum corneum construction with its dense corneocytes and intercellular fluid was first referred to as a brick-and-mortar model by Michaels et al. in 1975 and is depicted in Figure 1.4. We know at present that the skin barrier is probably far more complicated than was previously understood due to the organization of the intercellular lipids (Forslind, 1994).

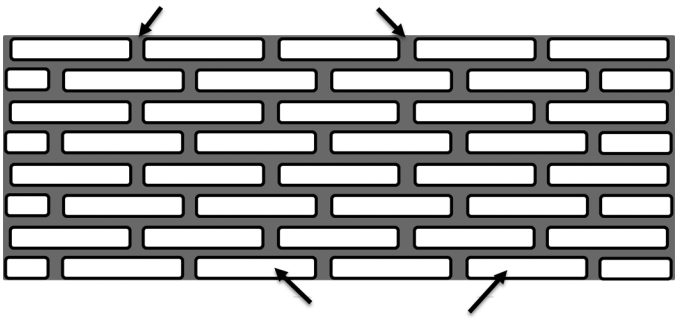


Figure 1.4: Brick-and-mortar model illustrating the organization of the corneocytes (bricks) and intercellular lipids (mortar) of the stratum corneum.

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Flame-Retardant Chemical Protective Clothing

12

By Nur-Us-Shafa Mazumder, MS
and R. Bryan Ormond, PhD*

Abstract

Flame-retardant chemical protective clothing (CPC) plays a critical role in safeguarding individuals exposed to various occupational hazards. Professionals in diverse fields benefit from CPC, such as military personnel, firefighters, first responders, oil-field workers, and those in various industrial sectors. These professionals depend on this specialized clothing to shield them from flames, hazardous chemicals, splashes, electric arcs, and molten materials. The choice of flame-retardant fibers for these protective garments is designed to meet specific requirements, offering options from inherently flame-retardant fibers to those treated with flame-retardant finishes. This chapter provides a comprehensive exploration of combustion principles, textile flammability, and the array of fibers used in the production of flame-retardant textiles. Additionally, the chapter delves into material and ensemble-level testing methods to assess thermal protective performance (TPP) and flame retardancy. The fundamental theory of repellency and the chemistry of durable water repellents are discussed, along with the evaluation methods for repellency against different liquids. The chapter concludes by shedding light on emerging issues and advancements in this crucial field of protective clothing.

Introduction

Flame-retardant fabrics serve various purposes, including in firefighting gear (Prezant et al., 1999), uniforms for military and law enforcement personnel (Adanur and Tewari, 1997; Duran et al., 2007), work clothing for industrial workers (Mandal et al., 2021a), home furnishing like upholstery (Kamath et al., 2009), textiles used in commercial buildings and transportation materials (Flambard et al., 2005), and specialized sleepwear for children and older individuals (Gaan et al., 2011; Horridge and Timmons, 1979; Horrocks et al., 2004). To make textiles flame retardant, three main approaches are commonly used: (1) utilizing inherently flame-retardant fibers such as aromatic polyamides (e.g., Nomex), polybenzimidazole (PBI), and poly(p-phenylene-2,6-benzobisoxazole) (PBO); (2) treating standard textile fibers with flame-retardant substances; or (3) incorporating flame-resistant additives into polymer bulk before fiber spinning (Gaan et al., 2011).

The history of flame-retardant chemicals traces its roots back to a remarkably early period, with records dating as far back as 1735 indicating the use of substances like borax, vitriol, and other mineral compounds in England (Weil and Levchik, 2008; Wyld, 1735). The production of flame-retardant theater curtains can be traced back to 1821 when the first systematic study on this subject was conducted in France. During that period, ammonium phosphate, which is still in use today, was identified as a highly effective flame-resistant material (Weil and Levchik, 2008). However, the majority of advancements in flame-retardant chemicals happened during the 1950s and 1960s (Horrocks et al., 2005). This aligns with the awareness of the significance of flame retardancy, particularly in the aftermath of the Second World War. Subsequently, the demand for enhanced performance of flame retardants and the need to replace existing flame-resistant materials due to safety concerns led to significant innovations in the development of flame-retardant fibers and thermal protective clothing for firefighters and industrial workers during the 1990s (Bajaj, 2000). Today, flame-retardant clothing is essential for various professionals such as firefighters and emergency responders, as well as in numerous other applications. This clothing is crucial in protecting individuals from thermal hazards as they carry out their occupational responsibilities (Schindler and Hauser, 2004).

