CHALLENGE®[1] – THE ULTIMATE IN CB BARRIER MATERIALS

Ruth A. Jamke
Saint-Gobain Performance Plastics
702 Daniel Webster Highway
Merrimack, NH 03054

ABSTRACT

High temperature, multi-layer, CB barrier composites are manufactured utilizing multi-layer, cast perfluoropolymer films laminated to lightweight, high strength aramid or other reinforcements. The paper will address the unique cast fluoropolymer film and laminating technologies and processes which allow: 1) a very broad range of performance characteristics within these very thin films/laminates (including the highest level of CB protection, IR spectral matching, blackout, bi-color constructions, color-coding to identify severity of abrasions while in use, UV barrier, static dissipation); and 2) fluoropolymer films to be laminated to dissimilar (low temperature) reinforcement materials such as polyester.

INTRODUCTION

In light of uncertain (unknown) initial environmental conditions, in-field personnel must be provided the broadest CB barrier protection. Saint-Gobain Performance Plastics (SGPPL) is a producer of high performance fluoropolymer composites. In the segment of the company formerly known as Chemfab Corporation, films, coated fabrics and laminates are combined in various ways into protective systems which include both clothing and shelters, offering extraordinary resistance to a broad range of chemicals and live agents. The objective of this paper is to present the materials and technology that have made the development of these systems possible and to underscore the performance features of both the materials and the systems produced from them.

DISCUSSION

SGPPL is known worldwide as a designer, producer and fabricator of flexible fluoropolymer composites for use in applications that are extremely demanding. These applications range from use in permanent architectural structures, industrial belting, food processing applications, chemical processing (flexible joints in power plant ducts, for example), all the way to aerospace and communications. These applications share one feature—they are extremely challenging in one or more ways—they demand excellent high temperature properties, good durable release properties, broad chemical resistance, and/or long term weathering resistance (moisture, UV). The systems which are of interest to COLPRO conference attendees are those made from the CHALLENGE® product line, such as the STEPO suit (Self-contained Toxic Environment Protective Outfit) in Figure 1, Improved Toxicological Agent Protective Suit (ITAP) in Figure 2, or the mobile and rapidly deployable shelters (CBPSS, Chemically Biologically Protective Shelter System) intended for use as a forward medical treatment system shown in Figure 3. This unit may stand alone with its vehicle but is often interconnected with many others to form a large network.

The materials used in these systems are based on perfluoropolymers—that is, on fluoropolymers composed only of carbon and fluorine—no significant hydrocarbon content, very little oxygen, except as a side chain modifier. After the carbon-carbon single bond, the carbon-fluorine bond is about the

Figure 1. STEPO suit of CHALLENGE ULTRAPRO®[1] barrier laminate.

Figure 2. ITAP suit of CHALLENGE ULTRAPRO® barrier laminate.

Figure 3. Chemically and biologically protective shelter system (CBPSS) of CHALLENGE® X-22 barrier laminate.

strongest single bond in organic chemistry. It is the nature of the chemical structure of this family of polymers that results in its very broad chemical resistance. The most common member of this family is polytetrafluoroethylene, PTFE, known by any number of trade names, the most familiar of which may be the Dupont Teflon®[2] resins.

PTFE is remarkable in that it is virtually unaffected by contact with most laboratory or industrial chemicals. Table 1 is a table taken from a Dupont brochure[3] which lists just some of the chemicals with which PTFE and its sister compounds, FEP and PFA, are compatible. There are many compounds that are not on this list, of course—this is only a representative collection of chemical types.

TABLE 1[1]. Typical Chemicals with which TEFLON® Resins Are Compatible[2]

