

PESTICIDE AND FLAME PROTECTION CHARACTERISTICS
OF CANDIDATE MATERIALS FOR AERIAL
APPLICATOR PROTECTIVE CLOTHING

By

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CHAPTER I

INTRODUCTION

Pesticides are chemicals introduced in the environment for the purpose of controlling and destroying pests. Today in agriculture, pest control is essential not only for producing more food but also for production of better quality food products. So widespread is the use of pesticides in agriculture that the yearly consumption of some 1400 chemicals used as pesticides amounts to more than a billion pounds in the United States (OPA 138/0, 1980). Agricultural workers who apply pesticides as well as those working in the fields face the danger of pesticide exposure. Pesticide exposure in humans has been linked with death, disability, neurological and behavioral disorders, sterility and birth defects (Davies, Freed, Enos, Barquet, Morgade, and Danauskas, 1980). As the dangers associated with pesticide exposure are recognized, attention has been focused on developing protective clothing for agricultural workers involved in handling pesticides, thereby limiting dermal pesticide exposure.

Justification of the Study

As much as two thirds of pesticide application in the United States is done aerially (Boraiko, 1980). Due to the nature of their occupation, pesticide aerial applicators face the risk of pesticide exposure. Several studies (Hayes, Wise, and Wier, 1980, Cohen, Richter, Weisenberg, Schoenberg, and Luria, 1979, Ganelin, Mail, and Cuetoc, 1961) have documented aerial applicators exposure to pesticides.

Pesticide exposure studies have reported three primary routes through which pesticides can enter the body, ingestion, inhalation and dermal absorption. Durham, Wolfe, and Elliot (1972) reported that dermal absorption accounts for about ninety seven percent of the pesticide detected in the body. Protective clothing that offers a barrier against pesticide penetration could minimize dermal exposure. The degree of protection offered by the clothing would depend on the ability of the clothing material to resist penetration/ permeation by the pesticide. Materials that offer barrier protection are especially important in designing protective clothing for aerial applicators, as Carter (1985) reported that majority of the aerial applicators in her study handled high toxicity pesticides. The pesticides that came in contact with the aerial applicators' skin were usually liquid pesticide

formulations diluted to field strength. She also found that the majority of the applicators reported not changing clothing immediately after an accidental spill of full strength pesticides on their clothing. Thus ample opportunity for dermal absorption of pesticides exists for aerial applicators. High temperature, sweating, exposure lasting several hours and delays before showering have also been reported to enhance dermal exposure (Cohen et al., 1979).

An aerial applicator's job involves technical skill as well as competence. Besides being aware of the type of pesticide being applied, the aerial applicator has to be concerned about controlling drift, as the Environmental Protection Agency has strict regulations about the same. One of the important factors influencing the amount of drift according to Overhults (1976) is the height from which the pesticide is released. This affects the time required for the droplet to reach the ground, the longer the time needed, the more opportunity the pesticide has to move away from its intended target. The wind velocity is also lower closer to the ground, thus drift problem can be minimized by holding the discharge height to the minimum. An article in World of Agricultural Aviation (November 1981) reported dramatic increases in drift losses when the applicators flew above 6 feet boom height over the crops. Therefore, in order to be accurate aerial applicators need

to fly fairly low and close to the ground.

An aerial applicator's job is a hazardous job having high potential for airplane or aviation accidents. Between 1970 to 1983 a total of 5523 accidents involving aerial applicators were reported, 438 accidents were fatal (figures compiled from yearly accident reports published in World of Agricultural Aviation July 1981, February 1983, July 1983, and June 1984). The causes of accidents included power loss just after take off, take off accidents due to loss of directional control, fuel exhaustion, downwind take off, hitting a fence or trees, hitting power lines, swathe run mishaps, flying into wires and into the ground, landing accidents and incapacitation due to pesticide exposure (World of Agricultural Aviation, February 1982).

In the event of an accident it is possible to survive the crash impact, since the aerial applicators fly fairly low, yet the possibility of a fire remains a threat to life. A general aviation study (Aviation Safety, June 1986) investigating aviation accidents from 1976 through 1981, found 2292 accidents involving fire. Out of the 2292 accidents 5.5 percent involved fire in the air, 2.4 percent involved airplanes that were on the ground when the fire broke out, while the remaining 92.1 percent were post crash fires.

As with any type of chemical protective clothing, the level of complexity of the hazards determine the type of

chemical, biological protection needed (Watkins, 1984). Aerial applicators face dual hazards, that of exposure to pesticides and fire. One of the preliminary but major steps for developing protective clothing for them would be evaluating the materials/fabrics, for their barrier properties against pesticide penetration and fire.

Purpose Of The Study

The purpose of the study was to examine the pesticide barrier protection properties and flame protection properties of the six selected flame resistant fabrics.

Objectives

1. To evaluate the effectiveness of the six selected flame resistant fabrics as barriers to pesticide penetration.
2. To evaluate the flame protection properties of the six selected flame resistant fabrics.

Hypotheses

1. No significant differences exist in the barrier protection properties of the six flame resistant test fabrics to organophosphate pesticide malathion.

- 2-4. No significant differences exist in the after-glow time, char length and after-flame time of the six flame resistant test fabrics when exposed to a 12-second flame source.
- 5-7. No significant differences exist in the after-glow time, char length and after-flame time of the six test fabrics when exposed to a 30-second flame source.
- 8-10 No significant differences exist in the after-glow times, char lengths and after-flame times of the test fabrics exposed to a 12-second flame source and a 30 second flame source.

Limitations

1. Only a selected number of fabrics which are expected to possess good flame and heat barrier properties were tested.
2. Only one pesticide was used, therefore, the results cannot be generalized to other pesticides, formulations and concentrations.

Assumptions

1. A standardized test method was used for evaluating fire protection property of the materials. This method has been rigorously tested and is accepted as a standard

test method for evaluating fabrics meant for protective clothing for flame/heat environment. However, it may not simulate a plane crash situation.

2. The penetration test procedures have been previously used and proved to be reliable.

Definition Of Terms

Aerial Applicator : Person who applies pesticide(s) from an air craft. (Carter, 1985, pg 6).

Pesticide : Chemical agent used to destroy pests, including fungicide, herbicide, rodenticide and insecticide.
(Farm Chemical Hand Book. 1982)

Penetration : Flow of chemicals through closures, porous materials, seams and pin holes, or other imperfections in clothing material. (ASTM subcommittee F23. 30 Schwope, 1983).

Permeation : Is the process by which chemical moves through clothing on a molecular level.
(ASTM subcommittee F23.30 Schwope, 1983).

Chemical Barrier Property : Is based on the ability of the fabric to prevent or inhibit the movement of the chemical through the fabric. (ASTM subcommittee F23.30 Schwoppe, 1983)

Flame Resistance : The property of a material whereby flaming combustion is prevented, terminated or inhibited following application of a flaming or nonflaming source of ignition, with or without subsequent removal of the ignition source. (ASTM D:4391-84)

CHAPTER II

REVIEW OF LITERATURE

The review of literature includes two main sections corresponding to the two phases of the research. The first major section focuses on the flammability and heat protection and the second reviews the pesticide penetration research. Subsections on commonly used methodologies are also included under each major heading.

Flammability And Heat Protection

Desired Protective Clothing Performance Characteristics.

A distinction must be made between exposure to heat versus flame. The primary purpose of protective clothing in any kind of thermally hazardous environment is to protect the wearer against burn injury. Protective clothing may be designed to protect the skin from either exposure to intense heat and or flame, for example the primary function of fire fighters' clothing is to provide protection against heat transfer. Clothing designed to protect against the effects

of fire exposure would need to be made from materials that do not catch fire or ignite. If the clothing is made from material that catches fire or does not self extinguish, it becomes a prolonged source of heat, contributing towards further burn injuries to the wearer.

It is also equally important that the insulating value of the protective clothing be sufficient, to prevent damaging heat transfer, that could result in serious burn injury (Abbott and Schulman, 1976). Further the fabric should be able to maintain strength and integrity at high temperatures (Benisek, Edmondson, and Phillips, 1979), in order to continue as a barrier between the skin and the heat hazard. The fabric should be thermally stable, it should not shrink or melt. If the fabric shrinks, it exposes the skin surface to the heat and flame source. If the fabric melts, the molten mass can drip on the skin causing burns. Melting also causes hole formation in the fabric, which, again leaves the skin exposed to flames and heat (Ross, 1980).

The fabric should have the ability to deflect molten substances (Brewester and Barker, 1983). The fabric should be easy to clean and should maintain its flame retardant property after repeated washings. Garments made from such protective fabrics should be durable and should withstand wear and tear. Their design features should not contribute in any way towards facilitating burn injury potential. The garment should be able to protect the wearer against all

types of flame/heat hazards, including exposure to fire, convective heat flames, convective and radiation heat, continuous exposure to radiant heat and exposure to molten metal droplets and splashes.