Mechanism of Combustion

To understand flammability and flame retardancy, it is imperative to have a comprehensive understanding of the combustion mechanism in fibers (Figure 12.1). Combustion is an exothermic reaction that necessitates the presence of heat, oxygen, and a suitable fuel for initiation and propagation. In the event of a fire, combustion becomes self-sustaining, persisting as long as there is an adequate supply of oxygen, fuel, and excess heat or until the material undergoing combustion is exhausted. Although the polymer composing the fiber does not burn by itself, it does release flammable gases as it thermally degrades. These gases contribute to the continuation of the flame, even if the polymer itself is not burning. Polymer materials experience heating when they burn, causing their temperature to rise. When the polymer's temperature reaches its pyrolysis point, it undergoes decomposition, producing a mix of

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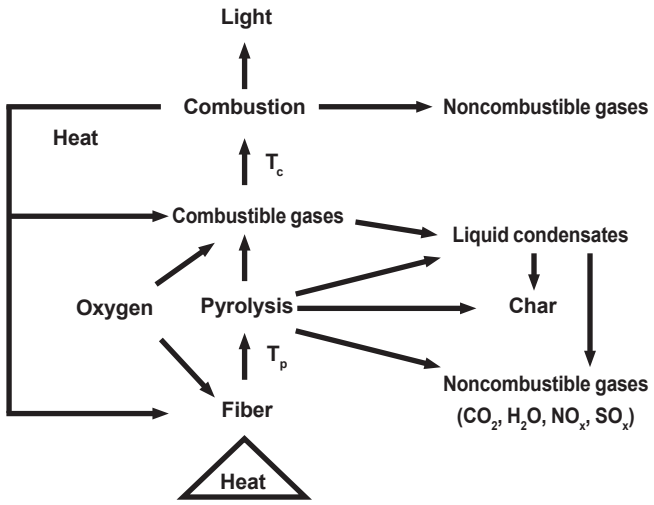


Figure 12.1: Mechanism of the combustion cycle in fibers (Mazumder and Islam, 2021; Schindler and Hauser, 2004).

combustible and noncombustible gases. At the combustion temperature, these combustible gases engage in a free-radical reaction with oxygen, generating a highly exothermic reaction that emits substantial heat and light energy. This release of heat further contributes to the degradation of polymers, leading to the generation of more combustible gases. These combustible gases effectively serve as fuel, sustaining and promoting the growth of fires. The continuation of a flame depends more on the rate of heat released during polymer degradation than on the total amount of heat released. Maintaining a flame depends on the availability of fuel and the rate at which heat is generated. The influence of these two factors is shaped by the type of material and the specific conditions in which combustion takes place. To impede the progression and expansion of a fire, flame-retardant chemicals or fibers must disrupt this cycle of heat and flammable gas generation (Dombrowski, 1996; Mazumder and Islam, 2021; Schindler and Hauser, 2004).

Mechanism of Flame Retardancy

A variety of strategies have been developed to disrupt the combustion cycle, as shown in Figure 12.1, through the use of flame retardants. One approach involves incorporating low-melting compounds that release water vapor and create a foamed glassy surface when exposed to fire. This surface acts as insulation—shielding the fiber from heat and oxygen—and prevents the completion of the combustion cycle, resulting in flame retardancy. Another approach is to influence the pyrolysis reaction. This results in the formation of less flammable volatiles and more residual char, which enhances flame retardancy. Additionally, flame-retardant materials that undergo strongly endothermic reactions, referred to as a "heat sink," can be used. When these materials absorb sufficient heat through endothermic reactions, the pyrolysis temperature is not reached, preventing combustion. Based on their mode of action, flame retardants can be classified into the following three categories: gas-phase action, condensed-phase action, and other mechanisms (Mazumder and Islam, 2021; Schindler and Hauser, 2004).

Gas-Phase Action

The primary characteristic of the gas-phase mode is the generation of reactive species, and it is in this context that halogen and phosphorous-based flame retardants are predominantly categorized. Radicals derived from halogen (X°) or phosphorous derivatives serve as the reactive species, functioning as free radical hunters within the vapor phase. The release of halogen from halogen-based flame retardants can result in the formation of hydrogen halide (HX), with hydrogen sourced from either the polymer or the flame retardants themselves. This hydrogen halide species has the potential to disrupt the combustion cycle by engaging in further reactions with hydrogen and hydroxyl radicals produced through the decomposition of the polymers (Gaan et al., 2011; Mazumder and Islam, 2021; Schindler and Hauser, 2004).

Condensed-Phase Mode

In the condensed-phase mode, a protective barrier is established between the heat source and the pyrolyzing polymer, which is the consequence of a reaction between the flame-retardant additive and the polymer during thermal decomposition. The catalytic interaction of flame retardants with the polymer induces polymer decomposition at lower temperatures. The effect of flame retardants can be categorized in the following two ways: they either modify the pyrolytic pathways of thermal decomposition or alter the rate of formation of combustible gases. For example, when phosphorous acid species interact with hydroxyl-containing polymers such as cellulose, a substantial amount of water molecules are released. In some cases, the decomposition of phosphorous compounds may yield phosphoric acid, which forms a thermally insulating barrier on the surface of decomposing polymers. The presence of external nitrogen additives like urea, guanidine, and melamine can enhance the condensed-phase action of phosphorous flame retardants. Chemical reactions between the decomposed nitrogen and phosphorous compounds further amplify the efficacy of phosphorous flame retardants, ultimately resulting in the formation of a protective coating (Gaan et al., 2011; Mazumder and Islam, 2021; Neisius et al., 2014; Schindler and Hauser, 2004).

