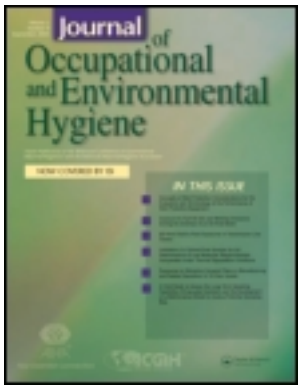

Journal of Occupational and Environmental Hygiene
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uoeh20

# Plasticizer Contamination of Firefighter Personal Protective Clothing - A Potential Factor in Increased Health Risks in Firefighters

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Accepted author version posted online: 27 Jan 2014.Published online: 14 Apr 2014.

To cite this article: Column Editor Steven Lacey, Reported by Barbara M. Alexander & C. Stuart Baxter (2014) Plasticizer Contamination of Firefighter Personal Protective Clothing - A Potential Factor in Increased Health Risks in Firefighters, Journal of Occupational and Environmental Hygiene, 11:5, D43-D48, DOI: 10.1080/15459624.2013.877142

To link to this article: http://dx.doi.org/10.1080/15459624.2013.877142

*Journal of Occupational and Environmental Hygiene*, 11: D43–D48
ISSN: 1545-9624 print / 1545-9632 online

DOI: 10.1080/15459624.2013.877142

# Case Study
# Plasticizer Contamination of Firefighter Personal Protective Clothing – A Potential Factor in Increased Health Risks in Firefighters

*Chemical exposures may be responsible for firefighters' elevated incidences of cancer and cardiovascular disease. This study characterized semivolatile chemical contamination on firefighter personal protective clothing to assess exposure of firefighters to these chemicals. Samples from used firefighter protective clothing, including gloves, hood, and one coat wristlet, were extracted with methylene chloride and analyzed by EPA method 8270 for semivolatile contaminants, including 20 polycyclic aromatic hydrocarbons (PAHs) and 6 phthalate diesters. Twenty-two of the chemicals of interest were found on at least one clothing swatch. Only di-(2-ethylhexyl) phthalate (DEHP), a plasticizer, added to polyvinyl chloride (PVC) to increase flexibility, was found on every swatch. DEHP concentrations were the highest of any chemical measured, and were 52 to 875 times higher than any PAH concentration measured. DEHP was also detected on most items of unused firefighter personal protective clothing, although at much lower levels. These findings suggest that firefighters are exposed to high levels of DEHP, a probable human carcinogen, and at levels much higher than PAHs, the semivolatile toxic combustion products most extensively studied historically. Firefighter exposure to DEHP and other phthalate diesters therefore merits further study.*

**Keywords** Di-(2-ethylhexyl) phthalate, DEHP, firefighters, exposures, phthalates, polycyclic aromatic hydrocarbons

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## INTRODUCTION

Firefighters are subject to an increased risk of coronary heart disease and several types of cancer.[1–4] A meta-analysis[1] of 32 studies of cancer in firefighters ranked elevated risks of testicular and prostate cancer, non-Hodgkin's lymphoma, and multiple myeloma in firefighters as "probable" They also reported a "possible" elevated risk of eight additional cancers including malignant melanoma and brain cancer.

Exposures proposed to be responsible for the above adverse outcomes include toxic gases, particulates, and a wide variety of organic chemicals in the vapor state or adsorbed onto protective gear and particulate matter.[5–7] Phthalate diesters make up a class of chemical agent which has recently been identified as a frequent, and often the most abundant, contaminant of firefighter gear.[6] Phthalate diesters, particularly di-(2-ethylhexyl) phthalate (DEHP), are found in high concentrations as plasticizers in polyvinyl plastic materials, such as wire sheathing, flooring, wall coverings, furnishings, and vinyl siding. The presence of phthalate diesters is of special relevance because several members of this class have been shown to display the same types of toxicity—cardiac and carcinogenic—in experimental animals as is found in firefighters.[8–10]

