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Development of Combined Performance Fabrics

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Overview

The need to develop combined performance fabrics for protective clothing has existed for many years. The combinations of chemical barrier with comfort or chemical barrier with flame resistance have been pursued by many companies. Attempts have been made to place existing products into new performance areas with limited success.

Traditional film-based chemical protective clothing, first developed and introduced in the mid 1980s, provided a high level chemical permeation barrier but offered no comfort. In addition, because they were based on polyolefin composites would melt and burn when exposed to extreme heat and/or flame.

Metalized films combined with fire resistant or fire retardant fabric substrates have been used for flame and thermal protection for many years. These garments have been used in combination with other garments to protect against intense heat encountered in close proximity such as firefighting, kilns and smelters, and other situations. These garments have also been used as over-garments for chemical suits that burn and melt; however, users found these combinations bulky, cumbersome and more expensive.

The Product Development Process

Kappler utilizes a stage and gate process for product development. The stages are *idea, concept, development, launch and commercialization.* In the case of this development, we had some ideas around the concept of a fabric that would provide high level chemical permeation barrier and flame resistance, and potentially thermal protection. We knew the first step was to listen to the user.

Concept Stage—Evaluation of User Needs

In August of 2007, Kappler met with approximately fifteen safety officers and hygienists working in the petrochemical industry in Baton Rouge, Louisiana. The purpose of the meeting was to discuss unresolved needs and issues in their facilities. An interesting story developed regarding a unique hazard scenario that involved both a chemical challenge and a chemical flash fire hazard. The scenario involved a line break, which is an activity that requires the maintenance crews to open piping containing skin hazardous chemicals that could ignite if exposed to an ignition source. When faced with a line break situation, the users felt they had to choose between chemical protection or flash fire protection. In most all cases, the users opted to use firefighter turnout gear, even though the expensive turnout gear would have to be disposed if contaminated. They needed a garment made from a fabric that combined chemical protection and flash fire protection.

Concept Stage: Review of Performance Requirements

During development of a prototype fabric to meet the combined chemical and flame/thermal needs of this unique application, we reviewed the requirements of several different NFPA standards to establish a baseline for minimum performance requirements. Upon completion of this review, we focused on three NFPA standards, NFPA 1991, NFPA 1992 and NFPA 2112.

NFPA 1991

In 1985, the NFPA standards council approved a project for development of these standards and assigned the project to the Technical Committee on Fire Service Protective Clothing and Equipment. Two and one-half years later they issued NFPA 1991*, Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies.*

NFPA 1991 addresses vapor protective ensembles designed to protect emergency response personnel against exposure to specified chemicals in vapor and liquid splash environments during hazardous materials emergencies. It requires chemical permeation resistance testing for primary suit materials, which include garment, visor, gloves and boots. Permeation testing is conducted on twenty-one chemicals, including fifteen liquids and six gases, specified in ASTM F1001, *Standard Guide for Chemicals to Evaluate Protective Clothing Materials.* Material testing is also performed for burst strength, tear strength, abrasion resistance, flammability resistance, cold temperature performance and flexural fatigue.

Chapter 3 on Definitions provides the following:

> Chemical Flash Fire. The ignition of a flammable and ignitable vapor or gas that produces an outward expanding flame front as those vapors or gases burn. This burning and expanding flame front, a fireball, will release both thermal and kinetic energy to the environment.
>
> Flammable or Explosive Atmospheres. Atmospheres containing solids, liquids, vapors or gases at concentrations that will burn or explode if ignited.

Annex A provides the following additional information:

> Chemical Flash Fire. A policy of wearing protective clothing is needed that recognizes the significant threat to fire fighters who can be exposed to flash fires in either structural fire-fighting or hazardous materials environments. It is hoped that fire fighters utilize awareness training on burn injuries caused by the ignition of the environment. There is a distinct difference between chemical flash fires and flashovers occurring in structural fire-fighting environments.