Other Mechanism

The intumescent mechanism operates by forming a foam-like barrier through the reaction of polyhydroxy compounds with phosphorous flame retardants, resulting in charring and the release of ammonia gases from nitrogen sources. This combined action of charring and foaming produces an intumescent effect. A phosphorous-nitrogen based intumescent system comprises an acid source, a

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thermal blowing agent, and a char-forming agent. During combustion, gases such as nitrogen or ammonia from thermal blowing agents become trapped within the char, leading to foaming. Metal hydroxides commonly exhibit the heat sink effect by releasing water when decomposed at higher temperatures, which absorbs heat and dilutes gases formed through polymer pyrolysis. This effect can be attributed to several factors, including the heat-absorbing properties of water, the endothermic nature of the decomposition process, and the dilution of gases through polymer pyrolysis (Camino and Lomakin, 2001; Gaan et al., 2008).

Flammability of Textiles

Textile flammability is a complex phenomenon influenced by multiple factors such as the polymer composition of fibers, fabric and yarn construction, chemical treatments, weight per unit volume, additives, and testing conditions. As a result of this diversity, the flammability of textiles can vary dramatically. Some textiles, such as those made from highly flammable cellulosic and common synthetic fibers, are very prone to catching fire, whereas others are inherently flame retardant and offer a higher degree of fire resistance (Weil and Levchik, 2008). Under the right circumstances of flame, heat, oxygen levels, and exposure duration, nearly all textiles can ignite (Gaan et al., 2011; Hull and Kandola, 2008; Mazumder and Islam, 2021). Furthermore, an ample oxygen supply tends to enhance a material's flammability. On the other hand, excessive ventilation can help dissipate excess heat, potentially limiting fire growth. Research has indicated that the type of fiber, yarn count, twist, and structural composition of knitted fabrics exert a significant influence on both the ignition time and the rate of flame spread within the fabric (Ozcan et al., 2003). Consequently, defining the flammability of a material can be challenging, and testing the same material under varying conditions may yield different results (Gaan et al., 2011; Hull and Kandola, 2008).

Fabric Construction

When assessing flammability, the primary consideration is the polymer's resistance to burning. Properties linked to fabric construction, such as weight, weave, and thickness, are viewed as secondary factors. However, when measuring TPP, fabric construction takes on a more significant role (Gaan et al., 2011; Udayraj et al., 2017). The availability of oxygen plays a critical role in flammability, and an open fabric structure may permit an excess of oxygen, leading to increased combustion and faster flame propagation. Conversely, a tightly woven fabric with highly twisted yarn may exhibit fewer flammability issues because of limited oxygen availability. The rate of flame spread, once ignited, is significantly influenced by the fabric's areal density. Studies conducted by Hirschler et al. (2006, 2007) have demonstrated that cellulosic, common synthetic, and blended fabric garments pose the greatest danger when they are lightweight, which typically corresponds to a low areal density. In addition to lightweight fabrics, there is also a high flammability risk associated with raised-surface apparel, especially for fabrics with a highly brushed texture. This is due to their susceptibility to easy ignition and rapid flame spread. Moreover, the choice of yarn type can impact flammability. For instance, open-end spun yarn, characterized by scattered fiber orientation at the core and lower density compared to ring-spun yarn, can contribute to increased flame propagation due to greater air spaces between fibers, which facilitates oxygen access and heat transfer (Hull and Kandola, 2008; Ozcan et al., 2003). Fabrics made from blended fibers can also display distinct flammability behaviors. For instance, although cotton fibers are inherently less flammable than polyester, they may burn more rapidly when blended with polyester (Gaan et al., 2011; Mazumder and Islam, 2021).

Fibers

The flammability of textile materials is predominantly determined by the type of fibers they are composed of. Fiber flammability can be categorized into the following three different groups (Nazaré and Horrocks, 2008):

1. Readily flammable. These fibers ignite easily and burn quickly. Examples include cotton, acetate, triacetate, and rayon.
2. Moderately flammable. These fibers are less prone to ignition and may exhibit self-extinguishing properties when removed from a flame. Wool, modacrylic, and aramids fall into this category.
3. Nonflammable. Fibers in this group do not combust after being removed from a flame. Asbestos, glass, and carbon fibers are examples of nonflammable fibers (Gaan et al., 2011; Nazaré and Horrocks, 2008).

Textile fibers can be broadly classified into natural, synthetic, and regenerated categories. Natural fibers include cotton, flax, jute, wool, and silk. Synthetic fibers encompass materials such as polyester, nylon, acrylic, aramid, and Nomex®. Regenerated fibers, like viscose, and lyocell, are human-made but derived from natural polymers. The flammability characteristics of these fibers vary, leading to classification based on their responses to flame exposure (Stegmaier et al., 2005).

The burning behavior of fibers depends significantly on various thermal properties. These properties include the glass transition temperature (T_g), which is a thermal transition temperature, and thermodynamic parameters like the melting temperature (T_m) of the polymer. Additionally, transition temperatures related to chemical changes, such as pyrolysis (T_p) and combustion (T_c), play a crucial role in determining the burning characteristics of fibers. A lower T_c, which corresponds to the temperature at which combustion begins, results in a higher flame temperature and greater flammability of the fiber (Gaan et al., 2011). Another key factor in assessing flammability is the limiting oxygen index (LOI) of fibers. The LOI represents the minimum oxygen concentration required for combustion and is an essential property in determining a fiber's flammability.