Abietic acid	Cetane	Ferric chloride	Nitrobenzene	Potassium
hydroxide				
Acetic acid	Chlorine	Ferric phosphate	2-Nitro-butanol	Potassium
Acetic anhydride	Chloroform	Fluoronaphthalene	Nitromethane	permanganate
Acetone	Chlorosulfonic acid	Fluoronitrobenzene	Nitrogen tetroxide	Pyridine
Acetophenone	Chromic acid	Formaldehyde	2-Nitro-2-methyl	Soap and
detergents				
Acrylic anhydride	Cyclohexane	Formic acid	propanol	Sodium
hydroxide				
Allyl acetate	Cyclohexanone	Furane	n-Octadecyl alcohol	Sodium
hypochlorite				
Allyl methacrylate	Dibutyl phthalate	Gasoline	Oils, animal and	Sodium
peroxide				
Aluminum chloride	Dibutyl sebacate	Hexachloroethane	vegetable	Solvents,
aliphatic				
Ammonia, liquid	Diethyl carbonate	Hexane	Ozone	and
aromatic[3]				
Ammonium chloride	Dimethyl ether	Hydrazine	Perchlorethylene	Stannous
chloride				
Aniline	Dimethyl formamide	Hydrochloric acid	Pentachloro-	Sulfur
Benzonitrile	Di-isobutyl adipate	Hydrofluoric acid	benzamide	Sulfuric acid
Benzoyl chloride	Dimethy1formamide	Hydrogen peroxide	Perfluoroxylene	
	Tetrabromoethane			
Benzyl alcohol	Dimethyl hydrazine,	Lead	Phenol	
	Tetrachloroethylene			
Borax	unsymmetrical	Magnesium chloride	Phosphoric acid	
	Trichloroacetic acid			
Boric acid	Dioxane	Mercury	Phosphorus	
	Trichloroethylene			
Bromine	Ethyl acetate	Methyl ethyl ketone	pentachloride	Tricresyl
phosphate				
n-Butyl amine	Ethyl alcohol	Methacrylic acid	Phthalic acid	
	Triethanolamine			
Butyl acetate	Ethyl ether	Methanol	Pinene	Vinyl
methacrylate				
Butyl methacrylate	Ethyl hexoate	Methyl methacrylate	Piperidene	Water
Calcium chloride	Ethylene bromide	Naphthalene	Polyacrylonitrile	Xylene
Carbon disulfide	Ethylene glycol	Naphthols	Potassium acetate	Zinc chloride
		Nitric acid		

1 From Dupont publication E-21623-1.
2 Based on experiments conducted up to the boiling points of the liquids listed. Absence of a specific chemical does not mean that it is incompatible with TEFLON resins.
3 Some halogenated solvents may cause moderate swelling.

The CHALLENGE laminates are composed of unique, multilayered perfluoropolymer films and coated reinforcing substrate(s) of high performance aramid fabrics. The structures are represented schematically in Figure 4 and are typically composed of two or three films and one or two substrates. The films are produced by SGPPL via a proprietary casting process. Figure 5 shows a cross section of one of our films, 4-mils (about 100 microns) in thickness. Each of the 12 striations seen in this actual photomicrograph represents a different layer of resin. Each of these layers may have a different composition—different polymers, different pigments, different fillers or other performance additives. The fact that there is this ability to vary the layers means a film may be tailored for the application. For example, outer layers might be a camouflage green or desert tan and underlying layer(s) a contrasting color in order to provide a visual indication of surface wear or damage. Pigments are also added to provide blackout properties, improve IR invisibility and to protect substrates from UV damage. The layers might be formulated so that different temperature properties could be achieved on opposite faces, making one side bondable at a different temperature than the other. The ability to tailor the bonding temperature is important in the manufacture of the laminate, in fabrication of the protective suit or shelters and in field repairs.

As for reinforcing substrates, for many applications SGPPL uses fabrics woven of fine continuous filament fiberglass for high strength, weatherability and high temperature capability. But for CB-resistant

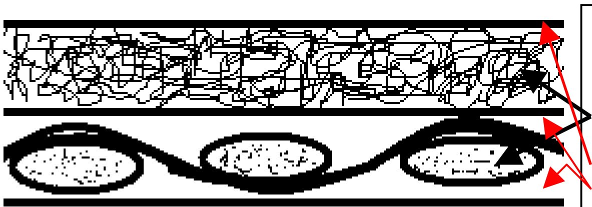

Figure 4. Schematic Representation of the Structure of CHALLENGE and ULTRAPRO Barrier Composites:

One or two woven or non-woven, coated aramid substrates

Two or three multilayer cast perfluoropolymers films

clothing and shelters, aramids have been the textiles of choice. Most people would recognize the Kevlar®[2] and Nomex®[2] brand names of the Dupont Company. These fibers and fabrics are chosen not only for their high strength and light weight, but also for high temperature capability. Processing of perfluorinated polymers is done at high temperatures, so the substrates must be able to retain most of their strength throughout the coating, lamination, and fabrication processes. A key performance feature of these fabrics is their flexibility and their ability to retain their strength after repeated strike and erect cycles or multiple donning and doffing.