Factors Affecting Performance Of Protective Clothing

Performance of protective clothing for protection against heat and flames depends upon a complex interaction between the properties of the thermal environment and fabric characteristics. In fact, it is the type of thermally hazardous occupation which determines the nature as well as the extent of thermal protection needed. A fireman's job requires that his clothing be able to protect him from exposure to radiant and convective heat flames, however, a worker handling a propane torch would need protection against convective heat flames. Clothing with certain characteristics may provide high levels of protection against a specific hazard but may completely fail to provide any protection against other type of thermal hazard. Hence, when choosing protective clothing for a thermally hazardous occupation, a careful evaluation of the environmental characteristics (Benisek et al., 1979) needs to be done. Based on this evaluation fabric characteristics which would offer highest level of protection for the specific hazard

can be chosen.

The burning characteristics of fabrics are influenced by the properties of the fiber, yarn, fabric structure and finishes. The chemical composition of the yarn used in a fabric affects its burning behavior. Fabrics made from cotton (cellulosic fibers) fibers were seen to ignite more readily than fabrics made from other fibers (Halcombe, 1983). Flammability in blended fabrics is influenced by the nature and proportion of the constituent fibers. Tesoro (1970) observed flammability of polyester to increase with increase in amount of cotton content in the blend from 0 to 15 percent. Presence of nonflammable fibers in blends may reduce flammability of the flammable component in the blend. Tesoro and Rivlin (1971) reported that in their study of nomex with cotton and other flammable fibers, increased oxygen index values were observed for the blends as the content of nomex increased.

Fabric characteristics like the construction, weight per unit area, moisture content and surface smoothness also affect flammability. Cohen (1982) stated that yarns with little twist, thin yarns, pile or napped surfaces are likely to be more flammable. Fabrics with loose construction having air spaces between them will tend to burn more rapidly due to availability of more oxygen (Cohen, 1982). Dense fabric construction in fabrics was seen to reduce tendency to ignite readily in some fabrics by Halcombe (1983). Fabrics

with napped surfaces will be more flammable than those with smooth surfaces.

Lightweight fabrics are likely to be more flammable than heavier fabrics (Cohen, 1982). Neilson and Richards (1969) found the heavier fabrics to burn more slowly than lighter fabrics. Heavier fabrics were found to be less easily extinguished than light weight fabrics by Krasny (1986), who suggests that such fabrics in spite of their slow flame spread rates may produce enough heat to cause burn injuries. Ignition time for cellulosic fabrics was seen to increase with increase in weight by Bernskiold and Schultz (1979) as well as Krasny (1986). Halcombe (1983) found that untreated lightweight wool fabrics were easily ignited however those weighing in excess of 250 g/m² failed to ignite.

Chemical finishing operations also affect flammability in fabrics, operations like mordanting during chrome dyeing of wool decrease fabric flammability (Thompson, 1966). Several flame retardant/flame resistance finishes are used on fabrics to enhance their flame protection properties.

Heat transfer and burn injury potential in fabrics is influenced by fabric thickness, fabric weight, moisture content and fiber content. Thermal insulation in fabrics was found to be dependent on fabric thickness, including the ability to maintain this thickness during the period of hazardous exposure (Freestone, 1971). This characteristic

held true when fabrics was exposed to radiant heat source (Stephenson, 1983 and Halcombe, 1983), convective heat (Abbott et al., 1976) and Conduction (Brewster et al., 1983).

Sufficient fabric weight along with fabric thickness was found to be essential in providing single layer protection against splashing iron (Barker and Yener, 1981). Shalev and Barker (1983), found a trend for increase in thermal protective properties (TPP) with increase in fabric weight and thickness.

Thermal insulation is also influenced by the entrapment of still air within the fabric structure, as the entrapped air contributes towards thickness and also increases the distance between the skin and the fabric. Burn injuries have been reported to be less severe when the distance between the skin and the fabric increased (Krasny, Singleton, and Pattengill, 1982). Clothing with multilayers of fabrics offer higher levels of protection than those with single layer of fabric for the above reason. Multilayers also help in reducing the maximum temperature reached by the skin (Abbott et al., 1976).

Freestone (1971) suggests that the degree of thermal protection offered is influenced by the initial moisture content in the fabric. Krasny and Fisher, (1973) also found moisture to decrease the protection offered by garments.

Fiber content has also been shown to influence the burn injury potential of fabrics. Krasny et al. (1973) reported

that cotton polyester blends had more likelihood for causing severe burn injury than hundred percent cotton or hundred percent thermoplastic fabrics. Halcombe (1983) exposed a ninety five percent wool and five percent polyester blend to a convective heat source. The blended fabric was observed to form holes, leaving the skin exposed to the heat source. Brewster et al. (1983) stressed the importance of component fibers being thermally stable in order to be able to provide protection in thermally hazardous environment. If protective clothing made of thermoplastic fibers soften, melt or coalesce when exposed to heat, then they form a conducting path for the heat and thus increase heat transfer to the skin. Further if this melted mass came in contact with the skin the burn injury would be more severe as the molten material releases latent heat on melting to the skin . Halcombe (1983) suggests that the thermoplastic content in any blend with non-thermoplastic fibers should not exceed 10 percent in materials that are used in making clothing for thermally hazardous environment.

Krasny (1986) reported that fabrics with short ignition time, high heat release rates and total heat release are believed to present relatively high burn injury hazard. In addition they also may have tendency to burn even after coming in contact with the skin, which increases the burn injury hazard.

Certain fabric finishes enhance the protective

performance of protective materials in specific hazards. When exposed to a radiant source of heat, fabrics with clean reflective (aluminized finish) surfaces offer higher levels of protection Krasny (1986). However level of protection seemed to decrease if the fabric surface became dirty. Stephenson (1983) found aluminum coated fabrics to greatly reduce heat transmission when exposed to radiant heat sources. Halcombe (1981) found that garments made from aluminum coated fabrics could not offer adequate protection against convective heat as aluminum is a good conductor of heat so it becomes a transfer medium between gases, fabric and the skin.

Baitinger and Konopasek (1986) found that color influenced the degree of protection offered against radiant heat, when they exposed fire retardant cotton fabrics to radiant heat source. Black color was found to offer least protection, yellow color fabrics provided highest levels of protection whereas white fabrics offered intermediate levels of protection.

Heat And Flame Test Methods

The degree of protection offered by protective clothing in thermally hazardous environment depends upon the interaction of fabric variables and heat environment. Different heat sources place different performance demands

on the fabrics. This has led to the development of many test methods for evaluating the fabric effectiveness under different types of thermal hazards. Selection of test methods for evaluating or comparing the performance of protective fabrics depends solely on the type of hazard and the level of protection desired. The tests can be divided into two broad categories, flammability tests and tests for measuring heat transfer and burn potential.

Flammability Test Methods. Flammability of fabrics (treated or untreated) is usually measured in terms of their ignitability and combustibility (Kasem and Rouette, 1972 pg.319). Combustibility focuses on the rate of flame travel along the fabric specimen under a given test procedure. Ignitability is a measure of ease with which the fabric enflames. Number of test methods have been developed for evaluating the flammability of flame retardant/resistant and untreated fabrics. Flammability for untreated fabrics in terms of combustibility and ignitability can be measured and compared by using test method AATCC 33-1962.

Flame resistance for flame resistant/retardant fabrics is evaluated in terms of after-flame time (time for which specimen continues to flame after the burner flame is shut off), char length (which is the distance from the end of a tear (made lengthwise) of the specimen through the center of the charred area) and after-glow time which is the time the specimen continues to glow after it has ceased to

flame. Vertical flame tests are usually used to measure the above test parameters. The federal test method 191-5903 involves exposing a vertically mounted test specimen to 1.5 inches flame source at its lower edge for a period of twelve seconds. The char length, after-flame time and after-glow time are recorded.

The National Fire Protection Standard 1971 for protective clothing for structural fire fighters specifies that when fabrics to be used in fire fighters protective clothing are tested by the above test method (191-5903) the length of the char should not exceed 100 mm, and that the flaming should cease within 2 seconds after flame is removed. Most high performance fabrics have good resistance to the vertical flame test. To determine the differences that exist in nonflammable fabrics investigators often increase the severity of tests by prolonging the exposure time or using hotter ignition sources (Barker et al., 1981)

Ignition Tests. The ignition properties of flame resistant fabrics have been measured by recording the number of seconds needed to produce ignition and the temperature of ignition. The ignition time has been defined by Bernskiold et al. (1979, pg. 106) as : the time for which an igniting flame must act on a specimen in order to ignite it, so that it burns with flames for a time longer than 1 second. The above is measured by holding vertically oriented fabric specimens against the Calrod heater that

has a thermocouple embedded near its surface. The temperature of the surface of the heater at the instant before ignition is approximately the fabric burning point. The time of contact to initiation of burning is also noted (Freestone, 1971). This test evaluates fabric flammability under simulated thermal environments under which apparel made from protective fabrics may occasionally have to perform.