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For instance, cellulose-based fibers typically exhibit lower LOI values, often below 19%, making them more susceptible to burning. In contrast, fibers with LOI values exceeding 21% tend to burn more slowly, whereas those with values between 26% and 28% typically pass small-scale burning tests. Wool, among natural fibers, stands out with a relatively high LOI value of approximately 25%, which has led to its common use in the production of flame-retardant clothing (Horrocks and Price, 2001). The heat release rate of fibers is another critical criterion that influences the flammability of these materials. The heat release rate is how quickly a material gives off heat when it burns. This greatly affects how flammable a fiber is. A higher rate indicates greater flammability, leading to faster fire growth and spread. The opposite occurs for lower heat release rates (Yang et al., 2010).

Textile fibers primarily consist of organic polymers as their main component. The evolution of manufacturing technologies has led to the substitution of natural fibers with synthetic counterparts in many instances. However, it is important to note that, in most cases, synthetic fibers tend to be more flammable than their natural counterparts. Materials like polyethylene, polypropylene, and polystyrene possess heating values that are similar to those of petroleum. Consequently, the polymer composition of the textile fibers serves as the principal determinant of a particular fiber's flammability. The physical and chemical alterations that occur in polymers when they burn significantly impact the overall flammability of the fiber (Gaan et al., 2011; Mazumder and Islam, 2021).

Flame-Retardant Textile Materials

Flame-retardant textile materials can be produced through two main methods: using inherently flame-retardant fibers or applying flame-retardant coatings or finishes to textile materials (Figure 12.2). Flame-retardant fibers can be created using the following materials:

- **Inherently Flame-Retardant Polymers.** These are fibers made from polymers that are inherently flame retardant. Examples include aramids, polyimide, PBO, PBI, melamine, glass, basalt, oxidized polyacrylonitrile, and polyphenylene sulfide-based fibers.
- **Flame-Retardant Comonomers.** This involves incorporating flame-retardant comonomers during the polymerization process. Modified acrylic and polyester fibers are common examples of materials containing special monomers with flame-retardant properties.
- **Nonreactive Flame-Retardant Additives.** This involves adding nonreactive flame-retardant additives during the fiber processing stage. Flame-retardant cellulosic fibers like flame-retardant viscose and Lenzing contain high concentrations of flame-retardant additives.
- **Coatings or Finishes.** Flame-retardant coatings or finishes can be applied to textiles during the fabric stage through a finishing and subsequent fixation process (Gaan et al., 2011).

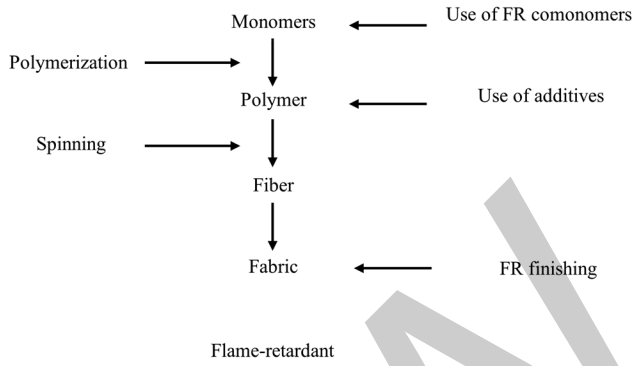


Figure 12.2: Methods to achieve flame retardancy in noninherent flame-retardant (FR) fibers (Tsafack and Levalois-Grützmacher, 2006).

Inherently Flame-Retardant Polymers

The high-level requirements for fire protective clothing are typically satisfied only by using inherently flame-retardant polymers. Some of these exceptional polymers include aromatic polyamides (meta- and para-aramids), PBI, PBO, and polyamide-imide polymers (Mäkinen, 2008). The following sections will delve into these specific polymers in greater detail.

Aromatic Polyamides or Aramids

Aromatic polyamides, commonly known as aramids (Figure 12.3), have emerged as one of the most prominent polymers used in the production of high-performance flame-retardant textiles, particularly in fire protective clothing and specialized industrial applications. These versatile fibers were initially developed in the 1960s and have since found widespread application in various industries. Meta-aramid polymers are particularly well-regarded for their lasting heat and flame resistance. As a result, they are ideally suited for use in fire-resistant clothing, heat-resistant filters, and various industrial applications. Para-aramid polymers, on the other hand, are known for their remarkable combination of high tenacity, high modulus fibers; heat resistance; and dimensional stability. Consequently, these fibers find their functionality in diverse products, ranging from automotive brake pads and other frictional materials to protective clothing, tire cords, and more. Additionally, these polymers have emerged as a safer alternative to asbestos in various applications (Bourbigot and Flambard, 2002; Gaan et al., 2011; Islam et al., 2020; Stegmaier et al., 2005; Weil and Levchik, 2008; Yang, 2007).

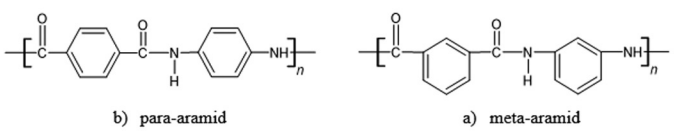


Figure 12.3: Chemical structure of aromatic polyamide polymers: a) para-aramid and b) meta-aramid.