The standard requires garment materials be tested for resistance to flame impingement in accordance with ASTM F 1358, *Standard Test Method for Resistance of Protective Clothing Materials to Flame Impingement*. It requires samples shall not ignite during an initial three second exposure, shall not burn a distance greater than four inches, shall not sustain burning for more than ten seconds, and shall not melt as evidenced by flowing or dripping during the subsequent twelve second exposure period. This requirement does not address the ability of the garment material to provide protection from heat or flame, rather just to show it would not contribute to the flame that already exists. In this method, sample garment materials are tested in a “folded edge” configuration.

The standard provides for optional chemical flash fire protection performance requirements for vapor protective ensembles and ensemble elements. The standard requires special labeling that states “limited chemical flash fire protection for escape only in the event of a chemical flash fire”.

The standard requires primary suit materials be tested for thermal protective performance (TPP) in accordance with ISO 17492 *Clothing for protection against heat and flame – Determination of heat transmission on exposure to both flame and radiant heat*, and shall have an average rating of not less than twelve when exposed to both flame and radiant heat.

The optional requirements include an overall ensemble flash test that involves placing a suited mannequin in the center of a flash chamber in an upright stationary position. The chamber is then filled with propane gas to a concentration sufficient to produce a visible chemical flash fire lasting seven seconds. The garment is then removed, and the mannequin and a gastight integrity test (pressure test) are performed on the garment. The standard requires the garment pass the test.

This method was developed and proposed during an ASTM symposium, *Performance of Protective Clothing: Challenges for Developing Protective Clothing for the 1990s*. The paper titled, “Developing and Selecting Test Methods for Measuring Protective Clothing Performance in Chemical Flashover Situations,” Stull, Veghte, Mann, and Storment, provided the results of a study that followed a two part approach. The first involved selecting a test for materials which simulates the relatively short, but high temperature exposure of a chemical flash. The phase involved comparing material performance in flame resistance, thermal protective performance (TPP), radiant reflectivity and small scale flash environment tests. The second part was aimed at conducting a whole ensemble test where the chemical protective suit was placed on a mannequin within an enclosed area which was then filled with propane and ignited. This test was developed such that the temperatures measured inside the suit can determine the extent of protection offered by the ensemble. The resulting overall condition of the suit is also a recommended means for assessing performance. Test data gathered showed conclusively the improved performance of materials that utilized an aluminized layer and/or two layers. In a subsequent revision of the NFPA 1991- 1995 edition, optional flash fire requirements were incorporated. The whole ensemble test was adopted, however, the entire issue of internal temperatures and survivability of the user was not considered by the committee. The only requirement was the post flash condition of the garment. This method has shown to be very difficult to perform, provide for inconsistent results, and never been adopted by ASTM, ISO or other standards organizations.

