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Occupational exposures to new dry cleaning solvents: High-flashpoint hydrocarbons and butylal

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Abstract

The dry cleaning industry is moving away from using perchloroethylene. Occupational exposures to two alternative dry cleaning solvents, butylal and high-flashpoint hydrocarbons, have not been well characterized. We evaluated four dry cleaning shops that used these alternative solvents. The shops were staffed by Korean- and Cantonese-speaking owners, and Korean-, Cantonese-, and Spanish-speaking employees. Because most workers had limited English proficiency we used language services in our evaluations. In two shops we collected personal and area air samples for butylal. We also collected air samples for formaldehyde and butanol, potential hydrolysis products of butylal. Because there are no occupational exposure limits for butylal, we assessed employee health risks using control banding tools. In the remaining two shops we collected personal and area air samples for high-flashpoint hydrocarbon solvents.

In all shops the highest personal airborne exposures occurred when workers loaded and unloaded the dry cleaning machines and pressed dry cleaned fabrics. The air concentrations of formaldehyde and butanol in the butylal shops were well below occupational exposure limits. Likewise, the air concentrations of high-flashpoint hydrocarbons were also well below occupational exposure limits. However, we saw potential skin exposures to these chemicals. We provided recommendations on appropriate work practices and the selection and use of personal protective equipment. These recommendations were consistent with those derived using control banding tools for butylal. However, there is insufficient toxicological and health information to determine

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the safety of butylal in occupational settings. Independent evaluation of the toxicological properties of these alternative dry cleaning solvents, especially butylal, is urgently needed.

Keywords

Alternative dry cleaning solvents; butanol; butylal; dibutoxymethane; dry cleaning; formaldehyde; high-flashpoint hydrocarbon; hydrocarbons

Introduction

There are about 36,000 commercial dry cleaning shops in the United States.[1] Most are owner-operated small businesses with fewer than 10 employees.[2,3] In addition, some dry cleaning shops may be owned and staffed by individuals with limited English language skills and may be marginally profitable–factors that may prevent the owner-operator from maintaining a safe and healthy workplace.[2,3]

Dry cleaning solvent alternatives to perchloroethylene

Increasing environmental regulations and awareness of the potential occupational hazards from the dry cleaning chemical perchloroethylene (PERC) has resulted in some dry cleaners switching to alternative solvents. Some of the PERC alternatives are promoted as safe and environmentally friendly, although their effects on human health and the environment have not been well characterized.

Perchloroethylene can irritate the skin, depress the central nervous system, damage the liver and kidneys, and is a potential human carcinogen.[1,4] a survey conducted in King County, Washington, in 2010 found that most local dry cleaners (69%) were using PERC, but 21% were using a high flashpoint hydrocarbon solvent.[2,3] Subsequent field observations in 2012 by the Local Hazardous Waste Management Program in King County, Washington (LHWMP) found that the most frequently used high flashpoint hydrocarbon solvent was ExxonMobil's DF-2000, a product similar to odorless mineral spirits. Since the King County survey, another dry cleaning solvent called SolvonK4 was introduced in the U.S.[5] SolvonK4 is an acetal manufactured by Kreussler GmbH in Germany.

DF-2000

According to its safety data sheet DF-2000 is a nearly odorless synthetic hydrocarbon fluid containing C_{11} to C_{15} aliphatic-branched hydrocarbons, with a boiling point range between 174-234°C.[6,7] The Chemical Abstracts Service (CAS) number for DF-2000 (64742-48-9) represents hydrotreated heavy naphtha (petroleum) or isoparaffinic hydrocarbon.[6] These naphthas are classified as National Fire Protection Association Class IIIA solvents.