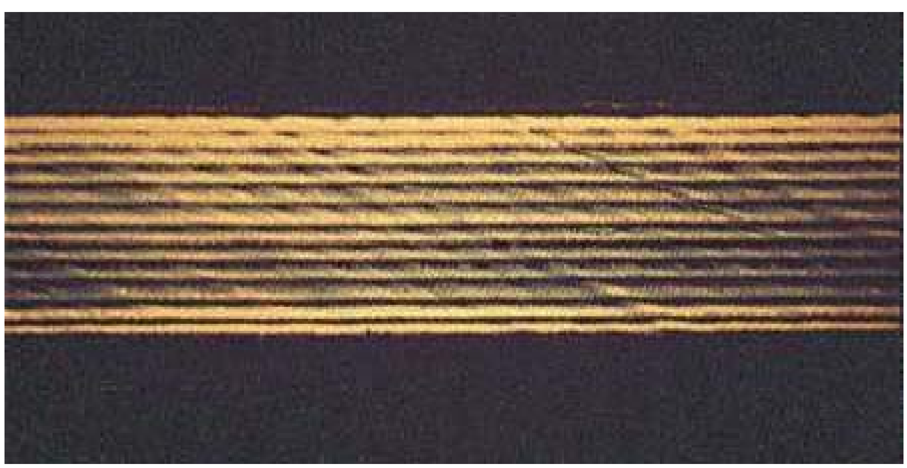

Figure 5. Cross-sectional photomicrograph of SGPPL cast PTFE film, 4 mils, 12 layers.

SGPPL may use commercially available fabrics, but for critical applications such as material for collective CB protection, it is far more likely that the fabric will be engineered from the yarn up. It is thus possible to design in the desired physical properties by weaving the textile in house. SGPPL is generally able to weave specialty fabrics (such as glass and aramids) in wider widths and higher quality than are available from commercial mills.

These substrates can be coated in multiple steps, again tailoring the coating composition from the fabric out so as to change the substrate properties. It is even possible to make the two sides of a substrate quite different by putting different formulations on each surface.

We have produced a number of different materials for CB-resistant systems. Their typical physical properties are summarized in Table 2.

TABLE 2. Typical Characteristics of CB Hardened Composites Produced by Saint-Gobain PPL

Product	Weight, osy	Thickness, mils	Breaking Strength, pli	Trapezoidal Tear Strength, lb	Relative barrier rating	Comments
CHALLENGE® X-22	~13	14-16	>350	35-45	Excellent	Shelters
CHALLENGE X-23	~15.5*	14-16*	>350*	>40*	Best**	Shelters, in development
CHALLENGE X-22/floor material	24-25	25-26	NT	NT	Best**	Shelter floors, highly damage resistant
ULTRAPRO® Vapor	14-16	22-24	Yields @ 20-40 PLI	ca. 40	Best**	Suits
ULTRAPRO Splash	10-11	18-20	NT	NT	Excellent	Suits

* Product is in development stages; values shown are nominal/expected.
** 5-layer construction, 3 barrier films.
All products: Useful temperature range of –40 to 500°F; exhibit no afterflame and will not burn unless in contact with an ignition source; will not support surface fungal growth.

Beyond the physical strength requirements, the chemical resistance of the composite is of paramount importance—not only to live agents, but also to decontaminating media. Because PTFE and its family of perfluoropolymers are so inert, there is little affinity of the composites for agents or other chemicals with which they come into contact. Figures 6-7 are plots of agent permeation and evaporation in the dual flow test of CRDC-SP-84010, method 2.2 (liquid agent contamination/vapor penetration method)[4], run at 70°F. There is virtually no permeation of distilled mustard (HD) during the 72 hour test and, in fact, all of the agent has evaporated from the exposed surface in a matter of less than 24 hours. Basically all of the agent is accounted for by that evaporation—none is held in the composite. The material tested here is the CHALLENGE® X-22 laminate. The total cumulative amount of HD detected on the opposite side of the cell was less than 0.75 $\mu g/cm^2$, over the entire 72 hour period.

