

Modernization of HAZMAT/CBRN PPE



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2021-05-25



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Modernization of Hazmat/CBRN PPE



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PPE Modernization



1980s to 2010s: Rubber to Teflon to Disposable to Hybrid Materials

Realities of Chemical Exposure

- Majority of exposures are short-term and are at low concentrations
 - Responders taught to avoid contact
 - Monitoring extensively used for detecting chemicals and other hazards
- Greatest exposure concerns exist for gaps in ensemble integrity
- Accidents more likely from loss of functionality than exposure



The selection of PPE for a given event must consider the **operational environment**, the **toxicity of the material**, as well as the **flammability of the material**. Your **task, location, and duration** are key considerations.

It All Started in Benicia, CA



- August 12, 1983
- Tank car loaded with dimethylamine
- Suit facepieces began to cloud over, crack, and melt reducing their visibility
- Leaks developed in seams of suits
- One responder's facepiece shattered

Information on the chemical compatibility of the suit with dimethylamine was relevant to the suit material only; *it did not apply to the visor or seams.*

Requirements for Level A Ensembles

- Encapsulation dictated by OSHA 1910.120
 - Appendix A defines protection levels
 - Appendix B indicates methods of evaluating Level A suits
 - Maintain positive pressure
 - Prevent inward leakage
 - Definition for total encapsulating suit and test methods are not in mandatory language of regulations



Why Do We Use PPE Standards?

- OSHA CFR 1926.65, Appendix B Recommends it

“As an aid in selecting suitable chemical protective clothing, it should be noted that the National Fire Protection Association (NFPA) has developed standards on chemical protective clothing.”

“These standards apply documentation and performance requirements to the manufacture of chemical protective suits. Chemical protective suits meeting these requirements are labeled as compliant with the appropriate standard.”

“It is recommended that chemical protective suits that meet these standards be used.”

CODES & STANDARDS

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NFPA 1990

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Standards for Protective Ensembles for Hazardous Material and Emergency Medical Operations

Please note: NFPA 1990 is in a custom cycle due to the Emergency Response and Responder Safety Document Consolidation Plan (consolidation plan) as approved by the NFPA Standards Council. As part of the consolidation plan, NFPA 1990 is combining Standards NFPA 1991, NFPA 1992, 1994, and NFPA 1999. For consolidated draft and revision cycle information, see the Next Edition tab.

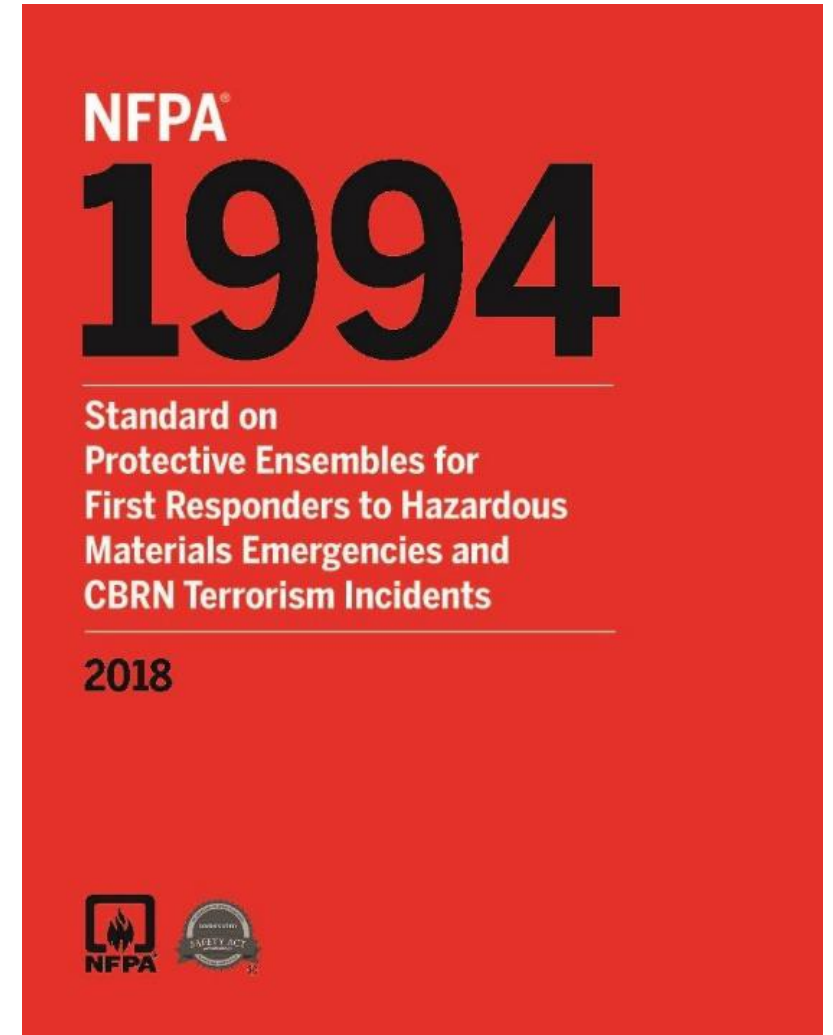
Current Edition: Proposed Standard

[Submit a Public Comment for the Next Edition](#) 

**NFPA 1990 Product Standard = NFPA 1991 + NFPA 1992 + NFPA 1994
NFPA 1891 Selection, Care, & Maintenance Document**

Ensembles Designed Specifically for Emergency Response

- Originally positioned to address terrorism concerns for a broader range of first responders
 - Classes established for different threats
 - 2018 edition incorporates recommendations from the NIJ Law Enforcement Chemical Protective Clothing committee, including updated chemical challenges and options for ruggedization and stealth
- NFPA 1994 now positioned for all hazardous materials responses
 - Class 1 provides alternative to NFPA 1991 Level A suits
 - Class 2 and 3 differentiate between IDLH and non-IDLH
 - Class 4 for particulates



Reconciling NFPA Standards with EPA PPE Levels



NFPA Standard	OSHA/ EPA Level	Respirator	NFPA Barrier Method(s)	Type of Challenge	Expected Dermal Protection from Suit(s)			
					Chemical Vapor	Chemical Liquid	Particulate	Liquid- borne viruses
1991 (2016)	A	SCBA	Permeation	24 TICs, 2 CWAs	X	X	X	X
1994 Class 1 (2018)	A	SCBA	Permeation	10 TICs, 2 CWAs	X	X	X	X
1994 Class 2 or 2R (2018)	B	SCBA	Permeation; viral penet.	5 TICs, 2 CWAs; Bacteriophage	X	X	X	X
1992 (2018)	B	SCBA	Penetration	10 TICs		X		
1994 Class 3 or 3R (2018)	C	CBRN APR or CBRN PAPR	Permeation; viral penet.	5 TICs, 2 CWAs; Bacteriophage	X	X	X	X
1994 Class 4 or 4R (2018)	C	CBRN APR or CBRN PAPR	Viral penetration	Bacteriophage			X	X
1999 Single-Use or Multiple-Use (2018)	C	APR (P100); PAPR with HEPA filter	Viral penetration	Bacteriophage				X

NFPA Standards vs. OSHA/EPA Levels

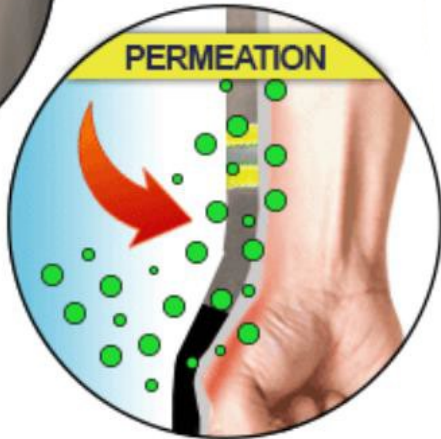
Protective Clothing Standards That Correspond to OSHA/EPA Levels

Ensemble Description Using Performance-Based Standard(s)	OSHA/EPA Level
NFPA 1991 worn with NFPA 1981 or NFPA 1986 SCBA	A
NFPA 1994 Class 1 worn with NFPA 1981 or NFPA 1986 SCBA	A
NFPA 1994 Class 2/2R worn with NFPA 1981 or NFPA 1986 SCBA	B
NFPA 1992 worn with NFPA 1981 or NFPA 1986 SCBA	B
NFPA 1994 Class 2/2R worn with NIOSH CBRN APR or PAPR	C
NFPA 1992 worn with NIOSH CBRN APR or PAPR	C
NFPA 1994 Class 3/3R worn with NFPA 1981 or NFPA 1986 SCBA	B
NFPA 1994 Class 3/3R worn with NIOSH CBRN APR or PAPR	C
NFPA 1994 Class 4/4R worn with NFPA 1981 or NFPA 1986 SCBA	B
NFPA 1994 Class 4/4R worn with NIOSH CBRN APR or PAPR	C
NFPA 1994 Class 5 worn with NFPA 1981 or NFPA 1986 SCBA	B