Little specific health information is available for DF-2000.[8,9,10] The manufacturer[6] reports that repeated exposure to the skin may cause skin dryness or cracking. When swallowed, this solvent may be aspirated and damage the lungs. At high concentrations, DF-2000 can also irritate the eyes, nose, throat, and lungs. Prolonged exposures at concentrations higher than the ExxonMobil Chemical suggested occupational exposure limit

(OEL) of 1,200 mg/m[3] can cause headaches, dizziness, drowsiness, unconsciousness, and other central nervous system effects, including death.[6]

A review by the California Environmental Protection Agency, Office of Environmental Health Hazard Assessment[11] of animal studies involving hydrocarbons similar to DF-2000 suggests they are safer than Stoddard solvent, which can contain aromatic hydrocarbons like benzene.[11] The German Social Accident Insurance Information System identifies substances with the same CAS number as DF-2000 as harmful and may cause lung damage if swallowed.[12]

The Federal Republic of Germany developed an OEL for a naphtha mixture with the same CAS number as DF-2000: Deutsche Forschungsgemeinschaft (DFG), maximum concentrations at the workplace (MAK) of 300 milligrams per cubic meter (mg/m[3]) (8 hr). The American Conference of Governmental Industrial Hygienists (ACGIH®) threshold limit value (TLV®) for a similar hydrocarbon mixture is in the range of 1142–1200 mg/m[3] (8 hr time weighted average [TWA]); range values were calculated using the reciprocal calculation mixture formula with two different group guidance values[13] and assuming 10% cycloparaffins and 90% paraffins.[12]

SolvonK4

SolvonK4 contains >99% butylal, with small amounts of n-butanol (<0.5%) and formaldehyde (<0.05%).[14,15] Synonyms for butylal include dibutoxymethane, 1-(butoxymethoxy) butane, and formaldehyde dibutyl acetal. The CAS number for butylal is 2568-90-3. SolvonK4 is a National Fire Protection Association Class IIIA solvent.

Little toxicity information is available for butylal. Published studies on its acute toxicity have focused on dermal and oral exposures.[16] The Toxics Use Reduction Institute (TURI) concluded that toxicological data are lacking for SolvonK4, rendering the human health assessment incomplete. [17]

The manufacturer of SolvonK4, Kreussler GmbH, reported low toxicity in animals exposed to butylal via ingestion and dermal contact.[15] The manufacturer also suggests that the airborne exposure risk to butylal at dry cleaning shops is low because the solvent has a low vapor pressure.[15] In a long-term inhalation study, no adverse effects were observed in rats after exposure to 478 parts per million (ppm) butylal over 13 weeks.[18] We are not aware of any studies that have evaluated respiratory sensitization or long-term inhalation exposures to butylal in humans. No toxicological data are available to characterize central nervous system effects or other target organ effects, reproductive or developmental toxicity, or other chronic health effects.

Kreussler states that short-term exposure to butylal does not elicit skin sensitization or irritation to the skin or eyes.[15] We are not aware of any studies that have evaluated longer duration exposures from ingestion or through skin contact. LHWMP determined that SolvonK4 exhibited lower toxicity to rainbow trout than PERC, but was more toxic than DF-2000.[19] Although the European Union has not classified butylal via REACH

(Registration, Evaluation, Authorization, and Restriction of Chemicals), the European Chemicals Agency (ECHA) has listed butylal as causing skin irritation.[18,20]

The dry cleaning process

Fabrics, including clothes, drapes, and other textiles, are received from customers, labeled, and sorted for cleaning. Prior to dry cleaning, stained fabrics may be pre-cleaned or "pre-spotted." Many different spot cleaning agents are used in the shops. These products are formulated according to the types of stains to be removed (i.e., hydrophilic or hydrophobic stains).

Modern dry cleaning machines use enclosed drums where the fabrics being cleaned are saturated with the dry cleaning solvent. Cleaning additives (e.g., detergent, sizing or fabric finishes, and stain repellant) are injected into the solvent flow line or into the drum of the machine (in contrast to an older method that involved predissolving the detergent in the solvent). When the cleaning cycle is complete, the solvent is drained, and the cleaned fabrics are placed under vacuum, heated, and tumbled to remove any remaining solvent. In our evaluations the duration of the dry cleaning cycle for SolvonK4 and DF-2000 machines was 70–80 min. Workers can manually spot-clean fabrics that are still stained or soiled after dry cleaning by using the same products used in precleaning. The cleaned fabrics are pressed (Figure 1) and ironed as needed, then hung on hangers and covered with plastic wrapping awaiting customer pick-up.