Figure 8 illustrates how different levels of abrasion are indicated by the appearance of the surface of the CHALLENGE Ultrapro laminate. This composite material provides, I believe, the highest level of military and commercial CB protection currently available. The material is fully decontaminable,

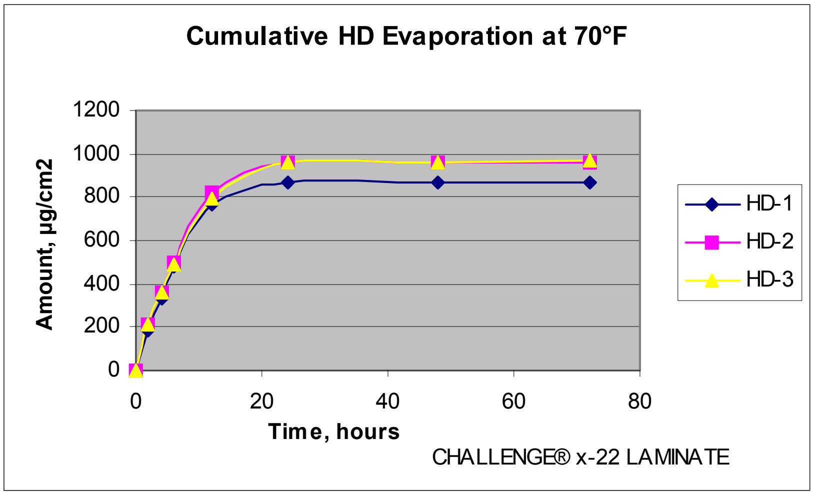

Figure 6. Cumulative evaporation of HD.

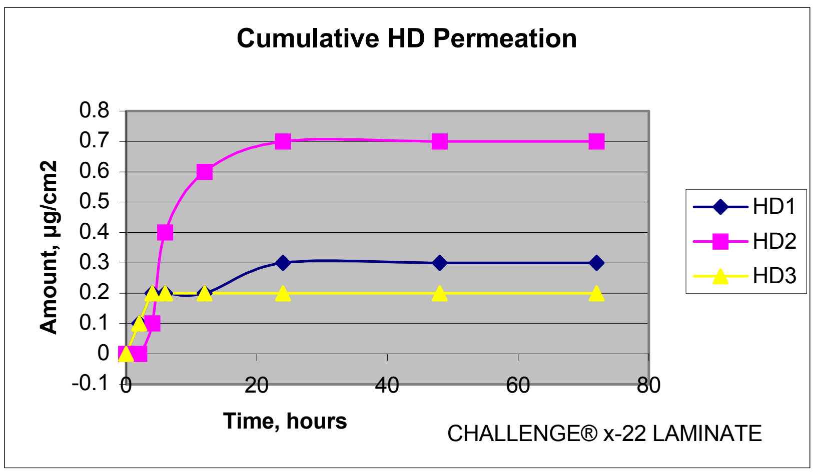

Figure 7. Cumulative permeation of HD.

statically dissipative and garments made from it may be used repeatedly. The Ultrapro material has been in field use for over two years as the US Army's Self-contained Toxic Environment Protective Outfit (STEPO). Even in the condition shown in the third image, the material will pass the static vapor penetration test of MIL-STD-282, method 204.1.2 (100 minutes).

Relative to actual barrier properties of the CHALLENGE laminates, there has been extensive chemical testing over the many years of development, as well as after commercial and military introduction of suits and shelter. Since, however, testing of every material to every chemical is hardly a practical task, several researchers have developed models to effectively predict the permeation behavior of fluoropolymer-based materials. The two most successful models that the author is aware of are one based on so-called RED affinity parameter[5] and one based on the molecular size and chemical structure of the challenge agent.[6,7] The affinity parameter approach of Hansen et. al. required that molar volume be