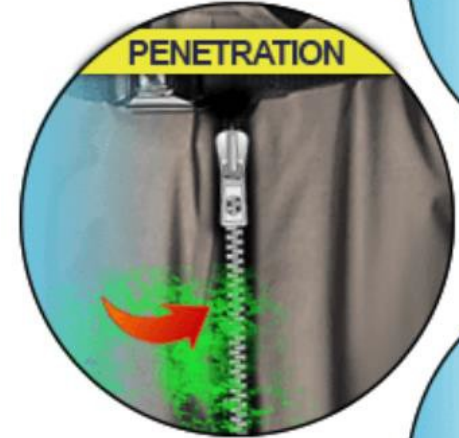
EPA/OSHA levels are design specifications while NFPA standards are performance specifications

- Material barrier performance describes how PPE materials protect the wearer from contact with hazardous substances with varying levels of effectiveness.
 - Testing demonstrates the ability to keep a hazardous substance from contacting the wearer
 - Level depends upon the intended application of the PPE ensemble and the hazards posed by the substance
 - Acceptable levels of material barrier performance are set by the NFPA standards
 - Together with the risk assessment, test results are a key consideration for selecting the most appropriate PPE available for the task at hand.

Modes of Exposure

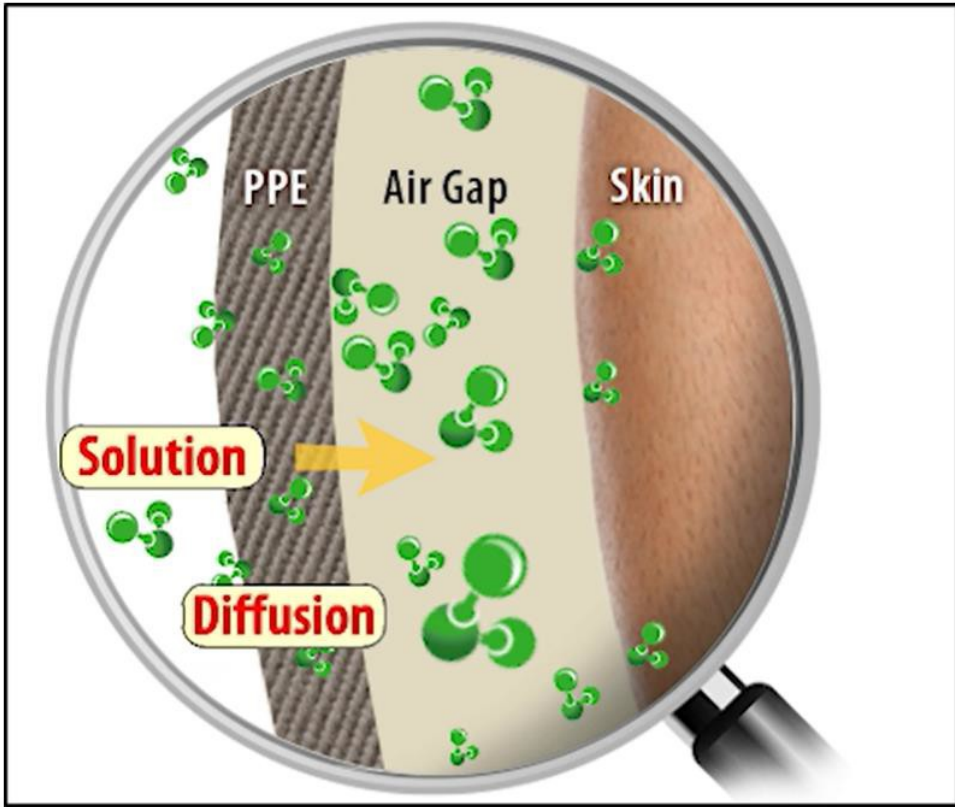


- **Degradation** – occurs when contact with a hazardous substance creates adverse changes in the barrier material
- **Penetration** – the passage of the hazardous substances in bulk (usually as a liquid or gas through PPE interfaces, seams, or other openings and sometimes materials)
- **Permeation** – the process by which a hazardous substance goes through barrier material at a molecular level



Permeation

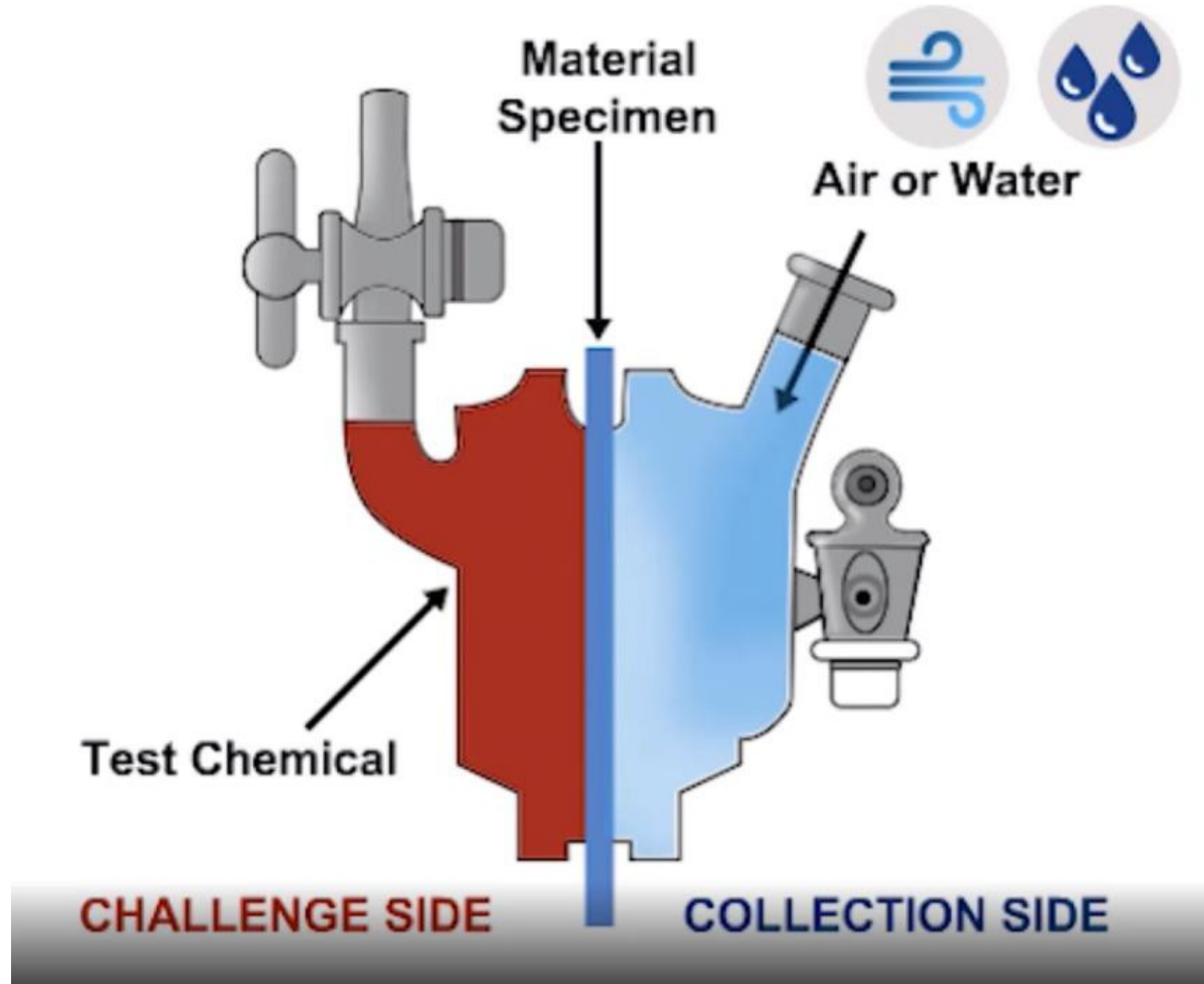
- Permeation occurs when a chemical moves through a barrier material at a molecular level
- Permeation is a major concern because it is invisible
- Three major factors
 - **Breakthrough time** – *time* between the substance contacting the suit and the substance getting through the material
 - **Permeation rate** – *how fast* the chemical moves through the material
 - **Cumulative permeation** – *how much* of the chemical gets through in a given period of time