Modern dry cleaning machines like the ones we evaluated minimize the release of solvent vapors to ambient air by recycling the solvent in a closed loop system and evacuating the air in the cleaning chamber before the machine is opened. The heated solvent vapors generated during the drying cycle pass through a refrigerated condenser. [21] The condenser cools the air and condenses the solvent vapor to be recovered. Recovered solvent is then pumped into a vacuum still. This distillation process prevents impurities from building up in the solvent. Steam coils in the still heat the solvent to boiling. The solvent vapors flow through a condenser to remove water. This distillation process generates a concentrated waste material called "still bottoms" that contains residual solvent in addition to nonvolatile components such as detergent, sizing, waxes, oils, and greases. After the machine has cooled (usually overnight), the still bottoms are manually transferred to a waste container (Figure 2) with a specially designed rake, usually by the shop owner. Depending on the volume of dry cleaning processed in a shop, the still bottoms are removed every 1–2 weeks.

Control banding

Control banding (CB) is a technique used to assess and manage workplace risks. It is a qualitative risk assessment strategy that determines a control measure (for example dilution ventilation, engineering controls, containment, etc.) based on a range or "band" of hazards (such as skin/eye irritant, very toxic, carcinogenic, etc.) and exposures (small, medium, large exposure). CB is especially useful in the absence of an OEL. More information on CB is available at: http://www.cdc.gov/niosh/topics/ctrlbanding/default.html.

Study objectives

Our objectives were to (1) assess occupational exposures in dry cleaning shops using SolvonK4 and DF-2000; (2) identify workplace conditions and practices contributing to exposures; (3) determine potential routes of exposure; and (4) identify ways to reduce exposures.

Methods

Investigators from the National Institute for Occupational Safety and Health (NIOSH) Health Hazard Evaluation Program evaluated occupational exposures to DF-2000 and SolvonK4.[22,23] In Washington State the LHWMP collaborated with NIOSH investigators to recruit the dry cleaning shops, and LHWMP officials provided help with language services, field assistance, and technical expertise. We spent at least 2 days evaluating each shop (Table 1). We collected bulk samples of the dry cleaning solvents and personal and area air samples of dry cleaning solvents and other chemicals that may be produced or used during dry cleaning. We observed work practices, the use of personal protective equipment (PPE), and the cleaning of the dry cleaning machine still bottoms. We used Korean-, Spanish-, and Cantonese-language services throughout the evaluations.

Bulk samples

We obtained a neat sample of DF-2000 from the manufacturer. We collected a bulk sample of SolvonK4 from inside the dry cleaning machine reservoir in shop A and an unused bulk sample from shop B. We stored the SolvonK4 samples in 40 mL glass vials and kept the samples on ice until analyzed. All of the bulk samples were analyzed by gas chromatography with mass spectrometry (GC-MS) and fame ionization detection (GC-FID). For SolvonK4 we compared our bulk analysis to a commercial butylal standard (TCI America, Lot# FIE01, purity 98%) to determine butylal content. The butanol content in SolvonK4 was measured using NIOSH Method 1401, [24] and the formaldehyde content was measured using OSHA Method 52.[25]

Air samples

We collected full-shift and task-based personal and full-shift and short-term area air samples for DF-2000 and butylal in the respective shops. In the shops that used SolvonK4 we also collected personal and area air samples for formaldehyde and butanol. We collected full-shift personal air samples from most production employees and the owners/operators.

We collected air samples for DF-2000 and butylal on 150-mg charcoal tubes using SKC model 210-1002 pocket pumps at a flow rate of 200 mL/min. We used NIOSH Method 1550 to analyze for DF-2000, with minor modifications. We developed an analytical method for butylal because none was available.[22] Samples of DF-2000 and butylal were extracted in carbon disulfide and analyzed using GC-FID, as described in the NIOSH report.[22]

Butanol was sampled and analyzed using NIOSH Method 1401,[24] and formaldehyde was sampled and analyzed using OSHA Method 52.[25] Formaldehyde was not sampled using NIOSH Method 2016 because laboratory testing revealed that this method resulted in false

positives for formaldehyde in the presence of SolvonK4 (butylal). More details are included in the NIOSH report. [22]

In the first SolvonK4 shop we evaluated we collected separate samples for butylal and butanol as the method for butylal had been developed to analyze butylal exclusively. However, after verifying in the chemical analysis that both butylal and butanol could be run simultaneously, we sampled butylal and butanol on a single sorbent tube at the second SolvonK4 shop. The results from personal air sampling were compared to OELs, when available.[13,26] We also evaluated butylal exposures using CB tools.