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Polybenzimidazole

Polybenzimidazole (PBI) (Figure 12.4) is an organic fiber renowned for its outstanding thermal resistance and pleasant texture. PBI possesses remarkable qualities such as being noncombustible in air, not melting, and not dripping when exposed to flames. This fiber's high LOI, combined with its excellent chemical resistance and moisture retention capabilities, renders it an exceptional choice for applications requiring fire-blocking. This includes safety and protective clothing as well as flame-retardant fabrics. Although PBI exhibits less-than-ideal physical properties (e.g., a rigid molecular structure, low tenacity, and poor resistance to UV degradation), it remains versatile and can still be processed using most types of textile equipment. Furthermore, PBI can be effectively blended with other materials, such as carbon and aramid fibers—a practice often undertaken for both performance enhancement and cost efficiency (Bourbigot and Flambard, 2002; Gaan et al., 2011; Mäkinen, 2008; Stegmaier et al., 2005).

Poly (p-phenylene-2,6-benzobisoxazole)

Poly (p-phenylene-2,6-benzobisoxazole) (PBO) fiber stands out for its remarkable heat and flame resistance coupled with superior mechanical properties, and it is surprisingly flexible as well (Figure 12.5). The beginning of PBO can be traced back to the Air Force Materials Laboratory within the U.S. Air Force Ordered Polymer Program. However, it was Toyobo that first introduced this high-performance organic fiber in 1999, naming it Zylon® (Zylon-Department, 2005). In its initial development stages, the strength of PBO fibers was on par with high-performance para-aramid fibers. However, following collaborative research between Toyobo Company and Dow Chemical Company aimed at enhancing the fiber's properties, the strength of PBO fibers nearly doubled that of para-aramid fibers. PBO fibers exhibit exceptional heat resistance, exceeding 100°C, compared to para-aramid fibers. This remarkable fiber can serve as a heat-resistant material in applications reaching temperatures of 550°C or higher. Additionally, the LOI of PBO surpasses twice the LOI of meta-aramid fibers, further underscoring its outstanding flame resistance. PBO's exceptional strength, high thermal stability, and chemical resistance make it indispensable in industries where extreme performance is required, from aerospace and defense to sporting and industrial applications such as ballistic protection, cut-resistant gloves, composite materials, etc. (Bourbigot and Flambard, 2002; Gaan et al., 2011; Kuroki et al., 1997; Lee, 1990; Stegmaier et al., 2005).

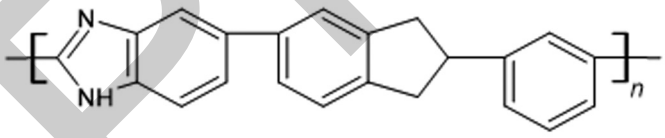


Figure 12.4: Chemical structure of polybenzimidazole (PBI)

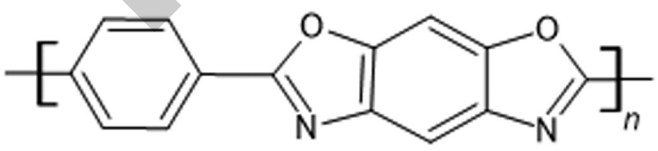


Figure 12.5: Chemical structure of poly(p-phenylene-2,6-benzobisoxazole) (PBO)

Polyimide

These fibers are manufactured through the polycondensation process of an anhydride with aromatic di-isocyanates, utilizing high-polarity solvents like dimethylformamide or dimethylacetamide (Figure 12.6). Remarkably, with a glass transition temperature of 315°C, polyimide (PI) fibers can be used in applications with temperatures reaching up to 250°C. These fibers are widely used in applications involving protective clothing, high-temperature filtration, and thermal insulation. It is important to note that PI fibers do not melt; instead, they undergo decomposition and carbonization at elevated temperatures. They exhibit a continuous operating temperature of 280°C, making them well-suited for high-temperature environments. Additionally, PI fibers feature a commendable LOI of 38%, which further emphasizes their excellent flame resistance (Bourbigot and Flambard, 2002; Sroog, 1991, 2018).

Flame-Retardant Copolymers

The key advantage of using reactive monomer and copolymer flame retardants, in contrast to other flame-retardant additives, is that a relatively low concentration is sufficient to impart flame retardancy. Reactive organophosphorus additives, primarily derived from phosphonic acid derivatives, are often used as comonomers to produce inherently flame-retardant polyester. Typically, a phosphorus content ranging from 0.7–1.0% is ample to achieve a satisfactory level of flame resistance. Phosphorus atoms in these polyesters can be integrated into the polymer's main backbone or exist as pendant groups attached to the main chain. Halogenated compounds based on bromine and chlorine and silicone-based flame-retardant compounds can be used as comonomers to achieve flame retardancy. Because these reactive flame retardants become part of the polymer's structure, they enhance the compatibility between the polymer and the flame-retardant agent. This integration reduces the detrimental impact on the mechanical properties of materials and minimizes the migration of flame-retardant agents to the material's surface (Gaan et al., 2011; Laoutid et al., 2009).