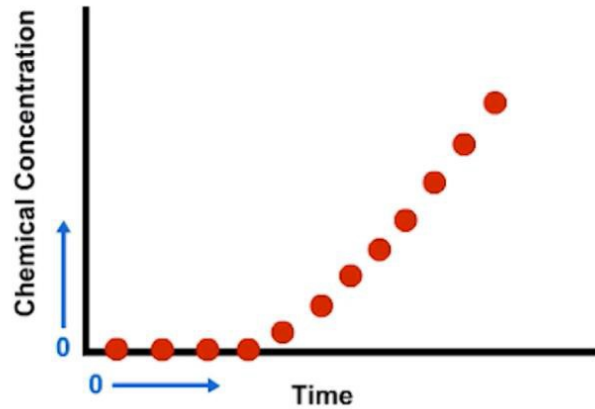
Limitations of Chemical Compatibility Charts

- **Common Misperception:** Principal barrier qualities of chemical protective clothing arise from the materials of construction only
- **Reality:** It is first integrity through suitable ensemble design, then barrier properties of the materials, seams, and closure, and then other design/material attributes of the clothing items that affect its durability, function, and comfort.
 - It is the combination of ***clothing design***, its ***integrity***, and ***material chemicals resistance*** that are the principal drivers of protection.
 - Chemicals take the path of least resistance
 - Gap between interfaces
 - Inadequate closure systems
 - Poorly constructed seams

Measuring Chemical Permeation

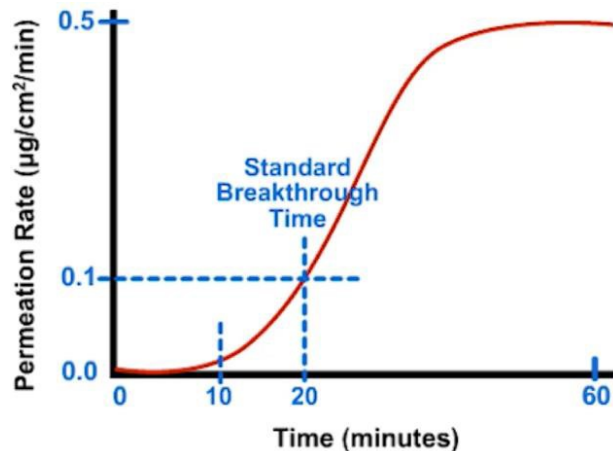


Chemical Permeation Test Results

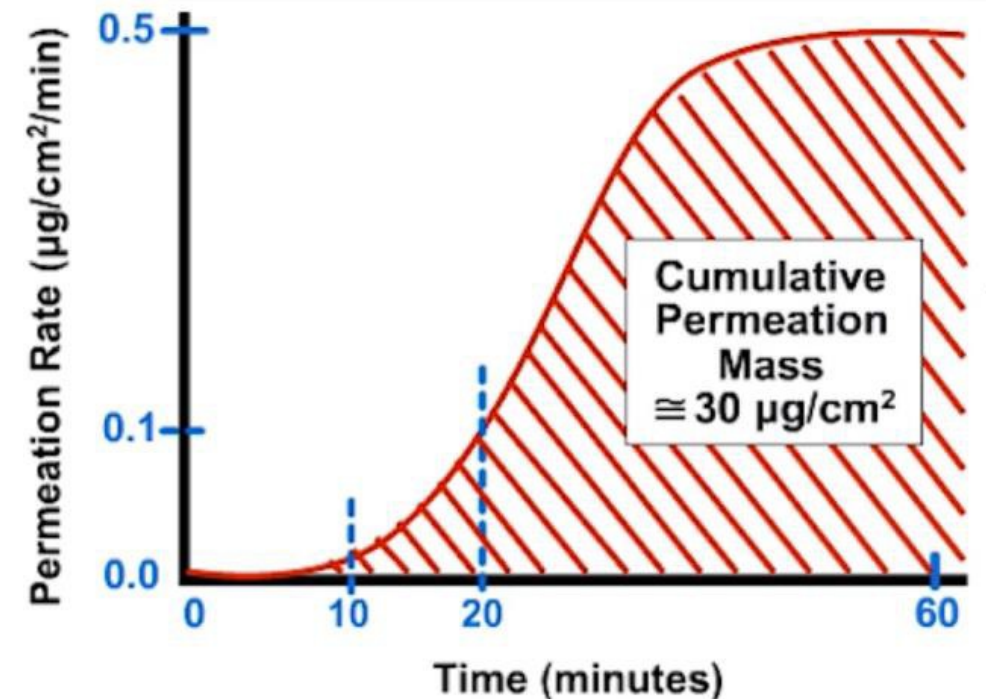


$$\text{Permeation rate} = \frac{\text{Mass of permeating chemical}}{\text{Area of exposed clothing} \times \text{time interval}}$$

- **Cumulative Permeation** measures how much of a chemical permeates the material.
- **Breakthrough Time** measures how fast a chemical permeates the material.
- **Normalized, or Standard, Breakthrough Time**, measures how fast a chemical reaches a specified permeation rate.



NFPA, HazMat and CBRN PPE standards use the Cumulative Permeation Mass.



Limitations of Chemical Compatibility Charts

Also called Chemical Breakthrough Charts or Chemical Permeability Charts

Permeation Data for ASTM Recommended List of Chemicals for Evaluating Protective Clothing Materials (ASTM F1001)

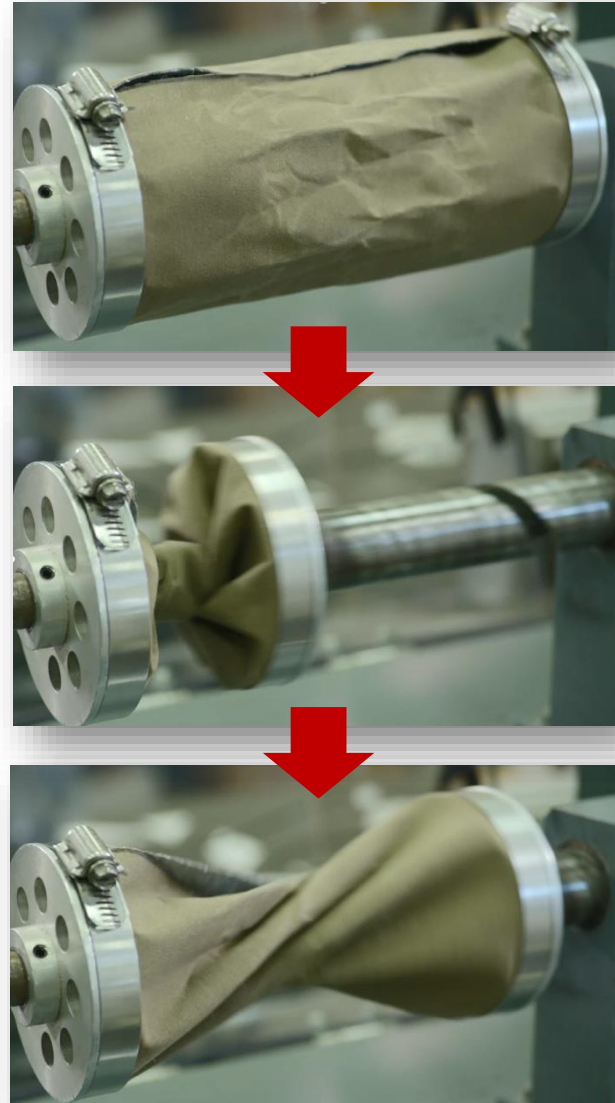
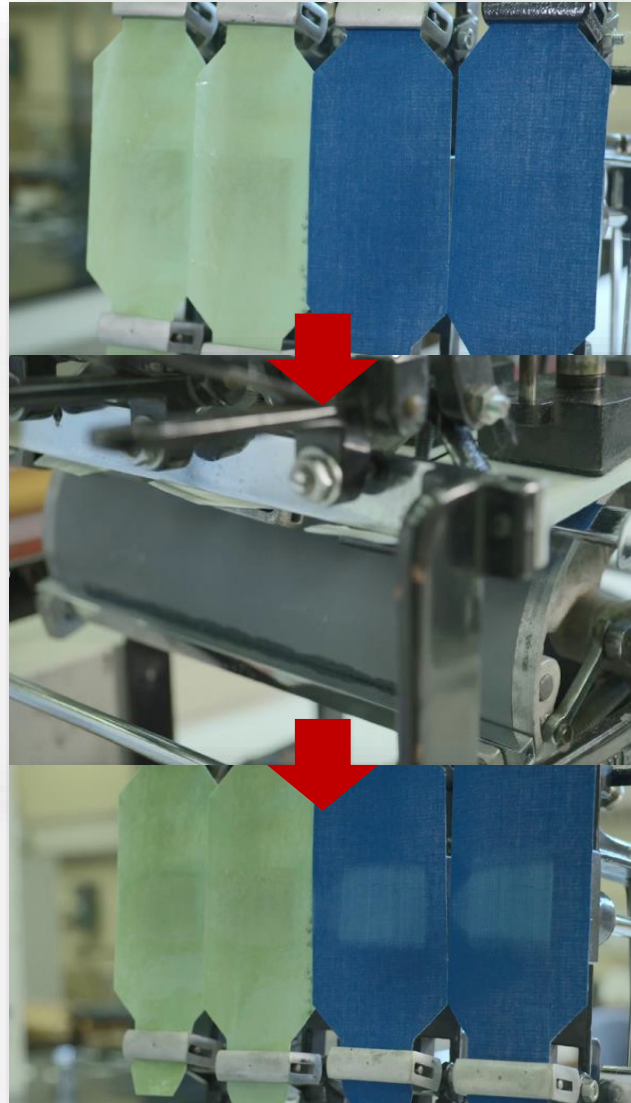
Chemical Name	Physical Phase	Normalized Break-through Time (min.)	CAS No.
Acetone	L	>480	67-64-1
Acetonitrile	L	>480	75-05-8
Ammonia (gas)	G	>480	7664-41-7
1,3- Butadiene	G	>480	106-99-0
Carbon disulfide	L	>480	75-15-0
Chlorine gas	G	>480	7782-50-5
Dichloromethane	L	>480	75-09-2
Diethylamine	L	>480	109-89-7
N,N-Dimethylformamide	L	>480	68-12-2
Ethyl acetate	L	>480	141-78-6
Ethylene oxide	G	>480	75-21-8
n-Hexane	L	>480	110-54-3
Hydrogen chloride	G	>480	7647-01-0
Methanol	L	>480	67-56-1
Methyl chloride	G	>480	74-87-3
Nitrobenzene	L	>480	98-95-3
Sodium hydroxide, 50%	L	>480	1310-73-2
Sulfuric acid (conc.)	L	>480	7664-93-9
Tetrachloroethylene	L	>480	127-18-4
Tetrahydrofuran	L	>480	109-99-9
Toluene	L	>480	108-88-3