**TABLE I. Firefighter Gear Sampled**

| Gear | Manufacturer | Description and Material |
|---|---|---|
| Protective Hoods (n = 3) | American Firewear (Dayton, Ohio) | Style HD 300 22887FNF, material - Nomex |
| Coat (n = 1) | Honeywell First Responder (Dayton, Ohio) | Morning Pride, Nomex wristlets |
| Structural Gloves (n = 2) | American Firewear (Ohatchee, Ala.) | Model 6500, outer layer - kangaroo leather, middle layer - Pyrotect, inner layer - Kevlar/Nomex, cuff - Nomex |

Exposure to these agents may result from inhalation, but deposition onto protective gear with subsequent skin contact creates the further possibility of exposure by transdermal absorption.[5] Since they are highly lipophilic, phthalate diesters would be expected to be readily absorbed through the skin, especially at the elevated skin temperatures experienced in firefighting situations.[11] In this study, phthalate diesters and polycyclic aromatic hydrocarbons (PAHs) were characterized and quantitated on firefighter personal protective gear, especially that which is in frequent contact with skin. Previous studies were extended by asking whether glove contamination extended to the inner layers of firefighter gloves. This addresses the question whether dermal exposure to such contaminants could occur not only by handling of contaminated gear, but also by direct exposure by skin contact even when gloves are being worn. Firefighter hoods and a coat cuff were analyzed in parallel to further assess the contribution to firefighter risk of the dermal absorption route.

## MATERIALS AND METHODS

### Sample Collection

Occupationally soiled firefighter protective clothing, and also unused clothing, including gloves, coats, and hoods, was donated to the University of Cincinnati by several Cincinnati metropolitan fire units. Detailed descriptions of the gear sampled are given in Table I.

Samples from different types of personal protective clothing were obtained using similar procedures. Hoods were composed of a double layer of a single type of material. A 10cm by 10cm sample was removed from the area of the chin, keeping both layers of fabric together. Samples were cut in half, from the chest edge to the chin edge, with one half being sent to the analytical laboratory for contaminant analysis, and one half being kept for future study.

The coat was fitted with double wristlets at the end of each sleeve. The entire right inner wristlet, which included a thumb loop, was removed from the coat, and the wristlet was cut in half from the hand side to the arm side. The half of the wristlet that included the thumb loop was analyzed.

The gloves were made up of three layers of different fabrics. The materials in the three layers are listed in Table I. A sample approximately 10cm by 10cm in the size of each layer was cut from the palm side of the glove. Samples were cut in half, from the wrist edge to the finger edge, with one half being sent to the analytical laboratory for contaminant analysis and one half being kept for future study. The three layers were extracted and analyzed separately. The sample halves were weighed and stored in a freezer at $-10^{\circ}$C until analysis.

### Analytical Methods

Samples were analyzed (ALS Datachem, Cincinnati, Ohio) for the presence of 26 phthalate diesters and PAHs following extraction with methylene chloride, according to EPA method 8270. The limit of detection for each analyte was 1 microgram.

## RESULTS

Of the 26 chemicals for which the analysis was performed, 22 were detected on at least one sample of protective clothing (Table I). DEHP was detected on every sample of occupationally used protective clothing. It was also detected on almost every sample of unused clothing at much lower levels. The only article of clothing that did not contain DEHP above the limit of detection was the unused hood.

The levels of phthalate diester contamination on soiled clothing samples, especially of DEHP, were much higher than those for PAHs, the semivolatile toxic combustion products most widely studied historically. In the glove and hood samples analyzed in this study, all agents were detected at concentrations several orders of magnitude higher than reported in a previous study.[6] Only the phthalate diester DEHP, albeit at low levels, was detectable on unused clothing samples, except for the outer layer of the unused glove. The outer layer, which was black kangaroo leather, also held low levels of several other phthalate diesters. None of the PAHs was detected on samples of unused clothing.