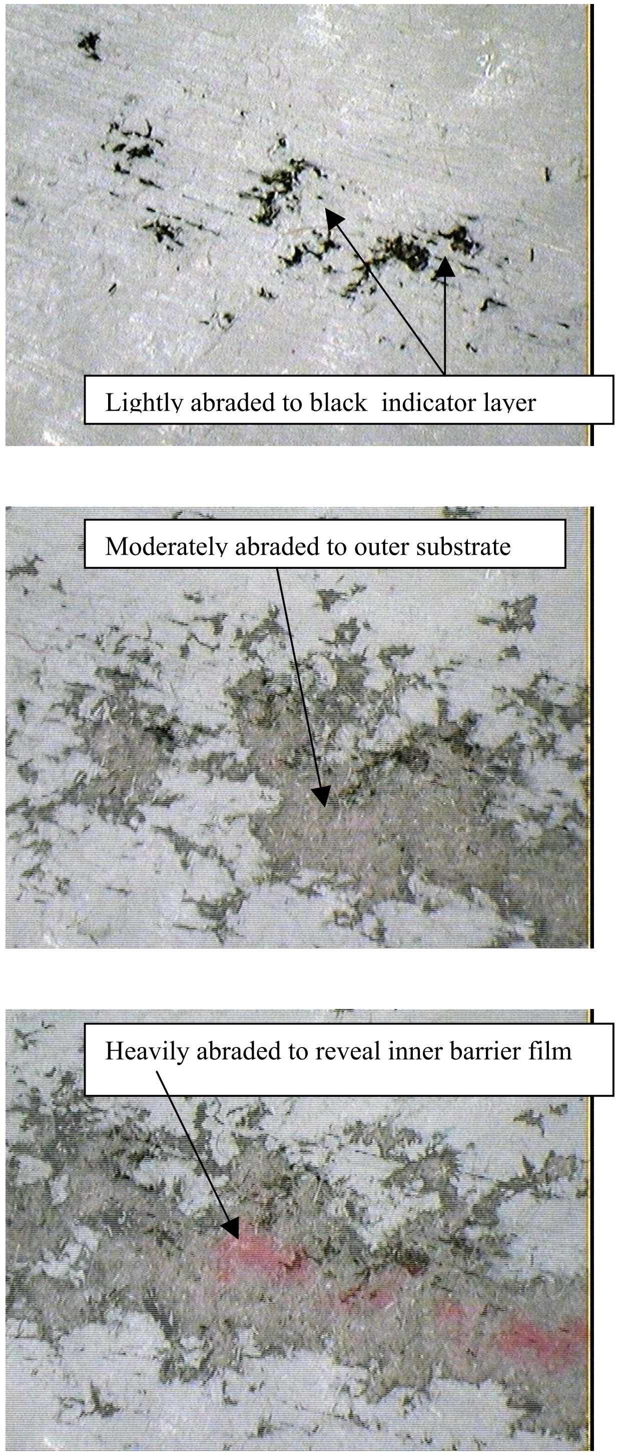

Figure 8. Effect of Abrasion on the appearance of ULTRAPRO® Barrier Laminate.

used to screen out certain chemicals. Substances with molar volumes greater than ~75-100 cm^3/mole simply do not permeate at a detectable level within the three or 8 hour test period. Goydan et. al. published a predictive method based on molecular size/weight and chemical structures. Table 3 shows a selection of chemicals and live agents and their predicted permeation behavior. Those predictions followed by a question mark are the author's best guess of behavior based on the published theories of each of the two predictive methods. The authors of the two methods neither tested live agents or made predictions about their permeation in the papers referenced. Nor did either address water vapor transmission, as water vapor is not a chemical hazard. Based on the type of information shown in this table, SGPPL has chosen WVTR at elevated temperatures (ASTM F-1249)[8] and trichloroethylene permeation testing via ASTM F-739[9] as effective screening methods for barrier materials.

TABLE 3. Predicted Permeation Behavior of Selected Chemicals and Live Agents through Fluoropolymer-based Barrier Systems

Chemical	**Molecular Weight**	**Density, g/cm^3**	**Molar Volume, cm^3/mole**	**# atoms, not H**	**Permeation predicted – Hansen et. al.[5]**	**Permeation predicted- Goydan et. al.[6,7]**
GD/Soman	182.2	1.02	179	>6	No	No
HD/distilled mustard	159.1	1.27	125	4	No?	No
VX	267.9	1.01	264	>6	No	No
TCE/trichloroethylene	131.4	1.465	89.7	5	Yes	Yes
Water	18	1	18	1	Yes?	Yes?

The two predictive models mentioned above were based on permeation testing of early CHALLENGE materials that were three layer/2-barrier-film constructions, similar to X-22 used in CBPSS. Obviously, if one adds additional barrier layers to a laminate, permeability of the laminate will drop, often dramatically. That is, in fact, our experience. While lab testing (Table 4) reveals a steady state rate of permeation for both water vapor transmission and permeation of trichloroethylene can be achieved in a typical testing period for three layer structures, no breakthrough of TCE through X-23 was seen in an 8 hour permeation test. The minimum detectable permeation rate in this testing was 0.001 µg/cm^2-min, a factor of 100 times more sensitive than the required by NFPA for level A suits.