> = greater than, L = liquid, G = gas

Note: Chemical Resistance Data is in accordance with ASTM F-739 test method. Testing is performed on fabric samples only, not finished garments. Sources for all test data are independent laboratory conditions and not actual use conditions.

- Only applied to primary ensemble materials, not seams or interfaces
- Materials are not abraded and flexed to simulate repeated use and test durability
- Testing performed at room temperature (25°C (77°F))
 - For example, sample permeation is measured at 32°C (90°F) and 80% Relative Humidity in the NFPA standards because permeation rates significantly increase with small increases in temperature
- Data is misleading as there is no relationship to protection, toxicity, or exposure limits
- Permeation is not uniform
- Results are variable
- Chemical has already permeated the suit by the time breakthrough is reported

Flexing and Abrading Material PRIOR to testing



What About the SCBAs?



- Current NFPA 1981/1986 SCBA tested for Mustard and Sarin (CBRN challenges)
- New full-scale testing underway (CB-PR-4177) to assess SCBA and PAPR/APR performance against toxic industrial chemical exposures
 - Initial tests show no permeation of chemicals tested to date against selected SCBAs and PAPRs

Chemical Battery Selection Factors

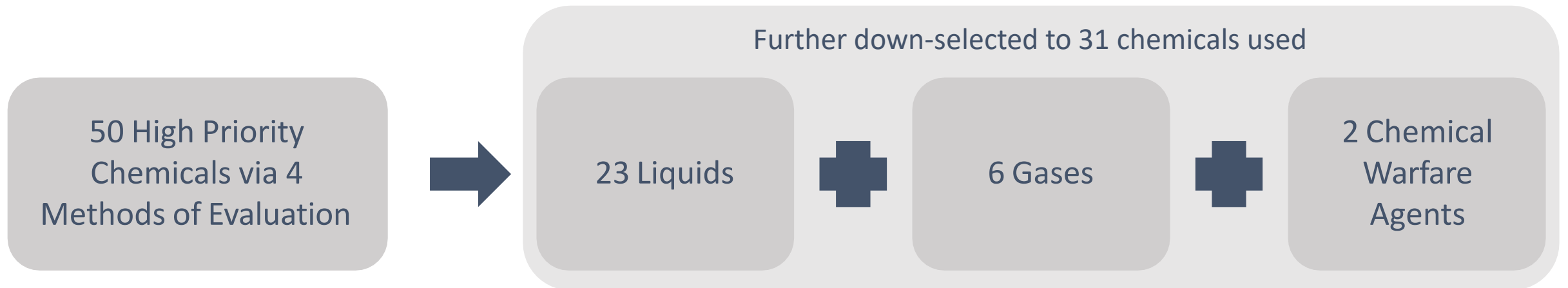
- Likelihood or frequency of exposure
 - High volume and more common hazardous chemicals
- Expected consequences of exposure (hazards)
 - Chemicals posing greater toxicity; carcinogens; skin-absorbing chemicals
- Persistency in environment
 - Low vapor pressure liquids; heavy vapor density gases
- Potential impact on material performance
 - Chemicals that easily permeate or degrade different materials
- Ability to analyze testing
- Availability and safety for testing

We evaluated 3 approaches to selecting chemical batteries during the NFPA 1991/1992/1994 process:

1. ASTM F1001 (1983)
2. Stull (US DoD/TSWG) (2008)
3. US DoD/NRL Approach (Industrial Chemical Assessment) (2011)

Selection of Chemicals in NFPA Batteries

- Now, it is important to take into consideration the worse case scenario for the dermal exposure as well as chemicals that permeate materials aggressively.
 - Lower vapor pressure
 - Lower surface tension
 - Known degradation on polymers
- In addition, several high use, high exposure likelihood chemicals are added (e.g., ammonia, chlorine)



NFPA 1991, 1992, and 1994 Chemical Batteries

NFPA 1991

Liquid Chemicals

Acetone
Acetonitrile
Acrolein
Acrylonitrile
Carbon Disulfide
Dichloromethane
Diethylamine
Dimethylformamide
Dimethyl Sulfate
Ethyl Acetate
Hexane
Methanol
Nitrobenzene

Liquid Chemicals

Sodium Hydroxide (50%)
Sulfuric Acid (93.1%)
Tetrachloroethylene
Tetrahydrofuran
Toluene

Gaseous Chemicals

Ammonia
1,3-Butadiene
Chlorine
Ethylene Oxide
Hydrogen Chloride
Methyl Chloride

Current NFPA 1994

Acrolein
Acrylonitrile
Ammonia
Chlorine
Dimethyl Sulfate

Additional Class 1 Chemicals

Diethylamine
Ethyl Acetate
Sulfuric acid
Tetrachloroethylene
Toluene

Current NFPA 1992

Butyl acetate
Dimethylformamide
Fuel H
Isopropyl alcohol
Methyl isobutyl ketone
Nitrobenzene
Sodium hydroxide
Sodium hypochlorite
Sulfuric acid
Tetrachloroethylene

Both NFPA 1991 and NFPA 1994 involve testing against GD and HD

Example for Inferring Chemicals

Class	Chemical Class/Subclass Name
120	Aldehydes
121	Aliphatic and alicyclic
122	Aromatics