Efforts have been directed at developing test methods by which flammability properties of fabrics may be characterized by numerical designations. Flammability index test method (Townesley, 1968) involves mounting the sample on a substrate of ashless filter paper and igniting the substrate. The flammability index is based on the minimum number of layers of filter paper needed to consume the sample during burning of the substrate. The method provides a measure of ease of ignition of the sample.

Limited Oxygen Index Method (LOI). This method for flammability rating of fabrics establishes the minimum fraction of oxygen which when mixed with nitrogen sustains burning of the fabrics. Tesoro (1970) found the oxygen index to be a function of the chemical composition of the fiber. Normally materials with LOI greater than 21 do not burn in air, while fabrics with LOI less than 21 burn in air (Krasny, 1986). Most fabrics have a LOI around 20.

Fabric/ materials with LOI of 25 are not easily ignited in air. Abbot et al. (1976) ranked fabrics with a LOI between 25 to 31 as essentially nonflammable under normal conditions. They would burn if there is sufficient air flow or heat flux. Fabrics having LOI between 35 to 40 could be considered truly nonflammable under fairly extreme conditions. The oxygen index tests have gained extensive acceptance by researchers because of the precision with which these values can be measured and the reproducibility of results. This method has been found to be a particularly valuable and useful quantitative measure in comparing flammability of nonflammable material (Brewster et al., 1983).

Test Methods For Measuring Heat Transfer And Burn Injury Potential. Performance of protective fabrics in heat/flame exposures cannot be realistically evaluated based on the flammability tests alone. In fact, Krasny (1986) found bench scale tests measuring heat released by burning fabrics to be a better predictor of fabrics' burn behavior than flame spread tests. The test methods for measuring heat transfer and estimating extent of burn injury basically involve measurement of the fabrics' thermal response by allowing time controlled exposures to regulated heat sources. The experimental equipment generally has a heat source, heat sensor, sample holders, timing and recording devices.

Radiant Heat Sources. Benisek et al. (1979) studied the transfer of radiant heat by exposing test fabric samples to 2.0 w/cm^2 flux levels from a gas fired radiant panel. He measured the time for temperature to rise by 25 degrees centigrade. Instrumented copper disc was used as a heat sensor. Perkins (1979) and Baitinger (1979) both used quartz heater set for radiant source of heat. The flux levels of heat ranged from $.84$ to 20.9 w/cm^2 . Perkins (1979) measured time to second degree burn and used a flux meter as a heat sensor. Baitinger (1979) recorded the time to blister and used instrumented copper disc as a heat sensor.

Convective (open flame) Heat Sources. Several researchers have studied convective heat transfer through protective fabrics. Meker burner has been used as heat source by many researchers like Freestone (1971), Perkins (1979), Baitinger (1979), Behnke and Seaman (1966), and Benisek and Phillips (1981). Benisek et al. (1981) used fischer burner while Ross (1977) used JP-4 fuel burner as a heat source. The heat flux levels in the above studies ranged from 5.4 to 13.8 w/cm^2 . The measurement of heat transfer was done by recording the temperature rise at three second exposures (Freestone, 1971), time to second degree burn (Perkins, 1979), time to blister (Baitinger, 1979, Benisek et al., 1981), Protective Index (Behnke et al., 1966), time to rise by $25, 50^\circ\text{C}$ (Benisek et al., 1979)

and time to cause injury in three second exposures (Ross, 1977).

The heat sensors used included NML skin stimulant (Freestone, 1971), instrumented copper disc (Perkins, 1979, Baitinger, 1979, Behnke et al., 1966, and Benisek et al., 1981) and aérotherm sensor (Ross, 1977).

ASTM D 4108-82 is a test method for measuring the thermal resistance and insulation of fabrics when exposed to convective energy levels of about 2.0 cal cm^2 for a short duration. This method can also be used to determine "The Thermal Protective Performance" (TPP) of fabrics. TPP rating is the exposure energy required to cause the accumulated heat received by sensor to equal the heat that will cause second degree burns in human tissue. The severity of skin burn is believed to depend upon rate of heat transfer at the skin surface and duration of exposure (Halcombe, 1981). Stoll, Chianta and Piergalline (1978) have established typical curves showing heat flux versus the time required to produce skin temperatures that exceed 44°C , which is the defined threshold temperature for skin damage. High levels of heat flux can be tolerated only for short times without injury while low levels of heat flux can be endured for longer periods without injury (Behnke et al., 1966).

Behnke (1977) developed the TPP rating system for ranking protective quality of protective fabrics. The

fabrics are rated according to the time required for heat transfer to cause second degree burns on the reverse side. This time is multiplied by the level of heat exposure to arrive at the TPP rating. The amount of heat transfer through the fabrics is measured by placing heat sensing devices behind the fabrics being tested. Some commonly used sensors are the NML skin stimulant developed at the Naval Materials Laboratory. It simulates the optical and thermal properties of the skin. Temperature changes are measured by embedding thermocouples .05 cm. below the NML surface to simulate the section of skin where actual damage occurs. NML skin stimulants are not reusable so other researchers like Behnke (1977, 1966) have used copper calorimeters consisting of copper disk embedded with four thermocouples to measure the flow of heat through the fabric.

Combined Radiant/Convective Heat Sources. Behnke (1977) exposed fabric samples to convective and radiant heat sources by using meker burner and T-3 quartz tubes to generate heat flux of 8.4 w/cm^2 . He used instrumented copper disc as a heat sensor for recordings the TPP rating. Ross (1977) used Meker burners and quartz burners to study time to injury in three second exposures by using a Aerotherm sensor.

Flammability Properties Of Some Protective Fabrics

Today there are number of commercial fibers that have varying degrees of resistance to burning. They include aramids, chemically modified cellulosics, modacrylic, polyimide, polybenzimidazole, polyamidimide, phenolic, and glass. These fabrics would not be expected to burn when a match is brought in contact with them at normal room temperature. The LOI is a way of assessing the relative resistance to burning of such fabrics. Fabrics with high LOI offer high levels of resistance to burning. Abbot et al. (1976) rated fabrics like wool FR cotton, Nomex , Kevlar, Dynel ,SEF, and PFR with LOI values between 23 to 31 as essentially nonflammable under normal conditions. Durette, Rhovyl, Polyimide fiber, HT-4, and PBI had LOI between 35 to 40 and were classified as truly nonflammable under fairly extreme conditions.

Freestone (1971) studied the burning rates of vertically oriented samples of nomex, PBI, and FR cotton. He measured the inches consumed per second. He used two techniques: ignition method of NASA burning tissue method and calrod type heater used for determining ignition temperature. PBI needed minutes of contact with heat source to produce ignition. Five seconds of contact produced ignition in Nomex and FR cotton fabrics. PBI had an ignition temperature of 1700 degrees, spun Nomex 1600 degrees and FR cotton 1450 degrees. Nomex and cotton were

found to burn in air but were self extinguishing. PBI fabrics did not burn in air.

Krasny et al. (1982) exposed various fabrics used in protective clothing for ten seconds to a flame source. They reported that chars of Aramid/ Novoloid blends and FR cotton were more embrittled than other fabrics studied. These fabrics would disintegrate readily under fire conditions than other blends of Aramid fabrics. The least embrittled char was observed in a blend of Kevlar/ Nomex. Economy, Wohrer, and Frechette (1972) tested Kynol under a variety of flame conditions from lighting a match to it to an oxyacetylene torch. Kynol was found to be nonmelting and nonburning. However, it was found to burn in atmosphere containing 40 percent of oxygen.

Ross (1980) evaluated the flammability characteristics of outer shell fabric and the insulation batting and covers used in air personnel's jackets. He used the Federal test Standard 191-5903 to assess their flammability. He found Kynol batting to be completely nonflammable. Nomex batting exhibited 1.5 seconds after-flame and 7.0 seconds glow-time. The wool back fabrics were all highly flammable. Continuous filament Nomex outer shell fabrics were seen to shrink and break open on flame contact.

Pesticide Penetration Through Fabrics

Laboratory Test Methods For Evaluating Barrier Protection Property In Fabrics

Fabric Assembly. A multilayer fabric assembly is commonly used for studying pesticide (liquid form) penetration through fabrics. The multilayer sample consists of the test fabric, the collector layer, aluminum foil, and a device to hold the three layers together. Gauze was used as a collector layer in liquid pesticide penetration studies by Orlando, Branson, Ayres, and Leavitt (1981) and Branson, Ayres, and Henry (1986). Leonas (1985) used 50% cotton 50% polyester jersey knit as a collector layer. Staiff, Davis, and Stevens (1982) used squares of alpha cellulose as a collector layer. Glassine weighing paper was used as backing under the alpha cellulose squares.