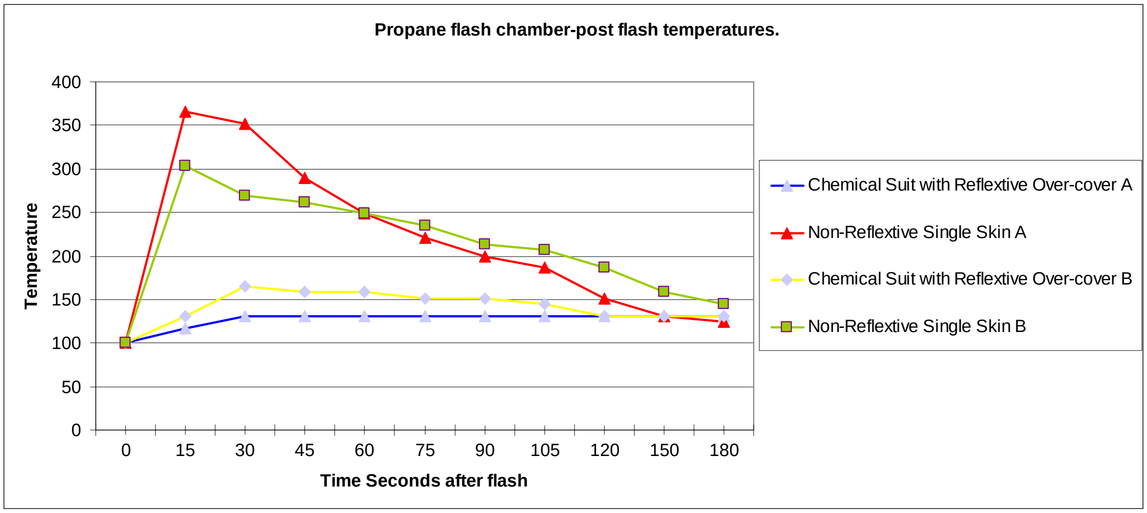

Figure 1. Propane Flash Temperatures

NFPA 1992

The technical committee also produced NFPA 1992, *Standard on Liquid Splash-Protective Ensembles and Clothing for Hazardous Materials Emergencies.* It addresses liquid-splash protective ensembles and clothing designed to protect against exposure to specified chemicals in liquid splash environments during hazardous materials emergencies. Chemical penetration resistance for five chemicals is required. It is structured similar to NFPA 1991 with respect to physical properties.

NFPA 2112

The NFPA Standards Council established the Technical Committee on Flash Fire Protective Garments in 1998. The technical committee produced two standards, one of which was NFPA 2112, *Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire*. Chapter Three on Definitions provides the following:

> Flame Resistance. The property of a material whereby combustion is prevented, terminated, or inhibited following the application of a flaming or nonflaming source of ignition, with or without subsequent removal of the ignition source.
>
> Flash Fire. A fire that spreads rapidly through a diffuse fuel, such as dust, gas, or the vapors of an ignitable liquid, without the production of damaging pressure.

Annex A provides the following additional information:

> Flash Fire. A flash fire requires an ignition source and a hydrocarbon atmosphere or atmosphere containing combustible finely divided particles (e.g., coal dust or grain) that contains a concentration above the lower explosive limit of the chemical. Both hydrocarbon and dust flash fires generate temperatures from 540 C to 1040 C (1000 F to 1900 F). A flash fire depends on the size of the gas or vapor cloud, and when ignited, the flame front expands outward in the form of a fireball. The resulting effect of the fireball's energy with respect to radiant heat significantly enlarges the hazard areas around the gas released.

This standard also requires fabric be tested for thermal protective performance (TPP), but deviates from the ISO 17492 and requires fabric has a “spaced” TPP rating of not less than twenty-five and a “contact” TPP of not less than 12.6.

It also requires fabric to be tested for flame resistance in accordance with ASTM D 6413, *Test Method for Flame Resistance of Textiles (Vertical Test).* It requires specimens have a char length of not more than four inches and an after-flame of not more than two seconds, and shall not melt and drip. In this method, garment materials are tested in a “straight cut edge” configuration.

It also requires fabric be tested for thermal shrinkage and shall not shrink more than ten percent in any direction.

NFPA 2112 requires garments be tested for overall flash fire exposure in accordance with ASTM F 1930, *Test Method for Evaluation of Flame Resistant Clothing for Protection Against Flash Fire Simulations Using an Instrumented Manikin,* and have an average predicted body burn rating of not more than fifty percent.

This method was also proposed during the same ASTM Protective Clothing Symposium in a paper titled, *Thermo-Man® and Thermo-Leg: Large Scale Test Methods for Evaluating Thermal Protective Performance*, Behnke, Geshury, Barker. These test systems provided for unique capabilities for evaluating the thermal protective performance of heat resistant garments in realistic simulations of fire hazard exposures. They utilized manikins or partial manikins that were surrounded by eight large industrial propane gas torches. The position and gas flow to the torches could be adjusted to deliver heat flux that varied but was set at 2.0 cal/cm2sec in order to simulate the flash fire conditions that might occur in a military or industrial accident. This exposure level is similar to the emergency fire hazard condition encountered by firefighters or the intensity of heat in a large pool fire and is equal to the TPP exposure specified in NFPA 1971, *Standard on Protective Clothing for Structural Firefighters.*

Each of the 122 heat sensors consists of a thermocouple embedded below the surface of an epoxy molded cone, which measures the temperature at a known depth. The authors of this paper were responsible for the development of copper calorimeters used on the ASTM F 1930 method today.