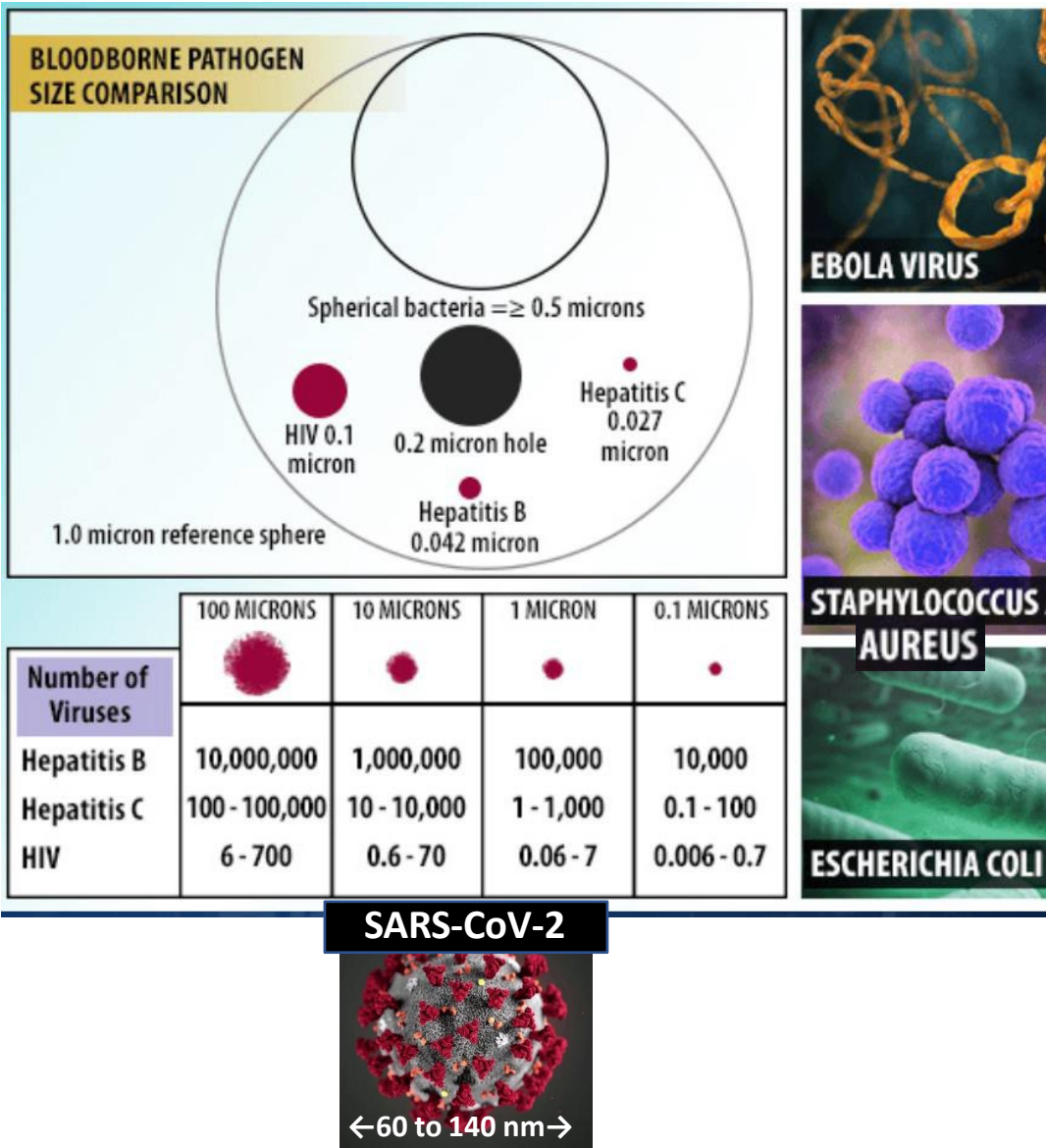
Aldehydes, Aliphatic and alicyclic
Acetaldehyde
Acrolein
Butyraldehyde
Crotonaldehyde
Decanal
Formaldehyde, gas
Formaldehyde, 30 -70%
Glutaraldehyde, 30-70%
Glutaraldehyde, < 30%
Isobutyraldehyde
Isovaleraldehyde
Trichloroacetaldehyde



Aldehydes, Aromatics
Benzaldehyde
Furfural
O-Phthaldehyde, 30-70%

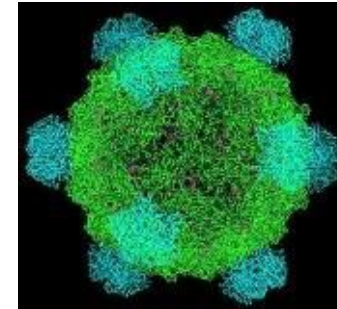
Acrolein is the simplest, unsaturated aldehyde

Biological Test Liquids



- Test liquid used to evaluate barrier materials and seams against penetration of biological liquids uses a very small, round surrogate microorganism

Phi-X174
Bacteriophage



←27 nm→

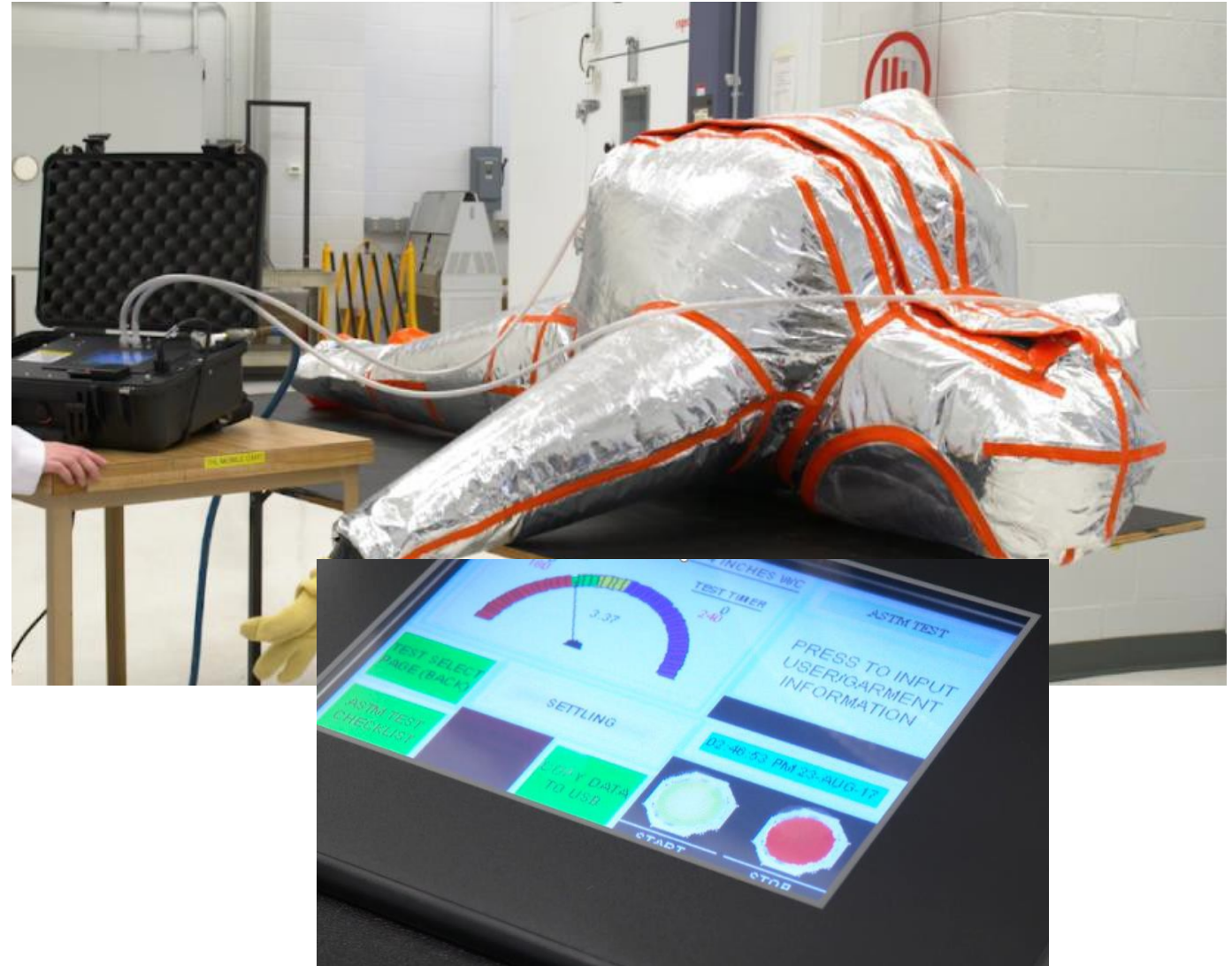
- The surrogate material is smaller than most pathogenic viruses and bacteria, including Ebola, E. Coli, and SARS-CoV-2
- Although a small amount of test liquid is used, the concentration of microorganisms is considerably higher than typically encountered
 - Many dangerous microorganisms multiply exponentially in blood, body fluids, and other media

Ensemble Integrity

- Integrity is a measure of an ensemble's ability to protect the wearer from hazardous materials
- Seams, closures, and interfaces are the most vulnerable parts of an ensemble
 - Glove/sleeve
 - Footwear/pants
 - Respirator/hood
 - Spaces between zipper teeth
 - End of zipper
 - Equipment pass throughs
 - Exhaust valves
- While some interfaces are liquid-resistant, few are liquid-proof
- If the PPE materials are liquid-proof but the zipper is only liquid-resistant, the integrity of the entire ensemble may be compromised