Control banding

We used CB tools to evaluate inhalation risks for butylal when loading, unloading, and hanging fabrics from the dry cleaning machine, and the inhalation and dermal risks for butylal when spraying and brushing fabrics with a spotting solution containing SolvonK4. We selected the following CB tools to evaluate inhalation and dermal risks associated with butylal:

- the Control of Substances Hazardous to Health (COSHH) Essentials inhalation tool,
- the Stoffenmanager inhalation and dermal tools, and
- the RISKOFDERM dermal tool.

We identified one risk phrase (R-phrase) for butylal, R38-Irritating to skin (from ECHA[20]) and used this R-phrase for all three CB tools. More information on these CB tools including inputs is provided in the supplemental document.

Results

Bulkanalysis

We found C_{11} to C15 aliphatic-branched hydrocarbons, with boiling points ranging from approximately 174–234°C in our bulk analysis of DF-2000. We did not detect benzene in the DF-2000 bulk sample, which is consistent with information provided by the manufacturer,[6] the NIOSH international chemical safety card for CAS number 64742-48-9,[26] and results from other reported bulk analyses.[8]

The amount of butylal in the two SolvonK4 bulk samples we analyzed was consistent with that reported by the manufacturer,[15] with trace amounts of butanol (0.05% and 0.06%) and formaldehyde (<0.00045% and 0.007%).

Personal air sampling

Full-shift personal exposures to DF-2000 ranged from 0.99–5.4 mg/m[3] (Table 2). Full-shift personal exposures to butylal ranged from 0.017–0.83 ppm and were similar between the two dry cleaning shops (Table 3). We measured the highest personal exposures for either solvent on the owner/operator.

Task-based personal exposures to DF-2000 and butylal were higher than those measured during the full shift. Task-based personal airborne exposures to DF-2000 ranged from non-detected (<3.8 mg/m$^{[3]}$) to 7.9 mg/m$^{[3]}$ (Table 4) and butylal ranged from 0.42-1.9 ppm (Table 5). The highest task-based exposures were measured when the owner/operator was closest to the dry cleaning machine and when employees pressed fabrics.

In the butylal shops formaldehyde was detected in one full-shift personal sample at 0.0087 ppm. This concentration was between the minimum detectable and minimal quantifiable concentration (MQC), meaning there is more uncertainty with this result than values above the MQC. However, this concentration is lower than the NIOSH recommended exposure limit of 0.016 ppm. Butanol was not detected (<0.001 ppm).

Area air sampling

The area air sample results are presented in Tables 6 and 7. Full-shift area air concentrations of DF-2000 ranged from 0.16–5.6 mg/m$^{[3]}$. The highest full-shift area concentrations of DF-2000 and butylal were measured in the area closest to the dry cleaning machine. Full-shift area air concentrations of butylal were also similar at the two shops, ranging from 0.0039–0.31 ppm. Short-term area air concentrations for DF-2000 ranged from 5.3– 37 mg/m$^{[3]}$. Short-term area air concentrations of butylal ranged from 0.17–1.9 ppm. In the SolvonK4 shops, formaldehyde was either not detected (<0.008 ppm) or below the MQC (≤0.2 ppm) (Table 7). Full-shift area air concentrations of butanol ranged from not detected (<0.001 ppm) to 0.0079 ppm. No butanol was detected in short-term area air samples.

Observations

All shops had one dry cleaning machine that was used mainly by the shop owner. All shops also had a commercial washing machine that used water and detergent for fabrics not requiring dry cleaning.