After completing the review and comparison of standards requirements, the testing required was summarized and is shown in Table 1:

	NFPA 2112	**NFPA 1991/1992**
SCOPE	**Flame Resistant Garments for Industrial Personnel Against Flash Fire**	**Vapor Protective Ensembles for Hazardous Materials Emergencies**
FLAME RESISTANCE	ASTM D 6413 Cut edge 12 sec w/ < 2 sec afterflame, < 4 in char length No melt or drip	ASTM F 1358 Folded edge 3 sec no ignition 12 sec w/ < 10 sec afterflame and char length < 4 inches
TPP	Spaced TPP > 25 Contact TPP > 12.6	Average TPP > 12

	NFPA 2112	**NFPA 1991/1992**
SYSTEM	ASTM F 1930 Pyroman 3 sec < 50% Body Burn	Chemical Propane Flashover 7 sec Pass Pressure Test 1991 Pass Shower Test 1992
HEAT STABILITY	500 degrees F for 5 minutes, < 10% shrinkage	Not applicable

Table 1. Comparison of Flammability Requirements

What came out of the concept stage was the development of two protective fabrics, the first that would be for the line break situations described by the petrochemical officers, that could be certified to NFPA 1992 and secondly, a hazmat fabric that would meet the requirements of NFPA 1991. Although we did not see the need for certification to NFPA 2112, the need to perform well in the pyroman testing was obvious.

Development Stage—Prototypes and Testing

In the beginning of development, two approaches were taken to obtain a heat sealed seam on the outer surface, which would be required for the level B splash application. Many types of heat seal tapes were evaluated to obtain seal to the aluminized surface. Although some produced reasonably good pristine seals, any amount of flexing, which would occur during use, would cause the seal to release. The second approach was to coat the aluminized film with another seal layer of a polyolefin. The general problem created is that the seal layer will burn away from the aluminized layer when exposed to flame impingement. At this point, we needed a way for something to absorb the heat energy away from the outer surface. We investigated the use of intermissence compounds, which have been used in the aircraft and aerospace industry. They behave in a way to prevent flammable materials from igniting and burning.

Development Stage—Design Verification

During the development process, multiple iterations of fabric design (including fire retardant treatment levels of the spunlace fabric) variations of thickness on the metalized film coating, and variations of the metalized thickness were produced. Multiple formulations of adhesive and thickness variations of the adhesive were also evaluated.

Extensive in-house and third party laboratory testing was conducted during development and at the conclusion to ensure the design input parameter were adequately verified. This testing included flame resistance to both ASTM F 1358 and ASTM D 6413. Sample results of this testing is shown in Table 2.

	ASTM 1358	**ASTM 6413**	**TPP Rating**	**Pyroman**
Reflective Chemical Splash Suit	Pass	Pass	16	<1%
Reflective Level A	Pass	Pass	16	0
Non-Reflective Chemical Splash Suit	Pass	Pass	19.9	16%

Table 2. Flame Resistance

We also needed to evaluate the whole suit performance specified by NFPA 2112 with the pyroman. Because of the expense and logistics of conducting this testing at a third party lab, we went back to the small scale flash chamber we developed in support of the ASTM paper. Based on knowledge obtained after review of ASTM 1930, copper calorimeters were obtained and the small scale flash chamber was modified to include twelve calorimeters, three each in three different towers. A multi-channel recorder was used to track the 12 different calorimeters and provide additional data that was beneficial. This allowed us to screen and compare many fabric combinations with immediate feedback. We found the testing in the small scale chamber correlated well against the results obtained in the full pyroman. The small scale chamber is shown in Figure 2.