Gas-Tight Integrity Test

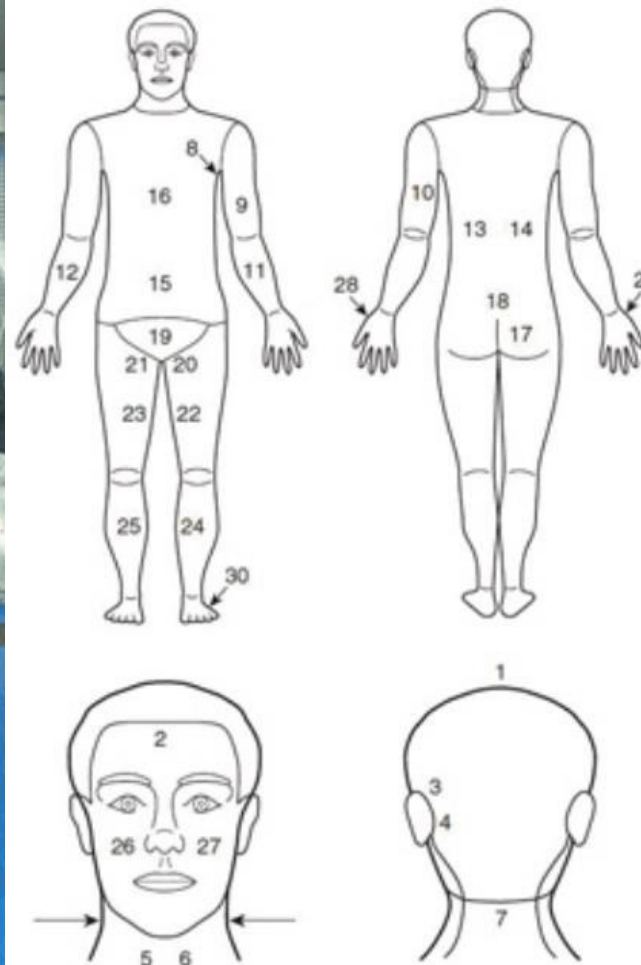
- The gas-tight integrity test evaluates a fully encapsulated ensemble's ability to hold an internal pressure
- Testing
 - Ensemble is inflated to a set pressure
 - If the pressure falls past a set threshold, it signals that the suit leaks, which may cause exposure to the wearer
 - The test is limited because it does not incorporate movement as a variable
 - Interfaces are more likely to be affected during movement.



Man-In-Simulant Test

24 ppm Methyl Salicylate (MeS) is used as a surrogate for chemical warfare agent for 30 minutes.

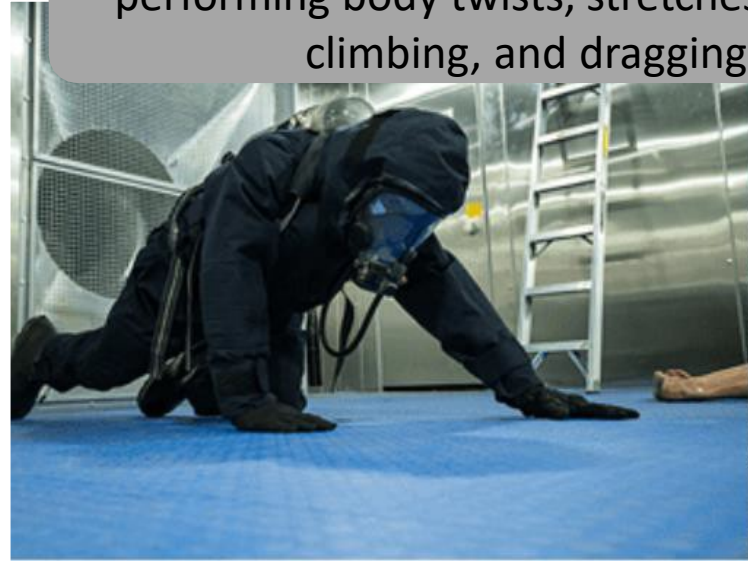
30 small personal absorbent dosimeters (PADs) are placed on the subject's body



Man-In-Simulant Test

Stress is induced on the ensemble by the wearer performing body twists, stretches, deep knee bends, climbing, and dragging a dummy

When the test is complete, the ensemble is washed down to eliminate cross contamination of test subject or PADs. PADs are collected for analysis.



Vapor Protection

Level	PPDF _i at each PAD location*	PPDF _{svs} *
Ultrahigh	≥ 1071	≥ 488
High	≥ 871	≥ 441
Moderate	≥ 481	≥ 328
Low	≥ 80	≥ 35

* Geometric means for all ensembles tested

NFPA 1991



Ultrahigh

Class 1



High

NFPA 1994 Class 2



Moderate

Class 3



Low

Increasing Protection and Heat Stress

Increasing Comfort and Tactility

30 min

20 min

15 min

15 min

Types of Ensembles

- Single Use (i.e., many “plastic” laminates)
 - Treat any non-certified gear as single use
- Single Exposure (i.e., Blauer suits)
 - Wash and reuse unless a significant exposure has occurred
 - Remember to Decontaminate on scene, wash according to manufacturers’ instructions, and disinfect (if needed)
- Multiple Exposure (i.e., Trelleborg VPS)
 - Remember to Decontaminate on scene, wash according to manufacturers’ instructions, and disinfect (if needed)

Liquid Integrity Testing

- Assesses whether each individual piece of an ensemble is liquid-resistant or liquid-proof
 - Test involves no movement
 - A manikin is dressed in a liquid absorbent garment, then the test ensemble
 - Surfactant-treated water is sprayed onto the manikin from all sides
 - The manikin rotates to evaluate different interfaces
 - Results are highly dependent on the proper fit of the ensemble
 - Liquid exposure times are longer than normal use conditions
 - The ensemble or garment fails if there is any evidence of liquid penetration into the garment or the ensemble interior



Liquid Splash Protection

NFPA 1994

Class 1



High

Class 2



High

NFPA 1992



High

NFPA 1994

Class 3



Moderate

NFPA 1994

Class 4



Low

NFPA 1994

Class 5



Low

COMING SOON



Level	Test Duration current edition (min)	Test Duration proposed edition (min)
Ultrahigh	60	60
High	20	20
Moderate	4	8
Low	0	4

Design Considerations

NFPA 1992 Garment Designs

Coverall



Beware of Bellows Effect!

Liquid Splash
Below the Knee

Hooded Coverall



Use care around zipper!

Liquid Splash
Below the Waist

**Encapsulated
Front Entry**



Liquid Splash Above Waist

**Encapsulated
Rear Entry**



CHEM Tape – When to Use It

- When wearing NFPA 1992 garments or NFPA 1999 garments (not sold or tested as ensembles), ChemTape is often used to create a glove-to-suit and boot-to-suit interfaces as well as holding zipper flaps in place. While these are often considered as “increased protection”, there is not way to test or prove that due to inadequate taping surfaces in the field.
 - To increase the glove-to-suit interface, I always recommend the use of a piece of PVC pipe as a taping surface or another commercial cone-ring type product.
 - The boot-to-suit interface is added to minimize the chance of any chemical splash following the suit down into the boot. Efforts are made to minimize the pooling of chemicals at the foot.
- ChemTape is often used to hold the zipper flaps in place. This can be helpful and it can be problematic, depending upon the circumstances.
 - Helpful: Most zippers on non-certified suits are problematic and leak. This is especially true with things like soapy water and sulfuric acid where the surface tensions allow the materials to find any penetration point.
 - Less than Helpful: The adhesive on the tape is often strong than the material to which it is taped creating a tearing hazard when doffing the gear. If the responder is “cutting out” of the gear, then this is eliminated, but care must be taken when removing the tape.

CHEM Tape – When NOT to Use It

- ChemTape should NEVER be used on/around the mask-to-suit interface. The respirator is the operator's last line of defense against the chemical and must be maintained as the last line.
 - The adhesive on ChemTape is very strong and can pull the mask away from the face when the suit is snagged on or pulled by something/someone.
 - The adhesive on ChemTape leaves a residue which is very difficult to get off of masks and can negatively impact visibility. In addition, nothing should be done to potentially limit the operators' visibility.
 - The adhesive on ChemTape is flammable and therefore should not be near the operator's face.
 - And finally, from NIOSH: *"If the original NIOSH respirator evaluation and approval was not done with taping, then there is no assurance that the use of taping is not negatively impacting the respirator fit and protection factor. Therefore, the use of CHEM Tape on the respirator could be perceived to be out of compliance of its certification."*

As a general rule, if you are applying ChemTape to a suit, you need to ask yourself if you are trying to increase its protection. If the answer is yes, then you likely chose the wrong suit to begin with. If the answer is no, and you are just trying to increase comfort, then tape away!