The three layers of the glove were separated and analyzed for one unused and one used glove (Glove 1). The outer layer of the glove provides cut resistance; the middle layer is a moisture barrier; and the inner layer insulates. For the soiled glove, a mass per unit weight concentration gradient was found for DEHP across fabric layers from the outermost to the innermost (Table II). For a second used glove (Glove 2), only the innermost layer was analyzed, as that is the layer worn in contact with the skin.

In almost every case, the levels of PAHs found on the middle layer of Glove 1 were higher than those found on the outer layer. Although a range of PAHs was detected on the middle and outer layers of Glove 1, only one PAH was found on the inner layer.

**TABLE II. Chemical Contaminant Concentration on Unused and Used Firefighter personal Protective Clothing**

| | Chemical contaminant concentration ($\mu$g/g sample) in different personal protective clothing[A,B] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Inner Glove Layer | | | Middle Glove | | Outer Glove | | Cuff | | Hoods | | |
| Chemical | Unused glove | Glove 1 | Glove 2 | Unused glove | Glove 1 | Unused glove | Glove 1 | Unused glove | Coat inner wristlet | Hood 1 | Hood 2 | Hood 3 |
| **PAHs:** | | | | | | | | | | | | |
| 1-Methylnaphthalene | | | | | | | | | | 1.4 | | |
| 2-Methylnaphthalene | | | | | | | | | | 1.4 | | |
| Acenaphthylene | | | | | | | | | 0.7 | 3.6 | | |
| Anthracene | | | | | | | | | | 0.9 | | |
| Benzo(a)anthracene | | | | | 2.3 | | 1.4 | | | 1.4 | | 0.5 |
| Benzo(a)pyrene | | | | | 0.8 | | | | 0.4 | | | |
| Benzo(b)fluoranthene | | | | | 2.0 | | | | 0.4 | | 0.5 | |
| Benzo(g,h,i)perylene | | | | | | | 0.5 | | 0.3 | | | |
| Benzo(k)fluoranthene | | | | | 0.8 | | | | 0.8 | | | |
| Chrysene | | | | | 3.5 | | 1.6 | | | 1.3 | 0.4 | |
| Dibenzo(a,h)anthracene | | | | | | | | | | 0.8 | | |
| Fluoranthene | | 0.7 | | | 7.9 | | 1.6 | | 0.5 | | 0.4 | |
| Fluorene | | | | | | | | | | 0.8 | | |
| Indeno(1,2,3-cd)pyrene | | | | | | | 0.5 | | 0.2 | | | |
| Naphthalene | | | | | | | | | 0.2 | 3.1 | | |
| Phenanthrene | | | | | 4.3 | | 0.7 | | 3.8 | | 0.4 | 1.1 |
| Pyrene | | | | | 8.4 | | 1.5 | | | | | |
| **PHTHALATES:** | | | | | | | | | | | | |
| Butyl benzyl phthalate | | 1.4 | 0.7 | | 7.3 | 0.4 | | | 8.0 | | | 2.0 |
| Di(2-ethylhexyl)phthalate | 1.4 | 320.0 | 30.0 | 4.4 | 830.0 | 4.5 | 1400.0 | 0.5 | 220.0 | 340.0 | 170.0 | 57.0 |
| Diethyl phthalate | | | | | 1.1 | 0.4 | 0.4 | | | | | |
| Di-n-butyl phthalate | | 2.2 | 0.8 | | 9.1 | 0.4 | | | | | 0.6 | |
| Di-n-octyl phthalate | | 1.3 | 1.6 | | 1.2 | 0.2 | 6.5 | | 1.8 | | 0.6 | |
| Detection Limit ($\mu$g/g clothing) | 0.7 | 0.7 | 0.6 | 0.9 | 0.6 | 0.2 | 0.2 | 0.3 | 0.2 | 0.3 | 0.3 | 0.4 |

[A] Blanks denote measurements below the limit of detection.

[B] No contaminant levels above the limit of detection (0.4 $\mu$g/g sample) were found in unused hoods.