We saw one DF-2000 machine operator cleaning the still while wearing a surgical mask, prescription glasses (not safety glasses or splash goggles), and nitrile gloves (3-5 mL thickness). This owner washed his hands after removing the still bottoms and before donning a new clean pair of nitrile gloves to transfer the still bottoms into a secondary waste container for disposal. We saw an operator transferring the still bottoms from a SolvonK4 dry cleaning machine to a waste drum, a task that lasted a few minutes, while wearing reusable leather gloves. This operator did not wash his hands afterwards. This operator added a manufacturer recommended acid-binder and stabilizer with deodorizers[28] to the dry cleaning machine after removing the still bottoms.

Employees at both SolvonK4 shops sprayed spot treatments daily onto fabrics prior to placing them in the dry cleaning machine (Figure 3). The spot treatment contained 40% SolvonK4, 40% PrenettK4 (a spotting agent containing alcohol and detergent), and 20% water. No local exhaust ventilation was available for spot cleaning. One SolvonK4 shop relied on natural ventilation, while the second SolvonK4 shop used both natural ventilation and a heating, ventilation, and air conditioning system (Table 1). Employees in the SolvonK4 shops did not use PPE during the unloading and loading of fabrics, however, one

operator wore a surgical mask. PPE was also not used while pressing fabrics or applying spot cleaners. Neither gloves nor safety glasses were available to employees.

We noted the characteristic intense, fruity odor of SolvonK4, especially near the operating dry cleaning machine. Employees told us that they preferred the odor of SolvonK4 to that of PERC.

Control banding

Table 8 shows a summary of the outputs of the CB tools. For both tasks we assumed small amounts of butylal (less than 0.5 L) were used per day. For the task involving loading, unloading and hanging fabrics from the dry cleaning machine we determined that the risk was low and recommended general ventilation. For the task involving spraying and brushing fabrics with a spotting solution containing SolvonK4 the risk estimate ranged from low to moderate, and our recommendations included general ventilation and PPE to reduce potential skin exposure. More detailed information regarding the outputs obtained from each CB tool is described in the supplemental document and supporting tables.

Discussion

The first objective of this study was to assess occupational exposures in dry cleaning shops that used SolvonK4 and DF-2000, cleaning solvent alternatives to PERC. The highest measured full-shift concentrations were associated with pressing and unloading/loading of fabrics from the dry cleaning machine and were up to 0.83 ppm (equivalent to 5.4 mg/m$^{[3]}$) for butylal and up to 5.4 mg/m$^{[3]}$ for DF-2000. DF-2000 levels measured were well below any of the OELs available.

The manufacturer reports that SolvonK4 is chemically stable in conditions ranging from moderately acidic (pH 4) to very basic (pH 14); however, it may hydrolyze in the presence of water, heat, and acid to yield formaldehyde and butanol.[15] We noted that the SolvonK4 shops followed the manufacturer's recommendation of adding an acid neutralizer product to the still after the waste had been removed. This neutralizer appeared to be effective. Although we measured low air concentrations of formaldehyde, it can be found at low concentrations in many indoor environments, originating from furnishings, clothing, and other materials.

The second objective was to identify workplace conditions and practices that may contribute to exposures. We measured exposures to dry cleaning solvents when fabrics were loaded and unloaded from the dry cleaning machine and during pressing of fabrics. We also found that spraying of a SolvonK4-containing spotting solution contributed to butylal exposures.

The third objective was to determine potential routes of solvent exposure. We found that employees could be exposed by inhalation and dermally. We saw potential dermal exposure to butylal when employees sprayed SolvonK4-containing spotting agents. Potential dermal exposure to both solvents also exists during still-cleaning operations and while handling fabrics that have recently been dry cleaned.