Figure 2. Small Scale Flash Chamber

After several down-selections of the optimum combinations of film thickness, metalized thickness, adhesive formulation and treated spunlace, garments were produced and pyroman evaluations were conducted at North Carolina State University. Testing on the line break three piece garments were performed first. We were quite amazed at the results, considering the standard allows fifty percent body burn as acceptable and some competitive products on the market claimed results in the fifteen to twenty percent body burn range. Our three piece designs were providing protection levels of five percent body burn or less. One problem emerged in testing the gas tight garment as it had to be cut to be placed on the mannequin. This prevented us from performing a gas tight leak test after the flash exposure. The gas tight configuration provided less than one percent body burn protection. Pre and post flash pictures of the gas tight configuration are shown in Figure 3.

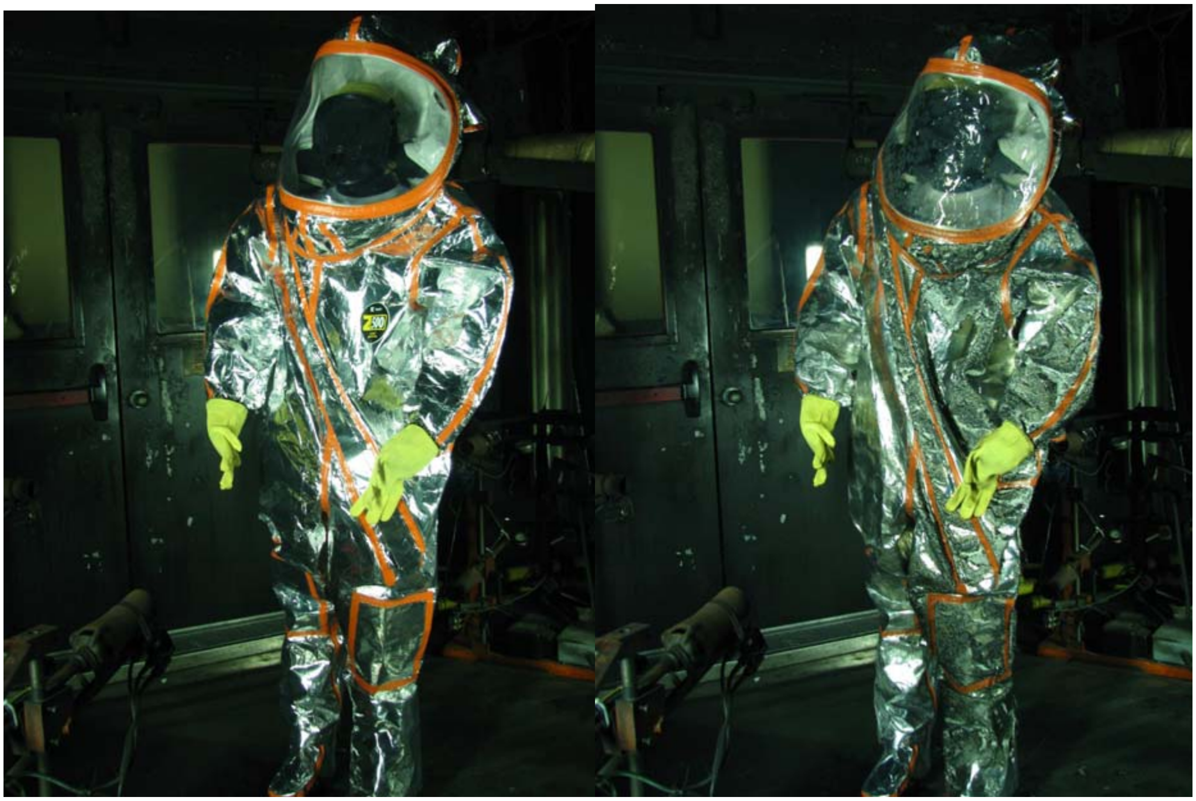

Figure 3. Pre and post flash pictures of the gas tight configuration

Launch and Commercialization

The design layout of the fabric now includes a fire-retardant treated spunlace fabric with the aluminized film laminated to the fabric with a thermoset adhesive that contains the interrmissent ingredients. This fabric configuration is capable of meeting the requirements of NFPA 1992. The garments using this fabric are designed as the traditional coverall style or a three piece that included bib trouser, jacket and hood. An additional film layer is added to the inner side to improve chemical resistance and provide for gas tight garment construction. This configuration is currently in process of certification to NFPA 1991.

