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Decontamination Effectiveness of Leather and Rubber Samples Specifically Treated for Fire Boot Applications

Abstract: PPE decontamination of residual toxic and dangerous fire ground chemicals is a concern for all firefighters. With respect to firefighting footwear, the long-held belief has been not only that rubber boots absorb less contaminants than leather boots, but also that rubber boots can be decontaminated more effectively than can leather boots. After Gore conducted a decontamination procedure on both rubber and leather footwear samples, this study shows that both parts of that assumption are false. Specifically it reveals that in most instances the leather footwear samples were more effectively decontaminated than were the rubber footwear samples.

Objective [1]

Firefighters are concerned about toxic and dangerous chemicals remaining in their gear after decontamination.[2] These chemicals can affect a firefighter's long-term health and safety,[3] and it is important that departments take this into account when purchasing gear. With respect to footwear, the ability to effectively decontaminate boots has been an important factor when departments are deciding whether to adopt leather or rubber footwear. Although firefighters are aware of the better fit, agility, and stability of leather footwear, a major concern has been the industry assumption that leather boots retain more chemicals than rubber boots after working exposures. To evaluate this premise technically, W. L. Gore & Associates, Inc., conducted a series of laboratory tests on samples of leather and rubber boot materials that manufacturers had treated specifically to be used in firefighting footwear. The objective of these tests was to determine the residual levels of chemical contamination after a decontamination procedure was completed.

Testing Protocol

To ensure that comparable samples were being tested, Gore only used newly purchased materials. Leather samples were supplied by a certified fire-boot manufacturer. To represent rubber boots, samples of new rubber materials used in fire boot applications were obtained. Because the process to manufacture rubber boots may further affect the rubber and yield different results than rubber fire-boot materials, another set of rubber material samples was cut directly from a pair of rubber NFPA 1971 certified boots.

The Gore testing protocol was based on the methodology used in the FEMA-commissioned study entitled "Non-Destructive Testing and Field Evaluation of Chemical Protective Clothing."[4] In this protocol, each sample was saturated for 30 minutes with one of the selected chemicals (see Chemical Selection). It was then rinsed with cold water for 30 seconds and scrubbed with a soft brush and 1.2 percent liquid detergent for 30 seconds. The samples then underwent another 30-second cold-water rinse and were air-dried in a well-ventilated area for 16 hours at room temperature.

To ascertain the amount of chemical remaining on and in each sample, Gore evaluated them for evidence of both gross (surface) contamination and matrix (within the sample) contamination. Initially, each sample was visually inspected for any residue spots or stains, which would indicate surface contamination.

Test specimens one inch in diameter were then cut from each sample to evaluate the matrix contamination level of each chemical (Figure 1: Leather Specimen, Figure 2: Rubber Specimen). Each specimen was then placed in a separate air-tight vial and subjected to thermal desorption at 160°C for 30 minutes to separate the residual chemical molecules from the sample. The off-gas residuals were collected, and the number of micrograms per one-inch disk of the sample was quantified using gas chromatography.

[1] The specific data provided in this paper is derived from tests performed in a laboratory environment. This data does not represent results that will be found in other tests or environments. The data in this report does not represent all results that could be derived from other tests or environments.

[2] NFPA 1851: Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting, 2008 edition, Annex A.7.1.1-A.7.1.4.2.

[3] WARNING: No products, including garments, footwear, or gloves, can offer absolute protection, even when new. Additionally, a product's performance will decline with wear, tear, abrasion, and other damage associated with use.

[4] Carroll, T. R., and Schwope, A. D., "Nondestructive Testing and Field Evaluation of Chemical Protective Clothing," Final Report, United States Fire Administration, Contract No. EMW-89-C-3045, Arthur D. Little, Inc., Cambridge MA, December 1990.

Figure 1: Leather Boot Specimen

Figure 2: Rubber Specimen

Chemical Selection

Referring to several NFPA personal protective equipment (PPE) standards,[5] Gore selected chemicals representing a broad range of physical characteristics for use in this testing (including vapor pressure, viscosity, and molecule size). The leather samples and rubber samples intended for fire applications were tested for evidence of contamination by 13 chemicals: carbon disulfide (CS_2), hexane, tetrachloroethylene, toluene, ethyl acetate, methanol, acetone, isooctane (gasoline), acrylonitrile, dimethylformamide (DMF), methylene chloride, diethyl amine, and liquid hydrochloric acid. In addition, Gore tested the rubber samples cut from the rubber 1971-certified boots for evidence of contamination by six of those chemicals: CS_2, tetrachloroethylene, isooctane, acrylonitrile, DMF, and diethyl amine. To gain reliable results, Gore tested three samples of each material for each separate chemical.

Results and Discussion

The visual inspection of all three sets of samples indicated that there was no evidence of gross (surface) contamination remaining after the wash, rinse and air dry decontamination procedure. Gore then evaluated the matrix (internal) contamination.