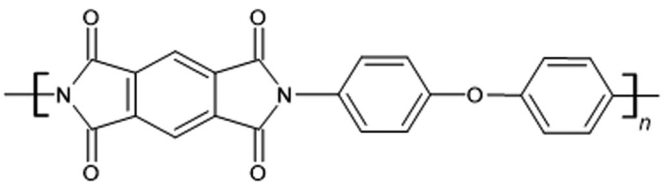


Figure 12.6: Chemical structure of polyimide (PI)

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Nonreactive Flame-Retardant Additives

The most common and cost-effective method of providing flame-retardant protection to polymeric materials is by incorporating flame retardants during polymer processing. However, the effectiveness of this method depends on selecting the right flame-retardant additives. These additives must be thermally stable, able to withstand temperatures up to 300°C without degradation, and easily disperse throughout the polymer matrix. They should also have a compatible melting point with the polymer's processing temperature, offer good dispersion to enhance flame-retardant properties, and not react negatively with the polymer. Failure to meet these criteria can result in decreased flame-retardant effectiveness and potential damage to the polymer material. The commonly used flame-retardant additives in melt spinning of PET fibers are halogen-containing organic compounds and organophosphorus compounds (Gaan et al., 2011; Koch et al., 1975). Organophosphorus-based pigment additives or silicon dioxide (SiO_2) flame-retardant additives are used in wet spinning for flame-retardant viscose fibers from cellulose.

Application of Flame Retardants by Finishing Treatments

Nylon fabric treatments for flame retardancy include brominated compounds, thiourea formaldehyde, and phosphonate esters. Finishing with hydroxy-functional oligomers is used for nylon-cotton blends. To ensure the durability of these finishes for up to 10 laundry cycles, melamine- and urea-based cross-linkers are used (Horrocks, 2003; Weil and Levchik, 2008). Conventional finishing treatments are difficult to apply to polyester fabrics due to the limited availability of reactive functional groups. Therefore, phosphorus or halogen-based flame retardants are used through thermoset methods for polyester (Weil and Levchik, 2008). For cellulosic textiles, chemical finishing treatments are the only option for achieving flame resistance. However, this presents a challenge because flame retardants must not compromise the fiber's properties, including strength, tactile characteristics, air permeability, and dyeability, and should not produce toxic gases when exposed to fire. Inorganic phosphates, organophosphorus compounds, and sulfur derivatives are used as flame retardants for natural cellulosic and protein fibers (Horrocks and Price, 2001).

Performance Evaluation of Flame-Retardant Clothing

Flame-retardant fabrics primarily serve the essential function of impeding the transfer of heat from the external environmental conditions faced by firefighters to their bodies. In this context, two pivotal properties that flame-retardant fabrics must deliver are thermal stability and insulative characteristics. The clothing's thermal stability can be assessed through parameters such as softening and melting temperatures, providing crucial insights into its performance under thermal stress. Complementing thermal stability tests, flammability testing is instrumental in confirming the clothing's integrity in a thermal environment (Song et al., 2016). A key metric for evaluating the effectiveness of flame-retardant clothing is TPP, which quantifies the thermal insulation capacity of the garment composite. The flame-retardant clothing's ability to insulate and restrict the transmission of thermal energy plays a critical role in mitigating the risk of burn injuries, thereby ensuring the safety and protection of the wearer [National Fire Protection Association® (NFPA), 2018; Song et al., 2016].

NFPA 1971: Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting outlines the minimum requirements for the design, performance, testing, and certification of protective gear used in structural and proximity firefighting. This includes coats, trousers, coveralls, helmets, gloves, footwear, and various interface components. In contrast, *NFPA 2112: Standard on Flame-Resistant Clothing for Protection of Industrial Personnel Against Short-Duration Thermal Exposures from Fire* specifies the design, performance, testing, and certification requirements, as well as the test methods for flame-resistant clothing. This standard covers garments, shrouds, hoods, balaclavas, gloves, and barrier face coverings intended for use in environments at risk from brief but intense thermal exposures. With the recent NFPA strategy to streamline and consolidate similar standards, NFPA is merging several existing standards into a single comprehensive document. The new *NFPA 1970: Standard on Protective Ensembles for Structural and Proximity Firefighting, Work Apparel, Open-Circuit Self-Contained Breathing Apparatus (SCBA) for Emergency Services, and Personal Alert Safety Systems (PASS)* will integrate the provisions of NFPA 1971 (firefighter turnout gear), NFPA 1981 (self-contained breathing apparatus), NFPA 1975 (station/work uniforms), and NFPA 1982 (personal alert safety systems).

Thermal Protective Performance

Bench-scale tests and full-scale manikin tests are both available for evaluating the flame-retardant clothing under various thermal conditions with varying intensities. The TPP of fabrics or their composites can be evaluated under various thermal conditions such as radiant heat, flame, hot surfaces, hot liquids, steam, and molten metal substances.