Kappler's traditional approach to marketing protective garments includes guidance on use of their products. These products are designed as multi use single exposure (MUSE). This means a garment will withstand repetitive wearing and still provide the protection. However, if the garment is exposed to chemical contamination and/or chemical flash fire or other thermal hazard, Kappler recommends the garment be disposed in accordance with local regulations.

One year after the meeting with the safety officers in Baton Rouge, Kappler introduced the splash garment and it is being offered commercially today. The gas tight configuration is in the final stages of approval for NFPA 1991.

Results and Conclusions

Several issues had to be addressed involving the discrepancy between the requirements of the chemical suit standards 1991/1992 and the flame resistant garment standard 2112. The pyroman testing in 2112 was much more analytical, repeatable and provided more meaningful results. However, the developed garments were not designed to be specifically flame resistant, so certification to that standard could be misleading to the user. However, the pyroman was a much better test than the overall propane flash test proposed in 1991/1992.

It is interesting to note the development of the test methods and standards themselves. Although both methods were originally proposed at the ASTM symposium in June 1991, the overall flash test was adopted into the NFPA standard within a couple of years, while it took about ten years to issue the NFPA 2112 with the pyroman method. This was probably the result of the more analytical challenge associated with the pyroman method.

The discrepancies that exist between NFPA 1991/1992 and NFPA 2112 need to be addressed. The Technical Committee responsible for the issue of NFPA 1991/1992 is currently in working session to reissue the standards, which is required by the NFPA every five years. Proposals will be submitted to request the Committee to consider the adoption of the pyroman testing to replace the full scale propane flash chamber. This will include the recommendation to remove the requirement for the gas tight garment to pass pressure test after flash. Considering the current labeling that says it provides protection for escape only, there is no need to pass the pressure test. Utilizing pyroman would better address the issue of survivability of the user, which is of course the mission we attempt to accomplish.

Bibliography

American Society for Testing and Materials. 2008. ASTM D 6413, “Test Method for Flame Resistance of Textiles (Vertical Test).” Conshohocken, PA: ASTM (withdrawn).

_____. 1999a. ASTM F1001, “Standard Guide for Chemicals to Evaluate Protective Clothing Materials.” Conshohocken, PA: ASTM.

_____. 2008. ASTM F1358, “Standard Test Method for Resistance of Protective Clothing Materials to Flame Impingement.” Conshohocken, PA: ASTM.

______. 2008. ASTM F 1930, “Test Method for Evaluation of Flame Resistant Clothing for Protection Against Flash Fire Simulations Using an Instrumental Manikin.” Conshohocken, PA: ASTM.

International Standards Organization. ISO 17492, “Clothing for Protection Against Heat and Flame - Determination of Heat Transmission on Exposure to Both Flame and Radiant Heat.” Geneva: ISO.

National Fire Protection Association, 1991. NFPA 1971, “Standard on Fire Fighter Protective Ensembles.” Quincy: NFPA.

______. 2005. NFPA 1991, “Standard on Vapor-Protective Suits in Hazardous Chemical Emergencies.” Quincy, MA: NFPA.

_____. 2005. NFPA 1992, “Standard on Liquid Splash-Protective Suits in Hazardous Chemical Emergencies.” Quincy, MA: NFPA.

_____. 2007. NFPA 2112, “Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire.” Quincy, MA: NFPA.

Stull, Jeffrey O., James H. Veghte, Philip C. Mann, and Steven B. Storment. 1992. "Developing and Selecting Test Methods for Measuring Protective Clothing Performance in Chemical Flashover Sitautions," *Performance of Protective Clothing* 4.

Wallace P. Behnke, Amotz J. Geshury, and Roger L. Barker. 1992. "Thermo-Man and Thermo-Leg: Large Scale Test Methods for Evaluating Thermal Protective Performance." *Performance of Protective Clothing* 4.