For each sample, Gore used the individual specimen results to calculate the mean and standard deviation of micrograms of residual contamination. For some of the specimens, the amount of residual chemical was below the detection limit of the analytical testing instrumentation; the mean values for these specimens are indicated with a less than sign (‹) and the lower detection limit of the instrument. If a specimen was saturated beyond the measurement capacity of the analytical instrumentation, the value is shown with a greater than sign (›) and the upper detection limit of the instrument. In both of these situations, the standard deviation does not apply since true values were not determined.

Figure 3 shows the residual values for each of the 13 chemicals tested in the leather specimens, and Figure 4 shows the residual values for the same chemicals tested in the samples of rubber intended for fire applications. Figure 5 lists the residual values for the six chemicals tested in rubber samples cut from purchased NFPA 1971 certified rubber boots.

Figure 3: Matrix Residuals of Chemicals Found in Leather Specimens (Measured in Micrograms per One-Inch Disk of Sample)

Chemical	Mean	Standard Deviation
Acetone	5.6	4.080
Acrylonitrile	‹ 0.25	Not Applicable
Carbon Disulfide	0.1	0.074
Diethyl Amine	86.8	40.223
Dimethyl Formamide	175.5	26.160
Ethyl Acetate	‹ 0.2	Not Applicable
Hexane	0.1	0.041
Hydrochloric Acid	1.9	1.644
Isooctane	‹ 0.2	Not Applicable
Methanol	1.6	0.404
Methylene Chloride	‹ 0.05	Not Applicable
Tetrachloroethylene	17.2	8.431
Toluene	5.4	3.802

[5] NFPA 1971: *Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting*, 2007 Edition, Section 8.28.4.2(4)
NFPA 1991: *Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies*, 2005 Edition, Sections 7.5.1(5), (8), (9), (19)
NFPA 1994: *Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents*, 2007 Edition, Section 8.7.4.2(2)(b).

Figure 4: Matrix Residuals of Chemicals Found in Rubber Specimens Intended for Fire Applications (Measured in Micrograms per One-Inch Disk of Sample)

Chemical	Mean	Standard Deviation
Acetone	534.0	26.727
Acrylonitrile	390.0	51.507
Carbon Disulfide	› 1,100.0	Not Applicable
Diethyl Amine	1,885.0	1,312.144
Dimethyl Formamide	434.0	125.020
Ethyl Acetate	› 800.0	Not Applicable
Hexane	› 688.0	Not Applicable
Hydrochloric Acid	0.0	0.0
Isooctane	732.0	21.000
Methanol	13.3	5.742
Methylene Chloride	434.3	181.087
Tetrachloroethylene	› 1,744.0	Not Applicable
Toluene	› 1,207.0	Not Applicable

Figure 5: Matrix Residuals of Chemicals Found in Rubber Cut from 1971-Certified Boots (Measured in Micrograms per One-Inch Disk of Sample)

Chemical	Mean	Standard Deviation
Acrylonitrile	3.6	0.586
Carbon Disulfide	2.7	1.650
Diethyl Amine	900.0	126.456
Dimethyl Formamide	270.7	13.614
Isooctane	288.5	31.820
Tetrachloroethylene	398.0	227.778

These results indicate that when compared to both types of rubber samples, the leather samples retained a substantially **lower** amount of all residual chemicals except hydrochloric acid.

Figure 6 shows the mean matrix residuals found in the samples for each the six chemicals tested with all three materials, while Figure 7 shows the mean matrix residuals found in samples for each of the seven chemicals tested only on leather samples and rubber samples intended for fire applications.

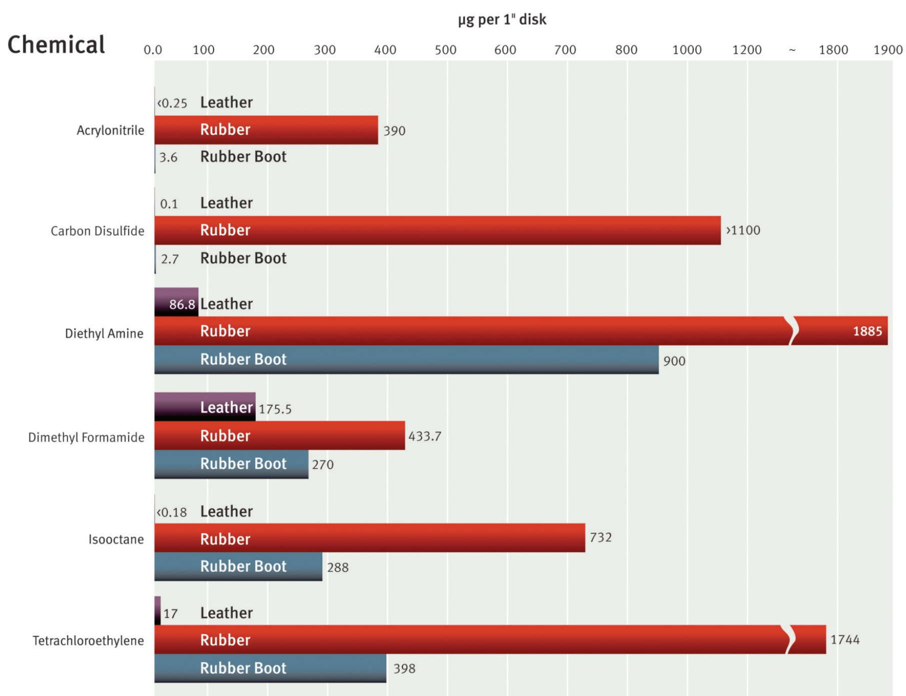

Figure 6:
Residuals of Chemicals Tested in Leather, Rubber Boot and Rubber Intended for Fire Applications