Kawar, Gunther, Serat, and Iwata (1978) studied the penetration of soil dust through woven and nonwoven fabrics. They used a multilayer fabric assembly consisting of the test fabric, filter paper, and aluminum foil held together in a specially fashioned holder.

Circular embroidery hoops were used by Orlando et al. (1981) for holding the fabric assemblies together. Branson et al. (1986) sandwiched the fabric assembly between two

metal plates. The top plate featured a circular hole for fabric contamination. Staiff et al. (1982) placed the fabric assemblies on plywood sheets and sealed the edges with masking tape. Kwar et al. developed a special shaking device for agitating the dust placed on the sample.

Methods For Contaminating The Samples. In order to simulate actual deposition conditions, researchers have used different methods for contaminating fabric specimens. Orlando et al. (1981) used the Beltsville experimental sprayer for depositing field strength pesticide using a nozzle on the test fabrics. Leonas (1985) used a table top adaptation of the Beltsville spray system which had an enclosed spray chamber designed to simulate field conditions of air blast spraying. Staiff et al. (1982) used a hand held sprayer to simulate light and heavy drift exposure. For assessing resistance of fabrics to aerosol sprays, Hobbs, Oakland, and Hurwitz (1986) used an airless spraying device for contamination of fabrics. The design of her aerosol spray test was based on ASTM method of salt spray test [fog testing (B117-7 1979)]. Branson et al, (1986), Branson and Rajadhyaksha, (1988) and Lillie, Livingston and Hamilton (1981) contaminated the fabrics by pipetting known volumes of pesticides on the fabric surface.

Methods For Measuring Pesticide Penetration. Quantification of pesticide residues is often done by using gas

chromatography techniques (Orlando et al., 1981), (Leonas, 1985). Branson et al. (1986) used C 14 isotopically labelled pesticide formulations for contaminating the fabrics, followed by scintillation counting for residue analysis. Hobbs et al. (1986) added methylene blue dye to the pesticide. The collector layer was examined visually for the blue stain, instead of being analyzed quantitatively for pesticide residue. This method cannot be used in comparative analyses, as it does not measure amount of pesticide extracted.

Factors Affecting Pesticide Penetration

Pesticide formulation, concentration, volume, and particle size all have impact upon the amount of pesticide penetration that occurs through fabrics.

Emulsifiable concentration (EC) formulations have been found to wet fabrics more readily than wettable powder (WP) or encapsulated materials (ENC) formulations (Laughlin, Easley, Gold, and Hill, 1985). Laughlin et al. (1985) also found significant differences between wicking and penetration properties of fabrics when EC, ENC and WP formulations were used. Laughlin suggests that EC formulations wetted and wicked most and also achieved most penetration as they have higher levels of surfactants or carrier solvent ingredients. These help in reducing the

surface tension of the fabric and thus increases penetrability. Slowest wicking time and lowest penetration levels were observed in ENC formulations, which could be attributed to the microencapsulated composition or less surfactant in its formulation. Staiff et al. (1982) also found EC formulations to achieve most penetration when they compared the penetration achieved by wettable powder, emulsifiable concentrate and flowable formulation for the same pesticide. Here WP formulations resulted in the lowest amount of penetration.

Branson et al. (1986) found a selected laminated fabric to be an effective barrier to pesticide penetration when field strength pesticides were used for contamination. However, in follow up work with a full strength pesticide Branson et al. (1988) found that the pesticide penetrated the same laminated fabric. Although the same pesticide was not used in both studies, these results suggest that the higher pesticide concentration maybe responsible for the decreased protection offered by the laminated fabric.

Branson et al. (1986) found pesticide volume to be a critical variable in determining effectiveness of protective fabrics. In general, an increase in pesticide volume resulted in a decrease in degree of protection offered by fabrics.

Pesticide penetration is also influenced by the particle size. The larger the particle, the more difficult

it is to achieve penetration. Particle size depends upon the spray and pesticide formulation. Kwar et al. (1978) reported that parathion mixed dust resulted in higher "PPM" levels with decrease in particle size. Kwar concluded that fine dust particles penetrating workers' clothing are likely to carry more toxicity per unit weight than coarse particles.

Awareness about the importance of protective clothing in limiting dermal exposure to pesticides has lead to the evaluation of all types of fabrics (wovens, nonwovens and knits) for finding materials that offer complete protection against dermal pesticide exposure. No fabric has yet been able to provide 100 percent protection but researchers have been able to identify fabrics that offer high levels of protection amongst currently available fabrics. The pesticide barrier protection property in fabrics is influenced by the fiber content, fabric structure, fabric construction, its thickness, air permeability and fabric surface treatments.

Lillie et al. (1981) evaluated clothing frequently worn by pesticide applicators for their ability to resist pesticide penetration. He found that 100 percent polyester fabrics offered less protection than 100 percent cotton fabrics against chlordane, diazinon, carbaryl and prometon pesticides. 100 percent polyester fabrics were penetrated to a much larger extent by all the pesticides than 100

percent cotton fabrics. However, the cotton fabrics in this study had a different yarn count and weighed more than the polyester fabric. Freed, Davies, Peters, and Parveen (1980) found that 100 percent cotton fabrics provided better resistance to pesticide penetration than 65 percent polyester/35 percent cotton denim fabric.

Laminated fabrics Gortex, a disposable nonwoven fabric Crowntex and Tyvek, a 100 percent olefin spun bonded nonwoven fabric were observed to give twenty five times more protection than treated chambray fabrics by Orlando et al. (1981). Jersey knit fabrics were completely penetrated by pesticide laden dust, as they allowed greater air flow than other materials tested by Kwar et al. (1978). Nonwoven fabrics were also found to be effective barriers to dust laden pesticide penetration by Kwar et al. (1978). In his study he found that the tested nonwoven fabrics allowed only .5 percent penetration of dust laden pesticide. Hobbs et al. (1986) also found nonwoven fabrics to offer higher levels of protection against aerosol spray penetration than woven fabrics. Serat, Vanloon, and Serat (1982) found 4 of the 5 nonwoven fabrics they tested, to offer more protection than knitted or woven fabrics.

Raheel and Gitz (1985) found drop absorbency rates to be higher in fabrics which had large interfiber and interyarn capillaries. Higher levels of wicking were observed in fabrics with small interfiber and interyarn

capillary radius. Fabrics that have smooth yarns, highly twisted fine yarns and dense weaves are likely to have higher levels of wicking. Properties of absorption and wicking both influence penetration levels. A tightly woven fabric with long smooth yarns will wick more due to the close packing of yarns (Freed et al., 1980). Wicking action moves the fluids closer to the skin, so closely woven fabrics will allow higher degree of pesticide transportation to undergarments and the skin. However, Serat (1982) found a cotton /polyester blend in tightest weave to be most restrictive towards pesticide deposition and retention.

Leonas (1985) found fabrics with twill construction to offer more protection than fabrics with plain construction. However, the thickness of fabrics with twill construction was more than the thickness of plain woven fabric. The different performance of the fabrics can be partially accounted for by the difference in thickness (Leonas, 1985, pg. 98). It has been shown that increase in fabric thickness leads to decrease in pesticide penetration (Leonas 1985). She also found that increase in fabric air permeability led to increase in pesticide penetration.

Water repellent, soil repellent, soil release, and fluorocarbon Scotchgard R finishes have been found to offer higher levels of protection against pesticides than unfinished fabrics. Laughlin et al. (1985) have shown that

fluorocarbon soil repellent finishes on fabrics increase the amount of protection offered by the fabrics. In fact Laughlin reports that for fabrics' treated with soil repellent finish, the initial pesticide contamination was only 20 percent that of the untreated fabrics. Durable press finishes were seen to enhance pesticide penetration by Leonas (1985). The fluorocarbon repellent finish, reduced penetration in light weight fabrics up to 50 percent (Leonas, 1985). Finished fabrics of heavier weights did not show as much reduction in pesticide penetration. Soil release finish applied on light weight fabric also reduced pesticide penetration up to 50 percent. When fabrics were coated with a nonporous coating, pesticide penetration was completely eliminated (Leonas, 1985). Kavar et al. (1978) observed up to sixty percent reduction in penetration of pesticide laden dust in fluorocarbon treated woven fabrics than untreated fabrics. Significant differences in levels of pesticide penetration between fluorocarbon treated and untreated chambray were observed by Orlando et al. (1981).

Fluorocarbon finishes on fabrics can lower surface energy of the fabric. Thus difference in surface energy of pesticide spray and fabric is increased. Increase in interfacial tension between the two surfaces leads to the likelihood of decrease in pesticide penetration. Freed et al. (1980) found that aqueous based fluoroaliphatic

formulation based finishes provided higher repellency than solvent based formulations. Scotchgard R finishes could offer up to sixty three percent repellency to pesticides and could reduce penetration rates.