Levels of DEHP comparable to those found on soiled gloves were found on three soiled hoods and a coat wristlet (Table II). Contaminants on the coat wristlet are listed next to the results for a cuff from an unused glove in Table II. Two hoods and the coat wristlet were also contaminated with other phthalate diesters. Much lower levels of a wide variety of PAHs were similarly found on the soiled hoods and coat wristlet.

## DISCUSSION

A large variety of phthalate diesters and PAHs were detected on the soiled protective clothing samples. In the samples analyzed in this study all agents were detected at concentrations falling midway between those reported in two previous studies.[6–12]

In the study by Stull et al., [13] samples from 3 heavily occupationally contaminated coats were analyzed, and levels of phthalate diesters and PAHs measured were much higher than those found in this study. Lower levels of phthalate diesters and PAHs were reported in the study performed by Fabian, or 8 weeks before analysis, while the materials in this study were used for an undetermined, likely much longer, period of time before being retired from active service. The study by Fabian et al. [6] suggested that phthalate diester contamination of firefighter protective gear is cumulative with time, which is supported by the current findings.

The common plasticizer DEHP was found on every sample of used firefighter protective clothing examined. Levels were from 52 to 875 times higher than that of the most abundant PAH found on the same clothing sample. PAHs are the most extensively studied semivolatile combustion products historically and include several recognized carcinogens. These results agree with those reported previously.[6–13] Levels of DEHP on 3 firefighters' used coats were previously reported to be from 15 to 33 times higher than the most prevalent PAH.[13] The second study reported DEHP levels that were at least 2.6 times higher than the highest level of any PAH on 8 used firefighter gloves, and at least 4.5 times higher than the highest level of any PAH on 8 used firefighter hoods.[6] The current findings are consistent with the ubiquitous presence of DEHP in many manufactured and/or processed domestic items and its ready transfer from burning materials to firefighter protective gear during fire suppression.

Ten to twelve different chemicals were detected on one hood (Hood 1) and a coat wristlet worn by the same firefighter. Both items of protective clothing had recently been worn in a structure fire before being taken out of service due to excessive contamination. Even though both were heavily contaminated, the chemicals found on the two items were almost uniformly different. The most abundant chemical found on both items was again DEHP.

The difference in composition of adsorbed chemicals between the wristlet and the hood could apparently not be explained by the difference in boiling points between the two sets of chemicals. Higher boiling point compounds might have been expected to be found preferentially on the wristlet, as they could be transferred more readily by direct transfer from burned materials rather than through volatilization and subsequent condensation on hoods, which are more distant from the combustion source. An ANOVA procedure with the Tukey's studentized range test (SAS 9.3, SAS Institute Inc., Cary N.C.), performed on the distribution of boiling points of the chemicals detected on the hood compared to those on the wristlet, suggested that this was not the case, since the distributions of boiling points were not significantly different ($P < 0.05$). Other factors, such as differences in affinity for different clothing material types may also play a role, but these have yet to be determined.

The greatest variety of chemical agents was found on the middle layer of Glove 1, with DEHP again having the largest concentration per unit mass of material relative to other agents. A mixture of phthalate diesters was found on all three glove layers, whereas PAHs were primarily present on the middle and outer layers. Some PAHs found on the middle layer were not observed on the outer layer. Other PAHs were found in higher concentrations on the middle layer than on the outer. PAHs are known to be more light-sensitive, therefore it is possible that some of these agents migrated in part through the outer layer of the glove to the middle layer, and were as a result protected from degradation due to light exposure. This is a potential area for further study.

The current findings show that phthalate diesters are present on inner layers of firefighter gloves, and therefore suggest that dermal absorption may result, and may represent an important route of exposure to these agents. This proposal is supported by the results of a previous study showing that the wearing of cotton undergloves or glove liners under fire gloves reduced PAH contamination on firefighters' hands by 80%.[12] The observation that the inner layers of the two used gloves examined both were dirtier in appearance on the side facing the firefighter's hand than on the side facing the middle layer of the glove suggest that contaminants might be present on this layer as a result of transfer from firefighters' hands.