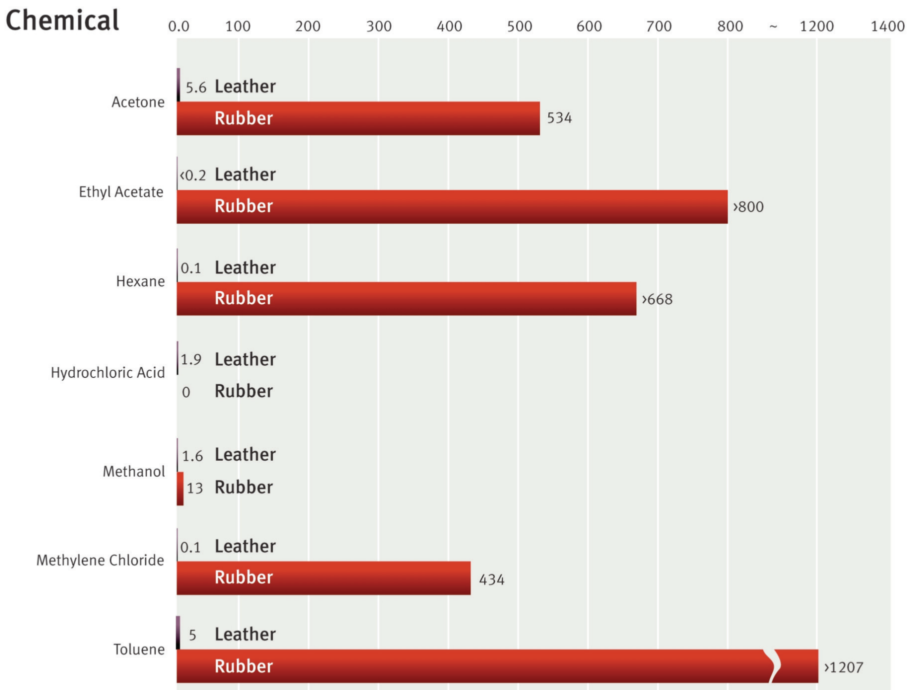

Figure 7:
Residuals of Chemicals Tested in Leather and Rubber Intended for Fire Applications

Perhaps the most significant results for firefighting professionals were those for isooctane (gasoline) because it is so frequently encountered at emergency scenes (Figure 8). The isooctane residuals after the decontamination procedures remained relatively high for the samples of rubber boot and rubber intended for fire applications even after decontamination. In contrast, the leather samples were almost fully decontaminated of isooctane by the normal decontamination procedures.

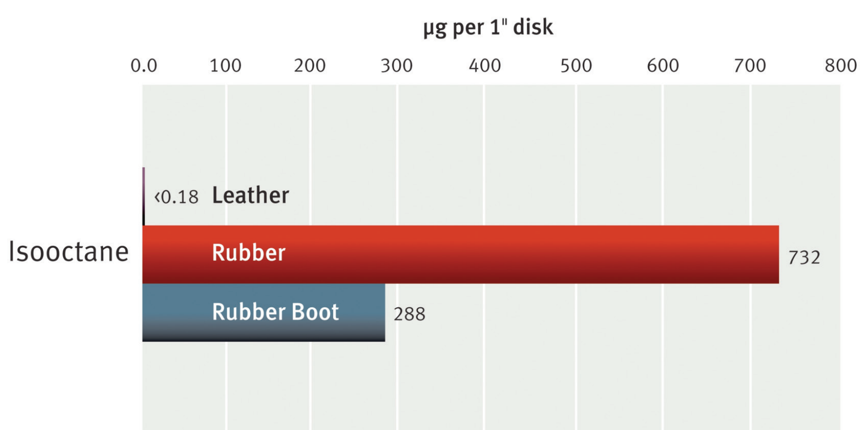

Figure 8:
Residual Values for Isooctane

Conclusions

During the course of their jobs, firefighters are exposed to many chemicals, and their gear must provide safety and protection in these extreme conditions. The fire industry has traditionally considered rubber boots to be easier to decontaminate after exposure, but firefighters have found leather boots to be much more stable, flexible, and comfortable. This study performed in W. L. Gore & Associates' laboratories indicated that leather boot materials retained substantially lower amounts of most contaminants at the matrix level than rubber boot materials after normal wash and air-dry decontamination procedures.