CHAPTER III

PESTICIDE AND FLAME PROTECTION CHARACTERISTICS OF CANDIDATE MATERIALS FOR AERIAL APPLICATOR PROTECTIVE CLOTHING (MANUSCRIPT FOR PUBLICATION)

Abstract

Pesticide aerial applicators need clothing that protects them against hazards of dermal pesticide exposure as well as fire. A two phase study was conducted to evaluate six flame resistant fabrics on the above two protective properties in order to make recommendations for developing protective clothing for aerial applicators. Phase I evaluated the barrier protection property of the fabrics to full strength EC formulation of malathion. Phase II examined the fire protection properties of the fabrics at two flame exposure levels using Federal test method 5903.

Fabric 2, an aramid, with a water repellent surface finish of Shellite was found to possess the most superior pesticide barrier protection property. Fabrics 4, and 6 offered the highest levels of flame protection as they

exhibited no after-flame time, low after-glow time and minimal char lengths. The level of protection offered decreased with longer flame exposures in five test fabrics.

Findings of this research suggest that none of the test fabrics offered high levels of protection against both the hazards of pesticide penetration and fire. Hence, recommendation regarding suitability of one particular fabric cannot be made. Fabrics 5 and 1 should not be considered for use in aerial applicators' protective clothing without modification as both fabrics allowed as much as 37-45 percent pesticide penetration. Fabric 5 had the most after-glow time while fabric 1 had longest char lengths for the 30-second exposure.

Introduction

Widespread pesticide use in modern agriculture places agricultural workers at risk of pesticide exposure, which is potentially hazardous to human health. As much as two-thirds of pesticide application in the United States is done aerially [2]. Pesticide exposure in aerial applicators has been reported by several researchers [6,7]. The routes for pesticide exposure in humans could be oral, respiratory or dermal, however, dermal pesticide absorption has been reported to account for as much as 97 percent of the pesticide detected in the human body [5]. Aerial

applicators' dermal exposure to pesticides would be reduced if their clothing prevented contact between the skin and the pesticides. Fabrics with high barrier protection properties to pesticides would be suitable candidates for aerial applicators' protective clothing.

However, the aerial applicators face another occupational hazard, that of fire. Aerial applicators fly their aircrafts fairly low and close to the ground, in order to spray the target fields accurately. This can be hazardous. In fact, figures compiled from the World of Agricultural Aviation [16, 17, 18, 19] show that as many as 5523 accidents involving aerial applicators have been reported between 1970 and 1983. As the aerial applicators fly fairly low it would be possible for them to survive the crash impact in event of an accident. However, the possibility of post crash fires remains a major threat to their lives.

While developing protective clothing, the level of complexity of the hazard determines the kind of protection sought [15]. Since aerial applicators face dual hazards their protective clothing would need to protect them against dermal exposure to different chemical classes and strengths of pesticides as well as against burn injuries. The extent of protection offered by protective clothing would largely depend on the clothings' ability to resist pesticide penetration and flames' as well as reduce heat

transfer to the skin.

The amount of pesticide which passes through the fabric surface is influenced by the characteristics of both the pesticides as well as the fabric. Pesticide characteristics affecting penetrability include: pesticide formulation, concentration, volume, chemical class, other ingredients in the pesticide mixture and particle size. Some of the characteristics responsible for higher penetrability are EC formulations [10], full strength concentration of pesticides [4], increased pesticide volume [3], and finer dust particles [9].

Fabric characteristics that have been shown to influence pesticide barrier protection include fiber content, fabric structure, construction, thickness, air permeability and fabric surface treatments. Enhanced barrier protection properties have been observed in laminated fabrics [13], nonwoven fabrics [8,9], fabrics with Fluorocarbon finishes [9], and fabrics with water repellent and soil release finishes [10,11]. Fabrics with twill construction were seen to provide more protection than fabrics of plain construction [11]. Pesticide penetration was seen to decrease with increase in fabric thickness [11]. Increase in air permeability was observed to decrease the pesticide barrier protection property in fabrics [11]. Fabrics containing cotton allowed less pesticide penetration than fabrics made of 100 percent

polyester [11].

The function of protective clothing in any thermally hazardous environment is to protect the wearer against burn injury. Although protective clothing can be designed to protect the wearer against specific hazards of heat and fire, clothing made for either situation would need to be made of materials that do not flame or catch fire and have sufficient insulating values so that heat transfer to the skin sufficient to cause burn injury is not allowed.

Performance of protective clothing in heat/flame environments depends upon the interaction between properties of the thermal environment and the fabric. It is the thermal hazard which determines the type and level of protection sought. Clothing made with fabrics with certain characteristics may provide excellent protection against a specific thermal hazard but may fail to provide any protection against another heat/ fire hazard. Thus, while developing protective clothing for any heat/fire hazard a careful evaluation of the worker's occupation, type of heat/flame source, amount of heat flux and maximum exposure likely to occur should be done [1]. Based on this evaluation, good candidate materials would be fabrics with characteristics that would offer highest levels of protection for that specific hazard.

The test methods for evaluating fabrics' can be categorized into flammability tests and heat transfer and

burn injury tests. Usually fabrics are first tested for their flame behavior. If they exhibit high levels of resistance to flames then they are further tested for heat protection properties for specific heat hazards.

The purpose of this study was to determine the effectiveness of six selected test fabrics as barriers to one pesticide and two flame exposure times. The study was viewed as a preliminary investigation into the problem of providing for the dual challenges of pesticide and flame protection in one fabric. A two phase study was conducted to meet this objective.

Procedures

Phase I Experimental Design

The study was conducted as a 6x1 completely randomized experimental design with three replications. The independent variables were the test fabrics and the pesticide used for the study.

Test Fabrics. Three of the test fabrics, Omniweave Nomex III Aramid (fabric 1), S/333 Nomex III Aramid (fabric 2), and Nomex III Aramid Denim (fabric 3) were made of aramid fibers. Fabric 4, Siltemp 84 CH, came from the family of silica textiles. PBI, fabric 5, was a blend of PBI and Kevlar fibers, while Flextra 42A060, fabric 6, was

an intimate blend of aramids, such as Kevlar and Nomex, wrapped around a Fiberglass core. Physical characteristics of the test fabrics have been given in Table I.

Pesticide. The pesticide used in the study was a commercial grade emulsifiable concentrate formulation of malathion, 57 percent active ingredient, xylene, 30 percent, and inert ingredients, 13 percent. It is from the organophosphate family of pesticides. Malathion was selected as a representative pesticide as it is frequently sprayed by aerial applicators.

Dependent Variable. The degree of barrier protection offered against pesticide penetration was measured by doing a gas chromatography analysis on the pesticide residue collected from a gauze collector layer placed beneath the fabric.

Protocol. The test method for determining the pesticide barrier properties of the test fabrics was adapted from Branson et al. [3]. The test procedure was the same, except that the fabrics were not contaminated with radio-labeled pesticides and the residue analysis was done by gas chromatography instead of scintillation counting. The test fabrics were given a prewash in distilled water at 25°C for 300 seconds and air dried. Fabric samples were cut in such a way that no sample contained the same warp and weft yarns. Fabric swatch edges were sealed by applying a narrow bead of seam sealer to prevent migration of

pesticide from the original contact location. The conditioned fabric assembly included the prepared test fabric sample, multiple gauze layers, and aluminum backing. These were placed between two, 50.8 mm square aluminum plates and secured with metal clamps. The top plate had a circular opening to permit pesticide contamination by pipet.

A hundred microliter Hamilton syringe was used to pipet 100 microliters of full strength malathion onto the test fabric surface. The contaminated fabric assemblies were disassembled after 28000 seconds. This time interval was chosen to simulate the approximate time period that an aerial applicator might typically wear his clothing before changing. The test specimens and gauze layers were separated and the gauze layer was placed in labelled amber colored bottles containing 50 ml. of acetone. These bottles were capped and placed in the refrigerator for about 28800 seconds to begin pesticide residue extraction. The extraction procedure was completed by shaking the bottles for 5400 seconds on a mechanical shaker.

The extracted pesticide residue was analyzed by a Tracor 560 Gas Chromatograph equipped with flame ionization detector. The glass chromatograph column was packed with liquid phase 5 % OV-1 on 80/100 mesh size supelcort. The carrier gas was helium, set at a flow of 37 ml/minute. The flame was fueled with air 300 ml/minute

and hydrogen 20 ml/minute. The selected conditions were oven temperature 200°C, injection pore 250°C and flame detector 226°C. Injections of 1 microliter of the pesticide residue were made on the gas chromatograph and the amount of pesticide residue in micrograms was calculated.

Phase II Experimental Design

A completely randomized 6x2 experimental design with five replications was used to study the flame protection properties of the selected test fabrics. The test fabrics were the same as those in Phase I. The dependent variables were char length, after-flame time and after-glow time. Char length is the distance from the end of the specimen, which was exposed to the flame, to the end of a tear (made lengthwise) of the specimen through the center of the charred area. After-flame time is time for which the specimen continues to flame after the burner flame is shut off. After-glow time is the time the specimen continues to glow after it has ceased to flame.