Thermal Protective Performance Under Radiant Heat Exposure

Standards such as ASTM F1939 and International Organization for Standardization (ISO) 6942 can be used to evaluate the TPP under radiant heat exposure. These standards provide methodologies for testing the radiant heat resistance of flame-retardant clothing materials. According to ASTM F1939, a fabric sample measuring 250 mm × 150 mm is vertically exposed to radiant heat from a quartz tube delivering heat at intensities of 21 and 84 kW/m^2. A thermal sensor consisting of a copper disc (often referred to as

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a slug) is positioned behind the exposed fabric. This sensor measures the total thermal energy transmitted through the specimen. The radiant heat resistance (RHR) is then calculated (in J/cm^2), serving as an indicator of the fabric's TPP under radiant heat exposure. Similarly, ISO 6942 offers a test method for evaluating materials and material assemblies when subjected to a source of radiant heat. This standard outlines procedures for assessing the performance of materials exposed to radiant heat, contributing valuable insights into their ability to resist radiant heat and protect against burn injuries (Mandal et al., 2021b; Song et al., 2016). The ASTM E1354 standard test method, titled *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter*, is used for assessing the fire behavior of diverse materials when exposed to radiant heat using a cone calorimeter. Although this instrument does not offer insights into TPP, it proves valuable for simulating radiant heat in a laboratory setting and is helpful in replicating the aging process of flame-retardant fabrics (Mazumder et al., 2022).

It should be noted that although ASTM F1939 is a well-established standard for evaluating the RHR of fabrics under continuous heating, it does not consider the thermal energy retained within the test specimen after the cessation of radiant heat exposure. The standard mainly focuses on assessing the fabric's ability to resist radiant heat during exposure, and the measurements are centered on the heat transmitted during the exposure period. This limitation suggests that the standard may not fully capture the potential impact of the accumulated thermal energy within the fabric after the radiant heat source is turned off. Users and practitioners should be aware of this aspect and consider additional assessments or complementary standards if a more comprehensive evaluation of the fabric's performance beyond the exposure period is desired (Song et al., 2016).

Thermal Protective Performance Under Flame and Radiant Heat Exposure

The ASTM test method D4108 was initially developed to assess the TPP of materials under flame exposure, but its application in the firefighting industry became perplexing due to the confusion over the measured performance. In response, the ASTM Subcommittee F23.80 developed a new standard, ASTM F2703, to address the confusion and provide a more accurate assessment of the protective capabilities of flame-retardant materials in predicting burn injuries. This standard incorporates both flame and radiant heat exposure and uses a TPP sensor, with or without a 6.4-mm air gap (Figure 12.7). The measured thermal energy value required to induce second-degree burn injuries is then used to estimate the TPP of the material (Song et al., 2016).

Thermal Protective Performance Evaluation Using Full-Scale Manikin Systems

Although the bench-scale evaluation methods discussed earlier are convenient, precise, and cost-effective, they have limitations in terms of simulating thermal exposure configurations and hazards. The results from these tests

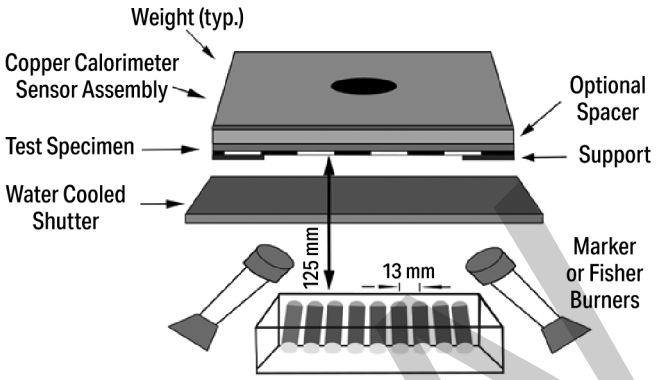


Figure 12.7: Simulated flame exposure tests in ASTM F2703. [Source: redrawn from Mandal et al., 2021a. *Int J Environ Res Public Health*. Open Access CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/)].

predominantly concentrate on fabric materials and often overlook crucial factors like microclimate and air gaps between the body and clothing. These factors are significant in predicting TPP. As a result, recent research efforts have shifted toward using full-scale manikin systems (i.e., life-sized, human-shaped models) to comprehensively evaluate TPP (McQuerry et al., 2018; Wang et al., 2015). This approach allows for a more realistic simulation of conditions and factors impacting the effectiveness of protective clothing in real-world scenarios.

The evaluation of full-scale TPP often involves the use of instrumented flash fire male manikins. Three notable examples are PyroMan™ at Textile Protection and Comfort Center, North Carolina State University; Thermo-Man® at DuPont; and Harry Burns at the University of Alberta. These instrumented manikins are used to predict the effectiveness of flame-retardant clothing in realistic flash fire simulations. The testing methods for these instrumented manikins are outlined in ASTM F1930 and ISO 13506-1, which are standard test methods for assessing flame retardant clothing's protection against flash fire simulations using an instrumented manikin (ASTM, 2023a; ISO, 2024).