Gloves are removed first when exiting the fire scene. As a result, contamination may be transferred from helmets, hoods, coats, pants, and boots to the firefighters' hands when protective clothing is doffed. The level of discoloration found on the inside layer of the glove may not accurately reflect the levels of the different chemicals present. The relative contributions to skin contamination from the inner skin-side glove layer, compared to that from migration from the outside of the glove through the glove layers cannot be determined from this study.

A principal purpose of firefighter hoods is to prevent dermal exposure to flames and heat; however they are worn next to some of the most permeable skin areas anatomically. Previous studies on regional differences in skin permeability have shown that the permeability of the skin of the jaw angle, forehead, and scalp is high and exceeded only by that of the scrotum.[14] Hoods become contaminated during fire events, and, if not cleaned, can continue to expose firefighters whenever they are

worn, donned, or doffed, even during training. Cleaning is infrequent following fire suppression.

Dermal absorption of DEHP has been found to be slow in animal experiments at ambient temperatures,[15] but would be expected to be markedly increased under the high temperature conditions to which firefighters are exposed,[11] making dermal exposure a potentially significant route of firefighter exposure. Prompt and frequent washing of gear and of the skin would be expected to reduce dermal exposures.

## CONCLUSION

Internal firefighter exposure to PAHs, but not phthalate diesters, has been previously studied.[16]. This is a serious deficit in information since the levels of DEHP found on occupationally soiled firefighter gear were far higher than levels of any PAH studied under the same conditions. Concentrations of phthalate diesters on firefighter gloves and hoods were several orders of magnitude higher than those reported after short periods of use, [6] suggesting that contamination of firefighter gloves and hoods increases with longer periods of use. DEHP exposure in experimental animals has been associated with several of the adverse health outcomes observed in firefighter populations, including cardiac effects and testicular cancer.[8–10] Further study of firefighter exposure to DEHP is needed.

Levels of human exposure cannot be deduced directly from measurements of contamination on personal protective clothing, because many factors interact to produce an effective internal dose at a target organ from a contaminant on clothing or skin. These include skin temperature, length of time of wear, heart rate, and frequency of cleaning and skin washing. Biomonitoring studies may help to quantify DEHP exposures in firefighters.

Experimental studies on the adverse health effects of DEHP have focused on ingestion. The current findings suggest that dermal absorption could also be a major route of exposure in firefighters, however. Determination of the major route of exposure to DEHP in this occupation is another area for future research.

## RECOMMENDATIONS

Results of this study suggest that contaminants accumulate in firefighter protective clothing over time. Prompt and frequent changing and washing of protective clothing, as well as showering, is recommended to reduce exposure to plasticizers and other toxic agents. The use of cotton glove liners would also reduce exposure by the dermal route, as would careful removal of turnout gear. Following decontamination principles at the scene of structural fires, much like at a hazmat incident, might be a small step in improving health protection. Any of these simple practices are doable at the scene of fires as well as during training sessions.



## ACKNOWLEDGMENTS

This research study was partially supported by the National Institute for Occupational Safety and Health through a Targeted Research Training grant, the Hazardous Substances Academic Training program of the University of Cincinnati Education and Research Center grant T42/OH008432-06, and a University of Cincinnati tuition scholarship.

The authors wish to acknowledge the significant contributions made by the members of Cincinnati metropolitan fire departments who cooperated with this study. They are grateful for the support given by ALS Datachem. They would also like to recognize the assistance of Carol Rice and Tiina Reponen of the Department of Environmental Health, University of Cincinnati.

Barbara Alexander is funded by Grant Number U45ES006184 from the National Institute of Environmental Health Sciences and C. Stuart Baxter funded by from the Department of Environmental Health, University of Cincinnati.

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