Analysis of variance and Duncan's multiple range tests were used to determine if the observed differences in the means of after-glow time and char length were significantly different. A two sample t test was used to see if differences between means of after-glow time and char length for the 12 second flame exposure were statistically

different from the means for the 30 second flame exposure.

Protocol. The test fabrics were subjected to the vertical flammability test, Federal Government Test Standard, 191-5903. This test involves exposing vertical strips of 304.8 mm x 50.8 mm fabric swatches to a controlled flame source for a 12 second exposure. The test is applied to fabric swatches cut with the longer edge parallel to the warp direction as well as a set of fabric swatches cut with the longer side parallel to the weft direction. The test fabrics were also subjected to a 30 second flame exposure to determine differences that might exist in the fabrics' flame protection properties when exposed to the flame source for a longer period of time. This time period also seemed to be a more realistic estimate of the time required to escape from a burning aircraft.

Results and Discussion

Pesticide Barrier Protection

The mean percent pesticide extracted from the gauze layers for the three replications is given in Table II. Anova results for pesticide penetration (Table III, row 1) revealed that the observed differences were statistically significant with a F value of 13.16 and p of .0002. The

Duncan's multiple range analysis revealed four groupings, with fabric 2, an aramid fabric with a Shellite finish, exhibiting significantly less pesticide penetration than the other five fabrics (Table II). Less than one percent of the full strength malathion was detected in the collection layer beneath fabric 2.

The superior performance against pesticide penetration observed in fabric 2 can be possibly attributed to the water repellent surface finish applied to it. Fabrics 1 and 3 which were made of similar blends but were treated with wickwell finish, allowed considerably more pesticide penetration. Wickwell finish is designed to improve the comfort properties, but it probably caused an increase in pesticide penetration due to enhanced wicking.

Maximum pesticide penetration (44.8 percent) was found for fabric 5 which was a PBI/Kevlar blend. Low fabric weight of only 152.60 g/m^2 could be one of the factors contributing towards this high pesticide penetration. Fabric 5 offered lower protection against pesticide penetration than fabrics 2, 3, 4, and 6, however, its mean was not different from that of fabric 1, an aramid fabric. Fabric 6, which was a blend of aramids wrapped round a Fiberglass core offered higher protection levels than fabric 5 and fabric 1. Mean pesticide residue percentages for fabrics 1, 3 and 4 were not different. Similarly, means for fabrics 3, 4 and 6 were not significantly different from each other.

Fire Barrier Protection

Twelve Second Exposure. None of the six test fabrics continued to flame after the flame source was removed. The Anova results for after-glow time and char lengths for both directions revealed statistically significant differences, as shown in Table III. The results from the Duncan's multiple range test for after-glow time for the twelve second exposure are given in Table IV. Fabric 5, a PBI/Kevlar blend had the highest mean after-glow time of 31.79 seconds in the warp direction and 27.81 seconds in the filling direction. Means of the remaining five fabrics ranged from 0.0 seconds to 2.75 seconds (both directions) and were not significantly different from each other.

Table V which presents Duncan's multiple range test results for char lengths for 12 second flame exposure, shows that 4 groupings were determined. In the warp direction fabric 2 possessed the highest mean char length of 28.85 mm. This was followed by fabrics 1 and 3 which were in the same group and had means of 20.9 mm and 21.94 mm. Fabrics 5 and 6 were in the third group having means of 7.11 mm and 3.25 mm. Fabric 4, a fabric made of silicon dioxide exhibited no char length. However, means of fabrics 4 and 6 were not significantly different. In the filling direction the Duncan's multiple range test indicated that means of fabrics 4 and 6 were not different enough to be

statistically significant, this group offered the highest level of protection in terms of char length. Fabric 5 offered the second best performance with a mean char length of 7.72 mm. Means between fabrics 6 and 5 were not statistically different. Fabric 1 had the most mean char length, 26.00 mm, and offered lower protection than fabrics 3, 4, 5, and 6. Fabric 2, with 24.9 mm char length was grouped with fabric 1 as its mean was not different from fabric 1. Similarly means of fabrics 2 and 3 were not statistically different.

Thirty Second Exposure. No after-flame was observed in any of the test fabrics even with the longer flame exposure. Anova results for after-glow time and char length showed statistically significant differences for both warp and filling directions, as shown in Table III. Results of Duncan's multiple range test for after-glow time for the thirty second flame exposure (Table VI) indicated that the performance of fabric 5 was significantly poorer than the other five fabrics. The mean after-glow time for fabric 5 was 35.88 seconds in the warp direction and 27.17 seconds in the weft direction. None of the other fabrics exhibited significant differences in their means, which ranged from 48 seconds to 3.14 seconds.

Duncan's multiple range test results for char lengths as shown in Table VII, determined four groupings for the warp direction specimens means. The group offering most

protection included fabrics 4 and 6, with means of 0 and 4.06 mm. Fabric 5 had a mean char length of 11.79 mm and offered the second best level of protection. This was followed by the group including fabrics 2 and 3 with means of 36.58 mm and 35.97 mm. Fabric 1 an aramid of nomex /kevlar blend with 40.84 mm mean char length offered least protection.

Results of Duncans' multiple range test for the filling direction show that again four groupings were determined. Fabrics 4 and 6 were placed in the same group and they offered the highest levels of protection. Their means were 0.0 and 4.27 mm. This was followed by fabric 5 with 11.79 mm mean char length. Fabric 3 with mean char length of 30.89 mm was next, its mean was not different from the mean of fabric 2 (36.37 mm). Difference between the means of fabric 1, mean 39.62 mm, and fabric 2, mean 36.37 mm were not statistically significant and this group offered the least protection.

Comparison of Results for Different Exposure Time. In order to determine the effect of a longer flame exposure time on the test fabrics and to determine if differences in levels of protection could be observed, a two sample t-test for each test fabric specimen for after-glow time and char length was performed. The test was applied at alpha .01 with 8 degrees of freedom for each fabric sample. In the (Table VIII) warp direction there was a significant

difference for after-glow time for only fabric 4. With the 30 second flame exposure, the after-glow time increased thus decreasing the level of protection afforded by fabric 4. In the filling direction significant differences were found for fabrics 1 and 4, with increased flame exposure resulting in increased after-glow time for these fabrics.

In the warp direction significant differences for char length were found for fabrics 1, 3 and 5, indicating that longer flame exposure resulted in increased char lengths for the above fabrics. In the filling direction, fabrics 1, 3, 5 and 6 exhibited significant differences, with increased char lengths found with increased flame exposure. Char lengths were not significantly different for both warp and filling direction for fabric 2 and 4. However, for fabric 2 there was an increase in char length for the thirty second exposure but it was not significantly different from the char length for the twelve second exposure.

Summarizing Phase II results in terms of after-flame time, after-glow time and char length, fabric 4 and fabric 6 exhibited superior fire protection properties. This finding for fabric 4 can be possibly attributed to its fiber content of silicon dioxide. The product information provided by the manufacturer reports that this fabric will not melt until temperatures exceed 1600°C. In this study, fabric 4 had the least after-glow time for twelve second

flame exposure and had zero or minimal mean char lengths when subjected to twelve as well as thirty second flame exposures. Fabric 4 also did not show any difference in level of protection for char length with longer flame exposure. It did exhibit tendencies of increased after-glow time for longer flame exposure, but its after-glow time for twelve second exposure was lower than all other fabrics. Its after-glow time for thirty second exposure was not significantly different from four other test fabrics in its group, see Table IX.

The superior flame protection performance exhibited by fabric 6 could also be attributed to its unique fiber structure and fiber content. According to the product information supplied by its manufacturer, fabric 6 is an intimate blend of aramids such as kevlar/nomex wrapped around a fiberglass core. This fabric also does not melt up to 538^oC. The after-glow time for both flame exposures ranged from 1.61 seconds to 2.8 seconds, and the after-glow time did not increase with longer exposure time. Its performance level for char length was comparable to that of fabric 4, as Duncan's multiple range test placed both fabrics in the same group. It did exhibit increased char lengths with longer flame exposure time, but the char lengths for this fabric for both flame exposures were considerably less than the char lengths for the other four fabrics.

Fabric 5, the PBI/Kevlar blend offered good protection

on the after-flame time and char length variable but, it had high after-glow time. The three Aramid fabrics (1, 2, and 3) as a group performed well on the after-flame time and after-glow time measures. However, they had longer char lengths than the other fabrics tested.

Conclusion

Each phase of the research identified fabrics that possessed excellent barrier properties. However, none of the fabrics tested offered excellent protection against both pesticide penetration and fire. Fabric 2 exhibited excellent pesticide barrier protection properties but exhibited long char lengths. Fabrics 4 and fabric 6 offered high levels of flame protection, as they had no after-flame time, low after-glow time and minimal char lengths. However, both fabrics allowed between 23 to 28 percent pesticide penetration.