Particle Inward Leakage Testing



- Adapted the fluorescent aerosol screening test from the military to assess an ensemble's ability to protect against very small solid particles
 - Wearer dons a black jumpsuit with the test ensemble over it
 - The operator performs a variety of movements for 30 minutes in a chamber with blowing fluorescent particle dust
 - The jumpsuit is visually inspected for any particle penetration under a black light

Particulate Protection

**NFPA
1991**



Class 1



Class 2



**NFPA 1994
Class 3**



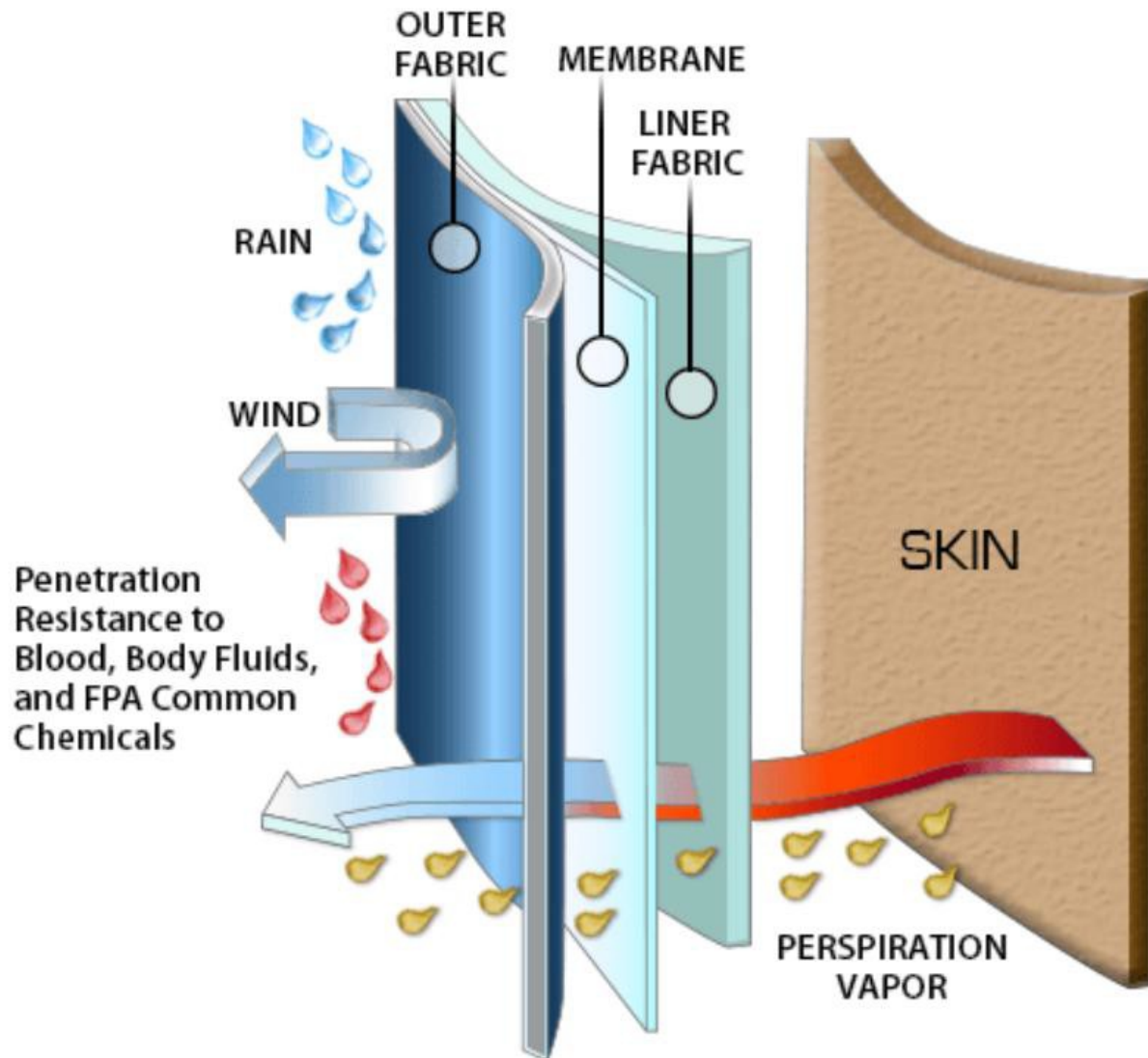
Class 4



← Increasing Protection and Heat Stress

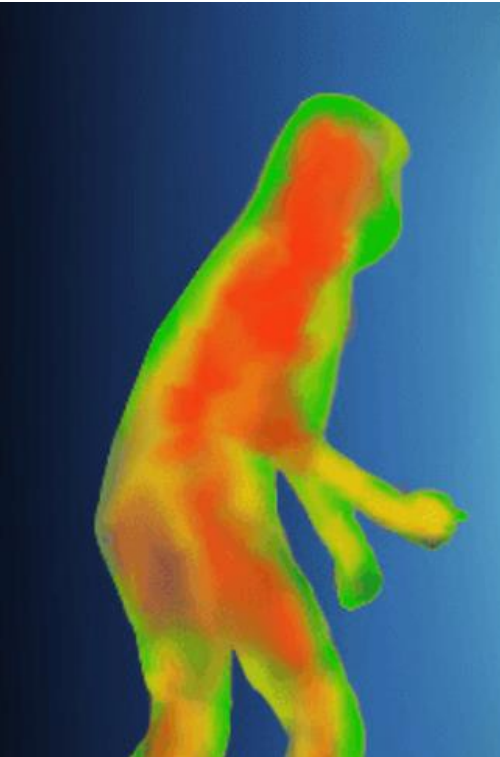
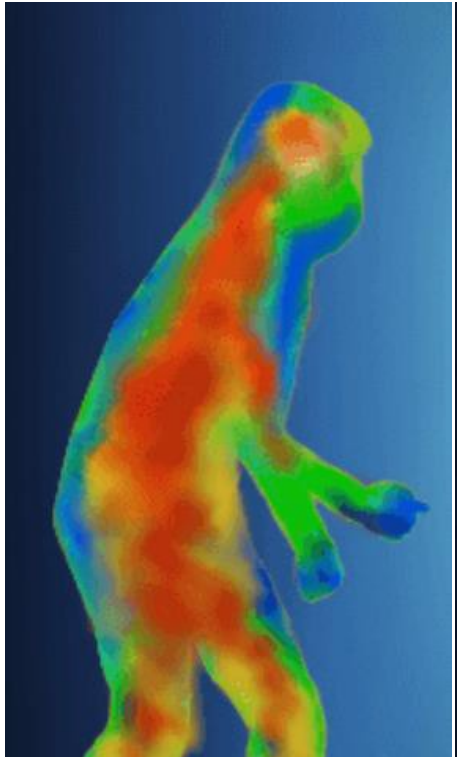
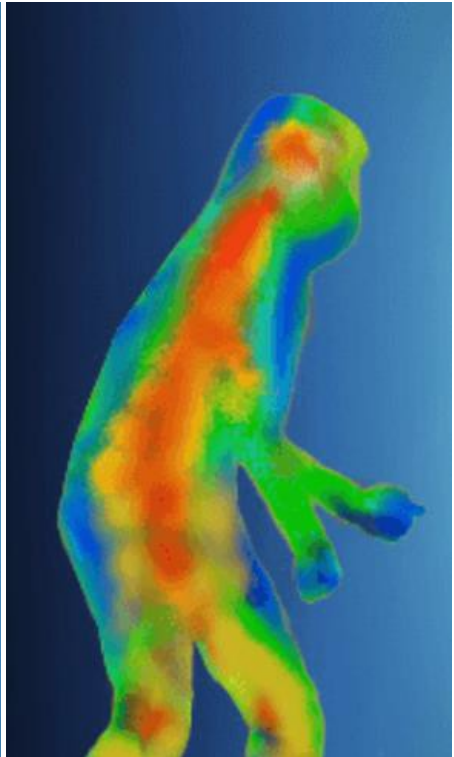
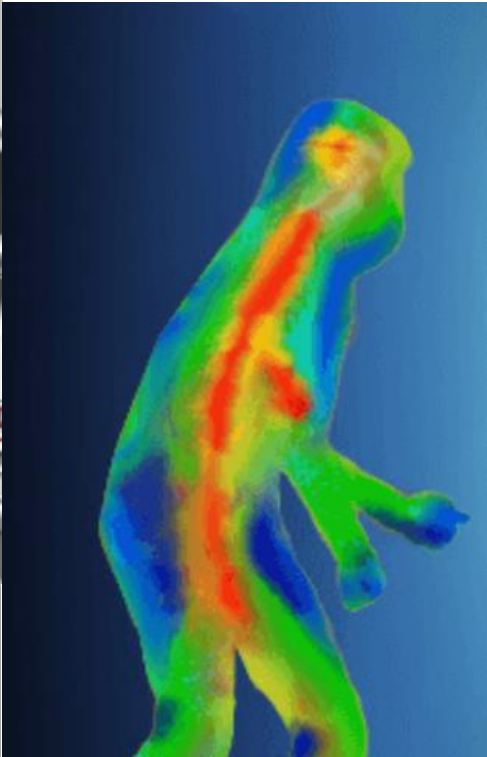
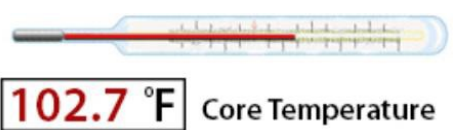
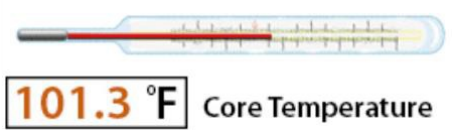
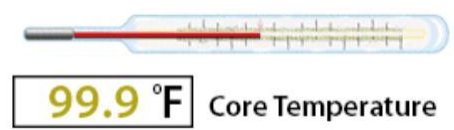
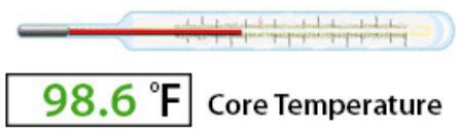
Increasing Comfort and Tactility →