TABLE 4. Permeability Comparison of Challenge X-22 and X-23

Test/Parameter	**X-22**	**X-23**
Trichloroethylene, 27°C, ASTM F-739		
Normalized breakthrough time, min	45 –60	>480
Max. or steady state permeation rate, µg/cm^2-min	0.5 avg	Not detectable
Minimum detectable permeation rate	0.001 µg/cm^2-min	0.001 µg/cm^2-min
Water vapor transmission rate at 50°C/100% RH, g/100 in^2-24 hr (ASTM F-1249)	0.4, typical	0.2*

* X-23 is a developmental material, available data is limited.

Because of the demonstrated lack of affinity of PTFE for most chemicals, decontamination of the composites is remarkably effective. Table 5 includes some decontamination studies of Garland et. al.[10] The data shows that the CHALLENGE material shows no absorption of the chemical used (nitrobenzene) and it was not possible to detect any by extraction, even without decontamination.

TABLE 5. Contamination of Various Barrier Materials with Nitrobenzene[10]

	Exposure Time*	% Contamination	% Decon, 1st wash (Freon®[2] 113)	% Decon, 2nd wash (Freon® 113)
Neoprene®[2]	75 min	46	66.7	92.4
Viton®[2]	150 min	3.9	82.9	99.1
Butyl	15 hr	3.3	44.7	89.5
Tyvek®[2]/Saranex®[11] 23	5 hr	1.5	Disposable	Disposable.
CHALLENGE®	24 hr	0	100**	100**

* Exposure time = breakthrough time plus one hour or 24 hours in the case of no detectable permeation.
** Nitrobenzene was not detected in the unwashed, exposed disk, or in either washed disk.

CONCLUSIONS

In summary, the CHALLENGE and ULTRAPRO laminates have the broadest chemical resistance of any barrier materials suitable for use in suits, shelters or other systems intended to provide individual or collective CB protection. This superior barrier performance is combined with inherent non-burning behavior, ease of decon, physical strength and tunable appearance to provide a range of products for use in protective shelters.

REFERENCES

1. Registered trademark of Saint-Gobain Performance Plastics.
2. Registered trademark of Du Pont.
3. “Teflon® Fluorocarbon Resin in Chemical Service,” Dupont publication no. E-21623-1.
4. CRDC-SP-84010, method 2.2 (liquid agent contamination/vapor penetration method).
5. Hansen, C.M., Billing, Jr, C.B., Jr. and Bentz, A.P., “Selection and Use of Molecular Parameters to Predict Permeation through Fluoropolymer-based Protective Clothing Materials,” *Performance of Protective Clothing: Fourth Volume, ASTM STP 1133,* James P. McBriarty and Norman W. Henry, Eds., American Society for Testing and Materials, Philadelphia, 1992, pp. 894-907.
6. Goydan, R, and Powell, J.R., “Development of a Model to Predict Chemical Permeation of the U.S. Coast Guard Chemical Response Suit,” Final Report No. CG-D-08-92, October, 1991.
7. Goydan, R, Powell, J.R., Bentz, A.P., and Billing, Jr, C.B., “A Computer System to Predict Chemical Permeation through Fluoropolymer-based Protective Clothing,” *Performance of Protective Clothing: Fourth Volume, ASTM STP 1133,* James P. McBriarty and Norman W. Henry, Eds., American Society for Testing and Materials, Philadelphia, 1992, pp. 956-969.
8. ASTM F-1249, “Test Method for Water Vapor Transmission Rate though Plastic Film and Sheeting Using a Modulated Infrared Sensor,” American Society for Testing and Materials, Philadelphia.
9. ASTM F-739, “Test Method for Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases under Conditions of Continuous Contact,” American Society for Testing and Materials, Philadelphia.
10. Garland, C.E. and Torrence, A,M., “Protective Clothing Materials: Chemical Contamination and Decontamination Concerns and Possible Solutions,” *Performance of Protective Clothing: Second Symposium, ASTM STP 989,* S.Z. Mansdorf, R.Sager, and A.P. Nielson, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 368-375.
11. Registered trademark of Dow.