Findings of this study also indicated that fabrics 5 and 1 would be unsuitable without modification for use in aerial applicators protective clothing, as both fabrics exhibited high levels of pesticide penetration (37 to 45 percent). Fabric 5 had no after-flame time, low char lengths and high after-glow time. Differences in levels of protection for char length were also found. Fabric 1 had no after-flame time, and after-glow time comparable to other

four fabrics. However, it had the longest char lengths (with the exception of the 12 second-warp specimens) and its after-glow time and char length increased with the 30 second exposure.

It would seem that the char length is a better indicator of the protection that could be anticipated in a real fire situation. Visual examination of aramid fabric samples after flame exposures revealed a charred and brittle appearance and a tendency to crumble. This raises questions regarding their ability to protect the skin against burn injuries, even if they satisfactorily meet the passing criteria specified by some standards for protective clothing used in thermally hazardous occupations. The NFPA [12] standard structural fire fighters clothing specifies that all fabrics to be used in fire fighters protective clothing should possess after-flame time of less 2 seconds and char length of less than 100 mm when tested by federal test methods 5903. All the fabrics tested in this study could have easily passed this standard, however, a brittle fabric with a tendency to crumble would expose the skin to the flames and cause burn injury. Fabric strength and integrity after flame exposure are important factors influencing the protection offered by the fabrics. These factors should be considered while assessing flammability test results.

The finding that five of the test fabrics showed an increase in after-glow time or char length when

subjected to thirty second flame exposure, suggests to the need for more stringent flammability tests. It also points to the fact that the protective characteristics of fabrics exposed to extreme flames as in case of a plane crash cannot be accurately assessed based on the prescribed twelve second flame exposure in the Federal test method.

Future research could focus on enhancing the barrier protection properties against pesticide penetration for fabrics (4,5 and 6) that exhibited good resistance to charring. The Shellite water repellent finish could be applied on the above fabrics for enhancing their pesticide barrier properties. It would be of importance to know if fabrics finished with the Shellite finish offered excellent protection against pesticide penetration to pesticides of other classes, formulations and concentrations. Ability of Shellite finished fabrics to provide continued excellent protection after repeated laundry needs to be investigated.

Fabric 4 is currently not suitable for use in clothing due to its poor seam and abrasion resistance. Research needs to focus on making this fabric suitable for use in clothing.

Table I. Physical characteristics of the test fabrics.

Fabric	Blend	Weave	Weight	Finish
1 - Omniweave nomex.	95% nomex/ 5% kevlar	plain	203.46g/m ²	wickwell
2 - S/333 nomex	95% nomex/ 5% kevlar	duck	203.46g/m ²	shellite
3 - Denim nomex	95% nomex/ 5% kevlar	twill	288.24g/m ²	wickwell
4 - Siltemp 84CH	98% amorp- hous silicon dioxide	satin	610.38g/m ²	hydro- carbon
5 - PBI	40% PBI/ 60% kevlar	Twill	152.60g/m ²	---
6 - Flextra 42A060	Aramids such as kevlar and nomex wrapped around a Fiberglass core	Twill	322.15g/m ²	weave set

Table II. Mean percent pesticide penetration and Duncan's multiple range test groupings.

Variable	Mean % Pesticide	N	Duncan's Grouping*
Fabric 5	44.8	3	A
Fabric 1	36.6	3	A, B
Fabric 4	28.4	3	B, C
Fabric 3	23.8	3	B, C
Fabric 6	22.7	3	C
Fabric 2	0.7	3	D

* Means with the same letter are not significantly different at 0.05 level.

Table III. Anova Table.

Variable	Source	Degree of Freedom	Mean Square	F-Value	P-Value
Pesticide% in gauze	Fabric	5	675.843	13.16	.0002
After-Glow 12 second exposure	Warp	5	810.205	81.22	.0001
	Weft	5	616.704	22.07	.0001
After-Glow 30 second exposure	Warp	5	985.790	15.57	.0001
	Weft	5	574.028	14.96	.0001
Char Length 12 second exposure	Warp	5	6.686	39.88	.0001
	Weft	5	6.278	28.41	.0001
Char Length 30 second exposure	Warp	5	16.191	161.11	.0001
	Weft	5	14.388	57.36	.0001

Table IV. Duncan's multiple range test results for twelve second exposure after-glow time.

Variable	Mean (seconds)	Number	Duncans Grouping*
<u>Warp Direction</u>			
<u>After-Glow Time</u>			
Fabric 5	31.79	5	A
Fabric 6	1.61	5	B
Fabric 3	0.92	5	B
Fabric 1	0.31	5	B
Fabric 2	0.27	5	B
Fabric 4	0.20	5	B
<u>Weft Direction</u>			
<u>After-Glow Time</u>			
Fabric 5	27.81	5	A
Fabric 6	2.75	5	B
Fabric 3	0.54	5	B
Fabric 2	0.32	5	B
Fabric 1	0.00	5	B
Fabric 4	0.00	5	B

* Means with the same letter are not significantly different at 0.05 level.

Table V. Duncan's multiple range test results for twelve second exposure char length.

Variable	Mean (mm)	Number	Duncan's Grouping*
<u>Warp Direction</u>			
<u>Char Length</u>			
Fabric 2	28.85	5	A
Fabric 3	21.94	5	B
Fabric 1	20.90	5	B
Fabric 5	7.11	5	C
Fabric 6	3.25	5	C , D
Fabric 4	0.00	5	D
<u>Weft Direction</u>			
<u>Char Length</u>			
Fabric 1	26.00	5	A
Fabric 2	24.90	5	A , B
Fabric 3	19.10	5	B
Fabric 5	7.72	5	C
Fabric 6	2.64	5	C , D
Fabric 4	.20	5	D

* Means with the same letters are not significantly different at 0.05 level.

Table VI. Duncan's multiple range test results for thirty second after-glow time.

Variable	Mean (seconds)	Number	Duncan's Grouping*
<u>Warp Direction</u>			
<u>After-Glow Time</u>			
Fabric 5	35.88	5	A
Fabric 3	3.14	5	B
Fabric 6	2.80	5	B
Fabric 4	0.80	5	B
Fabric 2	0.66	5	B
Fabric 1	0.60	5	B
<u>Weft Direction</u>			
<u>After-Glow Time</u>			
Fabric 5	27.17	5	A
Fabric 6	2.36	5	B
Fabric 4	0.86	5	B
Fabric 2	0.60	5	B
Fabric 3	0.59	5	B
Fabric 1	0.48	5	B

* Means with the same letters are not significantly different at 0.05 level.

Table VII. Duncan's multiple range test results for thirty second exposure char length.

Variable	Mean (mm)	Number	Duncan's Grouping*
Warp Direction			
Char length			
Fabric 1	40.84	5	A
Fabric 2	36.58	5	B
Fabric 3	35.97	5	B
Fabric 5	11.79	5	C
Fabric 6	4.06	5	D
Fabric 4	0.00	5	D
Weft Direction			
Char Length			
Fabric 1	39.62	5	A
Fabric 2	36.37	5	A , B
Fabric 3	30.89	5	B
Fabric 5	11.79	5	C
Fabric 6	4.27	5	D
Fabric 4	0.00	5	D

* Means with the same letter are not significantly different at 0.05 level.

Table VIII. Table for two sample t test.

Fabrics	After-glow t- stat.	level of significance	Char length t- stat.	level of significance
Fabric 1 warp	1.825	.01	10.37	.01
Fabric 1 filling	3.533	.01	3.30	.01
Fabric 2 warp	1.27	.01	1.72	.01
Fabric 2 filling	.795	.01	2.28	.01
Fabric 3 warp	2.05	.01	5.07	.01
Fabric 3 filling	.120	.01	2.98	.01
Fabric 4 warp	4.17	.01	0.00	.01
Fabric 4 filling	4.88	.01	- 1	.01
Fabric 5 warp	.444	.01	3.94	.01
Fabric 5 filling	-.073	.01	2.90	.01
Fabric 6 warp	1.30	.01	1.37	.01
Fabric 6 filling	-.302	.01	3.63	.01

Table IX. Summary table.