Impact of Clothing Material



- Most PPE materials are impermeable, therefore no air exchange occurs with the outside environment
- PPE materials that protect against lower concentrations and particulate hazards may be breathable, offering some relief from heat stress
- With respect to breathable materials:
 - Moisture from sweating can transfer to the outside environment
 - Materials still act as barriers to chemicals, microorganisms, and particles
 - Breathable materials are less effective in hot, humid conditions or during strenuous work

Combined Clothing Effect



0 Minutes



15 Minutes



30 Minutes



45 Minutes

As heat builds up in the body, protective materials, especially those that encapsulate the wearer, create a microclimate between the body and the PPE that can prevent heat loss through perspiration

Cooling Systems

- Properly selected PPE can help to prevent exposure to hazardous materials, and also minimize the negative impacts of heat stress
 - Personal cooling systems may be worn to provide some degree of comfort
 - Passive cooling systems absorb heat using a cooling medium in a vest or similar garment
 - Active cooling systems circulate air or a cooling medium inside the ensemble

PASSIVE SYSTEMS



Evaporative



Non-Ice PCM



Ice PCM

ACTIVE SYSTEMS



Thermoelectric



Venturi Tube



Active Liquid

Ice-based
Liquid



Active Air

CAUTION must be exercised with the use of all passive cooling systems, during operations, as once the cooling medium is exhausted (ice, water, phase-change material) these garments become another insulating layer and detrimental to heat loss. The speed with which the cooling medium is exhausted will be governed by the environmental conditions and the work rate of the PPE wearer.

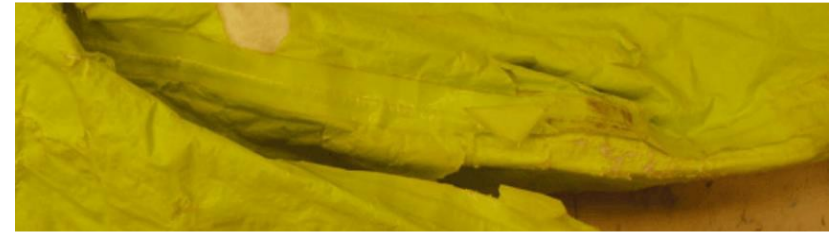
Cooling techniques that rely on evaporative cooling for their heat loss capability ie evaporative vests should NOT be used with encapsulating PPE.

Physical Hazard Resistance

- PPE must be durable to protect the wearer from chemical, biological, and radiological hazards throughout its intended service life
 - Physical Hazard Resistance
 - Ensembles must provide some degree of physical hazard resistance
 - Physical hazard resistance is a measure of the ability of an ensemble to resist stresses and hazards that result from operating in an incident environment
 - Durability
 - PPE is considered durable if it can stand up to the wear and tear caused by use, storage, and maintenance
 - Ensembles and the materials that comprise them are tested for levels of durability depending upon their expected uses and the exposure risks they may face
 - Proper storage and laundering are also important to long-term durability

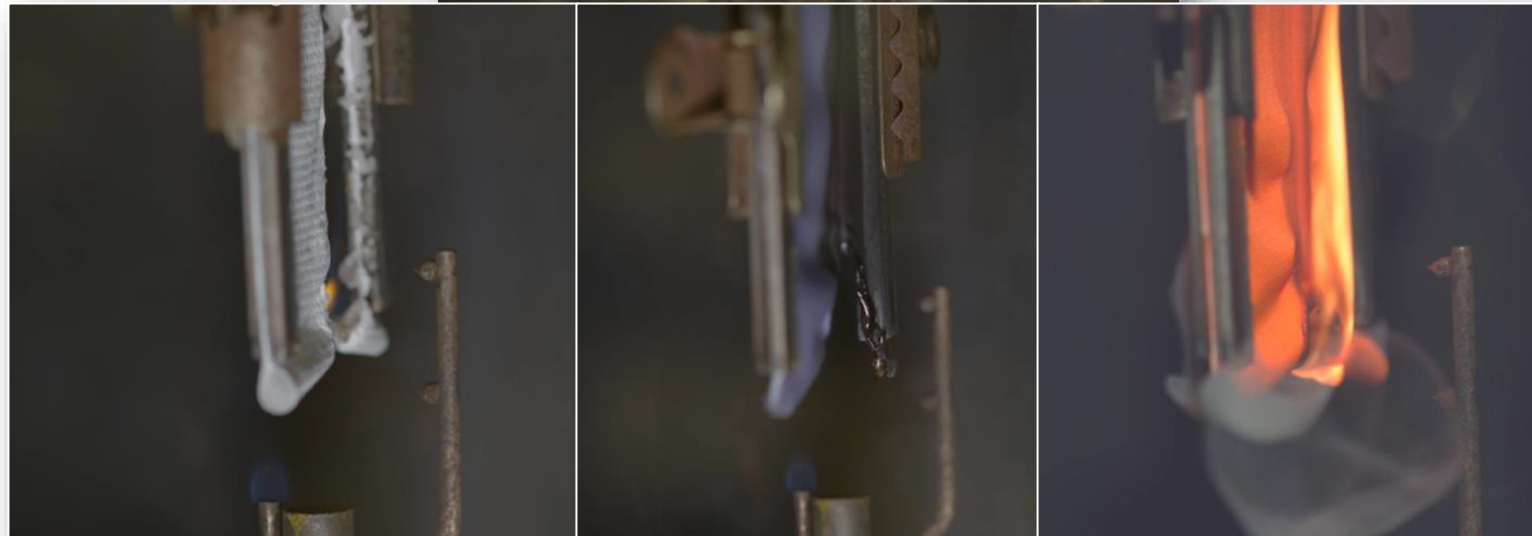
Loss of Durability

- When the ensemble materials or integrity break down or separate, the durability of the materials can be compromised. Less durable PPE can lead to gas/vapor, liquid, or particulate penetration
 - **Abrasion** – Materials that come into contact with physical hazards can lose durability and provide less protection even if they don't tear
 - **Flexing** – Repeated flexing and bending of PPE materials can cause a loss of durability
 - **Fatigue** – Continued donning and doffing can result in malfunctioning closures, tears at the seams, and other damage to PPE ensembles



Flame Resistance Testing

- Determines whether materials can be ignited and if they will continue to burn after ignition
- Key testing points:
 - Some ensembles are evaluated for a 3 second exposure to demonstrate that the suit will not contribute to injury if exposed to flame or high heat
 - Ensembles intended for flash fire protection are exposed for 12 seconds
 - Continued burning of material is reported as after-flame time which must be 2 seconds or less
 - Materials are also observed for melting and dripping



Flash Fire Testing



- The Ensemble Flash Fire Test determines ensemble integrity, durability, and the ability for the wearer to navigate away from an area during a replicated flash fire
- Key testing points:
 - A 6 to 8 second flash fire is created in a closed chamber using injected propane
 - Immediately after, the ensemble is observed for after-flame which cannot exceed 2 seconds
 - The ensemble is then tested for either liquid or gas-tight integrity, depending on the intended use
 - Passing ensembles must also afford the ability for an operator to see through the visor following exposure





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PERSONAL PROTECTIVE EQUIPMENT (PPE) MODERNIZATION

Modernization of HAZMAT/CBRN PPE



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2021-05-25



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