The PyroMan manikin (Figure 12.8), clad in U.S. size 42 regular male clothing, is constructed from flame-retardant polyester resin reinforced with fiberglass and suspended within the burn chamber. The manikin features 122 PyroCal heat sensors distributed uniformly on its surface, with leads connected to a data acquisition unit through heat-shielded cables. In the PyroMan testing setup, the flame exposure involves directing flames onto the manikin at heat flux levels of up to 84 kW/m^2. This exposure typically lasts for 3–5 sec and is facilitated by eight propane gas torches positioned around the manikin. The gas supply line is insulated and electrically heated to ensure a consistent fuel supply, unaffected by changes in weather conditions. To simulate wind conditions during testing, the manikin is surrounded by several fans capable of generating velocities up to 5 mph. This configuration allows for a comprehensive evaluation of thermal protective clothing under realistic fire and wind scenarios. The test sequence involves ensuring safe operating conditions, lighting pilot flames, exposing the garment

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to a flash fire, acquiring data, and ventilating the chamber with fans. Protective performance is evaluated based on the garment's ability to reduce heat transfer to the manikin. The acquired data are used to calculate incident heat flux and predict second- or third-degree burn injuries for each sensor location during and after the fire exposure. Graphical reports detailing burn injury predictions are generated for each test (NC State University, n.d.; Song et al., 2016).

The Thermo-Man, developed by DuPont, is a size 40 regular manikin constructed from a high-temperature flame-retardant polyester. This thermally instrumented manikin is suspended from the ceiling of a burn chamber equipped with a system capable of generating the equivalent of a fuel flash fire in a controlled exposure. The manikin features 122 embedded sensors distributed uniformly over the entire front and back of the body, with each sensor representing 0.82% of the body area. These sensors can measure incident heat fluxes in the range of 63–126 kW/m^2. For experimental purposes, the average heat flux level is set up to 84 kW/m^2. The flame is applied to the manikin through eight propane torches for a minimum of 5 sec. During flame application, sensors measure the thermal energy transferred through the clothing. The measured thermal energy data are then used to evaluate TPP, specifically the time required to generate second- and third-degree skin burn injuries (Behnke et al., 1992; DuPont, n.d.).



Figure 12.8: PyroMan™ manikin at Textile Protection and Comfort Center, North Carolina State University (NCSU). [Source: University Archives Photograph Collection, College of Textiles Photographs, UA 023.017, Special Collections Research Center, NCSU].

The Harry Burns flame manikin is a size 40 manikin constructed from fiberglass. This manikin is versatile, allowing testing in both clothed and unclothed conditions. The fire chamber features automatic control of supply and exhaust ducts for safe system startup and rapid removal of combustion/degradation byproducts after a test exposure. Flame application is executed through 12 propane gas torches, which are strategically positioned to engulf the manikin fully. The gas control panels, equipped with safety features, monitor pilot flames, gas supply lines, and safety devices to ensure secure operating conditions. Flame exposure typically lasts 3–4 sec, with heat flux values monitored up to 84 kW/m^2. Skin simulant sensors attached to the manikin collect thermal energy data, allowing measurement of the time required to generate second- and third-degree burns, which is crucial for assessing the TPP of firefighter clothing (Crown et al., 1998; Song, 2003; Song et al., 2016).

The three active flash fire manikin systems, namely Thermo-Man, PyroMan, and Harry Burns, operate on a common principle and produce real-time TPP reports specifically focused on second- and third-degree burn injuries. This report can be further expanded using sophisticated computer systems that facilitate a comprehensive analysis of test garment performance. Such analyses include determining the percentage of the body area subjected to second- and third-degree burns, calculating the total predicted burn injuries across the entire body by percentage, assessing the total accumulated heat received by the sensors, providing a table detailing the response of individual sensors, generating a plot depicting burn injury versus time, and presenting a manikin diagram illustrating the distribution of burn intensity over the body surface. Table 12.1 shows the basic comparison among the three different flash fire manikin systems.

Evaluation of Flammability

Flammability can be defined as how easily a textile material will burn or ignite in the presence of fire or combustion. Various parameters such as flame duration, the rate and extent of flame spread, ease of flame extinction, the temperature of burning fibers or fabrics, and the amount of heat during burning need to be considered for determining flammability. The selection of parameters for flammability evaluation depends on the nature and location of the ignition source, orientation of the test specimen, and environmental conditions. Therefore, various test methods are available to evaluate the flammability of the textiles (Kotresh, 1996).

Flammability of fabrics made from natural and synthetic fibers can be measured using the test method *ASTM D1230: Standard Test Method for Flammability of Apparel Textiles*. Clothes made from combustible fibers are dangerous to the wearer because of factors such as ease of ignition, flame spread time, amount of heat released, and design of the

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PREVIEW

Chemical Protective Clothing, 3rd edition

Edited by Derek A. Newcomer, DrPH, CIH, CHMM, CSP, REHS
and Robert N. Phalen, PhD, CIH, CSP, FAIHA®

This updated book provides a comprehensive overview of the considerations necessary for the implementation of a successful protective clothing and equipment program. The content is organized into three areas: Background, Fundamentals, and Theory; Manufacture, Design, and Testing; and Considerations for Proper Selection and Comprehensive Program Development. In addition, a new chapter on Flame-Retardant Chemical Protective Clothing has been added to highlight the emerging issues and advancements in this crucial field of protective clothing.

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