Variable Tested	Fabrics					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
% Pesticide penetration	36.6	.72	23.8	28.4	44.8	22.7
Duncan's grouping	A B	D	B C	B C	A	C
<u>12 Second After-glow time (seconds)</u>						
Warp direction	.31	.27	.92	.20	31.8	1.61
Duncan's grouping	B	B	B	B	A	B
Weft direction	.00	.32	.54	.00	28.0	2.7
Duncan's grouping	B	B	B	B	A	B
<u>30 Second afterm-glow time (seconds)</u>						
Warp direction	.60	.66	3.1	.80	35.9	2.8
Duncan's grouping	B	B	B	B	A	B
Weft direction	.48	.60	.59	.86	27.2	2.4
Duncan's grouping	B	B	B	B	A	B
<u>12 sec. char length (mm)</u>						
Warp direction	20.9	28.9	21.9	0.0	7.11	3.3
Duncan's grouping	B	A	B	D	C	C D
Weft direction	26.0	24.9	19.1	.20	7.7	2.7
Duncan's grouping	A	A B	B	D	C	C D
<u>30 sec. char length (mm)</u>						
Warp direction	40.8	36.6	36.0	0.0	11.8	4.1
Duncan's grouping	A	B	B	D	C	D
Weft direction	39.6	36.4	30.9	0.0	11.8	4.3
Duncan's grouping	A	A B	B	D	C	D

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CHAPTER IV

SUMMARY, CONCLUSION, IMPLICATIONS AND RECOMMENDATIONS

The purpose of this study was to determine the effectiveness of six selected flame resistant test fabrics as barriers to one pesticide and two flame exposure times in order to make recommendations for candidate materials for development of aerial applicators' protective clothing. This study was conducted as a preliminary investigation into the problem of providing for the dual challenges of pesticide and flame protection in one fabric.

A two phase study was planned to meet the above research objective. Phase I investigated the pesticide barrier protection property of the test fabrics to full strength EC formulation of malathion. The test method used was adapted from Branson et al. (1984). The pesticide barrier protection property was evaluated by analyzing the pesticide residue from collector layers placed under the test fabrics, using gas chromatography. Anova and Duncan's multiple range test were the statistical techniques used for analyzing data.

Federal government test standard, 191-5903 was used to

evaluate the flame protection property of the test fabrics. This test was a vertical flammability test which involved exposing fabric swatches to a controlled flame source for a 12-second exposure. The after-flame time, after-glow time and char lengths were recorded for the 12-second flame exposure.

The test fabrics were also subjected to a 30-second flame exposure and the after-flame time, after-glow time and char length were recorded. The fabrics were subjected to a 30-second flame exposure to determine the differences that might exist in the fabrics' flame protection properties when exposed to a flame source for a longer period of time. This time period also seemed to be a more realistic estimate of the time required to escape from a burning aircraft. The statistical techniques used for data analysis included Anova, Duncan's multiple range test and the two sample t test.

Results for the pesticide penetration phase indicated that fabric 2, which was an aramid blend with a water-repellent finish called Shellite, offered the highest level of protection. Less than one percent of full strength malathion was detected in the collection layer under fabric 2. Fabrics 1 and 3 were made of similar blends but were treated with a wickwell finish allowed considerably more pesticide penetration than fabric 2. The wickwell finish is designed to improve the comfort properties of fabrics, but

it probably caused an increase in pesticide penetration due to enhanced wicking. Maximum pesticide penetration of 44.8 percent was detected for fabric 5 which was a PBI/Kevlar blend. This fabric offered less protection than fabrics 2, 3, 4, and 6, but its mean was not significantly different from the mean (36.6 percent) of fabric 1.

Results from the flammability test indicate that after-flame time was not observed for any of the test fabrics during either the 12- or 30-second flame exposure. Fabric 5, a PBI/Kevlar blend, exhibited the highest after-glow time ranging from 27.17 seconds to 35.88 seconds for the 12 and 30 second flame exposures. The mean after-glow times for all of the other fabrics were not significantly different from each other for both the flame exposures. The mean after-glow for the other five fabrics ranged from 0 seconds to 3.14 seconds for both flame exposures. Fabrics 4 and 1 showed significant differences between the mean after-glow time for the 12- and 30-second exposure. This indicated that increased flame exposure increased the after-glow time for the above two fabrics.

Fabric 4, made of silicon dioxide and fabric 6 made of aramids wrapped around fiberglass core had least mean char lengths for both flame exposures (0.0 mm to 4.27 mm). Fabric 4 showed no difference between mean char length for 12-second and 30-second flame exposure. Fabric 5, a PBI/Kevlar blend had char lengths ranging from 8 mm to 11 mm

for both flame exposures. Fabrics 1, 3, 5 and 6 had significant differences between the mean char lengths of the two exposure times. These results indicate that the above fabrics had increased char lengths for the 30-second flame exposure.

The mean char lengths for the three aramid fabrics ranged from 19.10 mm to 28.85 mm for 12- second exposure and 30.89 mm to 40.84 mm for 30- second exposure. Duncan's multiple range test placed the mean char lengths of the three aramid fabrics in either the group offering the least protection or in the group offering slightly higher protection for both flame exposures.

Summarizing the results of the flammability tests fabrics 4 and 6 offered high levels of protection as they had low after-glow time, no after-flame time and minimal char lengths. Fabric 5 performed well on the after-flame and char length but had highest after-glow time. The aramid fabrics 1, 2, and 3 had no after-flame time and low after-glow time but they had longer char lengths than the other fabrics tested.

Conclusion

This research study was successful in identifying test fabrics that provided highest levels of barrier protection against pesticide penetration, as well as fabrics that

offered high levels of protection against fire. Fabric 2 offered superior penetration protection for malathion but it exhibited long char lengths. Fabrics 4 and 6 offered excellent flame protection properties, as they had low after-glow time, minimal char lengths and no after-flame time for both flame exposures. However, both fabrics allowed between 23 to 28 percent pesticide penetration. As none of the fabrics offered superior protection against both pesticide penetration and fire, recommendations regarding any particular fabric as candidate material for aerial applicators protective clothing cannot be made.

The findings of this study also indicated that fabrics 5 and 1 would be unsuitable without modification in aerial applicators' clothing. Both the fabrics allowed considerable pesticide penetration. Fabric 5 had the highest after-glow time, while fabric 1 had longest char lengths for 30- second exposure. Significant differences were observed in the means between 12- and 30- second exposure for glow time (fabric 1) and char length (fabric 5 and 1).

Implications

The finding that five of the test fabrics showed either increase in after-glow time or char length when subjected to a 30- second flame exposure, points to the fact

that protective abilities of fabrics that would perform under extreme flame hazard like in case of a plane crash cannot be evaluated on the basis of the 12- second flame exposure prescribed by the federal test standard.

The above finding about decrease in level of protection with longer flame exposure also points to the need for more stringent flammability tests for fabrics performing under extreme fire hazards.

It would seem that char length would be better indicator of protection that could be anticipated in a real fire situation. Visual examination of the aramid fabrics after flame exposure revealed a charred and brittle appearance and tendency to crumble. This raises questions regarding their ability to protect the skin against burn injury even if they have satisfactorily meet the passing criteria set by some standards for hazardous occupations. The NFPA standard for structural fire fighters clothing is that all fabrics used in fire fighters clothing possess after-flame time of less than two seconds and char length of less than hundred mm. All the fabrics tested in this study would easily meet this standard, however, a brittle fabric with tendency to crumble would expose the skin to the flames and cannot protect against burn injury. In order to realistically evaluate the flame protection properties of fabrics performing in thermally hazardous environment fabric strength, and integrity after flame exposure need to

be included and considered in assessing flammability test results.

Recommendations for Future Research

1. The superior pesticide barrier protection property of fabric 2 needs to be verified by testing it with pesticides of different classes, concentrations, volume and formulations.
2. The superior flame protection properties of fabrics 4 and 6 should be further assessed under longer time intervals of flame exposure.
3. Fabrics exhibiting high flame protection properties should be subjected to heat transfer tests to assess their burn injury potential
4. Protective clothing in thermally hazardous occupations are generally multilayer systems. The fabrics with superior flame protection properties should be combined with various insulating materials and these combinations need to be evaluated for their flame /heat protection properties.
5. Fabric 2 exhibited excellent barrier protection properties against pesticide penetration, its fire protection performance could be possibly enhanced if fabric of higher weight were used.
6. Flame protection properties for fabric 2 need to be evaluated in a multilayer system to see if that improves

its performance.

7. Research also needs to focus on ways to improve the pesticide barrier protection property of fabrics 4 and 6. One of the ways for improving their performance would be to combine them with lining materials that provide high levels of protection against pesticide penetration.
8. The manufacturer of fabric 4 has indicated that at current time this fabric has only industrial applications due to its poor seam and abrasion resistance. Research could focus on removing these deficiencies as well as suggest other ways to make this fabric suitable for use in protective clothing.
9. The pesticide barrier protection property of fabric 4 and 6 could perhaps also be enhanced by reducing the fabrics air permeability, or by applying water repellent finishes on the fabric surface.
10. Aerial applicators protective clothing would have to withstand repeated washings. The effect of laundry on the pesticide and fire barrier properties needs to be studied.
11. The superior barrier protection against pesticide penetration exhibited by fabric 2 could be attributed to a water repellent surface finish called Shellite, which was applied on the fabric surface. It seems that char length is a better indicator of protection that could

be anticipated in a real fire situation. Possibility of improving pesticide barrier protection property of fabrics 4, 5 and 6 which performed well on the char length variable by treating them with Shellite finish needs to be investigated.

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