The fourth objective was to identify strategies to minimize exposures to the dry cleaning solvents and other chemicals. When cleaning the still bottoms, we recommended that employees wear eye protection and use thicker (>8 mL) nitrile gloves for the DF-2000 machines, and neoprene or butyl rubber for the SolvonK4 machines.[29] We recommended that employees pour or brush the SolvonK4 spot cleaner rather than spraying, and perform this task with adequate ventilation. We explained that spraying this spot cleaner may also create a fire hazard because SolvonK4 is a combustible liquid.[15] We recommended that employees wear PPE when applying spot cleaners that contain SolvonK4, including safety glasses, a long sleeve shirt, and polyvinyl chloride or polyethylene protective gloves.[14,15] When using other spotting agents, we recommended that employees follow the products' safety data sheets. We also mentioned the value of periodically monitoring solvent exposures in shops that use SolvonK4, particularly if changes occurred in work practices and conditions. We referred these small businesses to local government agencies to help with this endeavor. Finally, we explained to employees that surgical masks did not protect them against dust or solvents[22,23] and were not considered NIOSH-approved respirators.

The recommendations to reduce butylal exposures obtained from the CB tools were consistent with those suggested from our industrial hygiene sampling. These included general ventilation while loading/unloading/hanging fabrics and when spraying spot cleaners. The CB tools also advised reducing dermal exposures to butylal while spraying spot cleaners. Although the CB tool recommendations did not require special treatment after inadvertent contact with butylal, we suggested handwashing after solvent contact and avoiding direct contact by wearing protective gloves and a long-sleeve shirt to prevent exposure.

A limitation of our study is that we only looked at four shops, all were using relatively new dry cleaning machines, and some had low workloads during the days of our visit. These shops are not representative of all dry cleaning operations. Nonetheless, we believe this is the first evaluation of employee exposures to DF-2000 and SolvonK4. More work is needed to evaluate potential exposures to these solvents at dry cleaning shops using retrofitted dry cleaning machines. For example, dry cleaning machines that have been retrofitted from PERC to 1-bromopropane have been previously documented as a source of solvent exposures to workers.[30]

Conclusion

Both SolvonK4 and DF-2000 are preferable in terms of human health to PERC because they are not chlorinated hydrocarbons. As an isoparaffinic hydrocarbon free of aromatic hydrocarbons like benzene, the toxicological properties of DF-2000 appear to be relatively well characterized in comparison to SolvonK4. However, independent toxicological studies have not been conducted on DF-2000, and the long-term respiratory and reproductive human health effects of SolvonK4 are unknown. Independent evaluation of the toxicological properties of these alternative dry cleaning solvents is needed.

As the use of these solvents continues to increase, there is a need to consider creating standard methodologies using the sampling and analytical methods developed for this study.

Additionally, as more toxicological information about butylal becomes available, the CB tools inputs could be further refined to provide more specific recommendations. An OEL for butylal could also be proposed as more human exposure, health, and toxicological data becomes available.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. National Institute for Occupational Safety and Health (NIOSH). [accessed January 2016] Dry Cleaning. Available at: http://www.cdc.gov/niosh/topics/dryclean/
2. Local Hazardous Waste Management Program (LHWMP). “A profile of the dry cleaning industry in King County, Washington.” by S. G. Whittaker, and C.A. Johanson. Final report LHWMP_0048 Local hazardous waste management program in King County, Seattle, Washington. 2011
3. Whittaker SG, Johanson CA. A health and environmental profile of the dry cleaning industry in King County, Washington. J Environ Health. 2013; 75(10):14–22.
4. Occupational Safety and Health Administration (OSHA). [accessed January 2016] Dry Cleaning. Available at https://www.osha.gov/SLTC/drycleaning/
5. LHWMP. “Characterizing alternative solvent dry cleaning processes.” by S. G. Whittaker, J. Taylor, and L.M. Van Hooser. Final report LHWMP_0155 Local hazardous waste management program in King County, Seattle, Washington. 2013
6. Exxon Mobil Chemical. Report number 92842583. Houston, Texas: ExxonMobil Chemical Company; 2015. Material safety data sheet for DF-2000 fluid. last updated 2001
7. Exxon Mobil Chemical. [accessed January 2016] DF-2000™ Fluid for Dry Cleaning. Available at http://www.exxonmobilchemical.com/Chem-English/brands/hydrocarbon-oxygenated-fluids-products-df-2000.aspx?ln=productsservices
8. LHWMP. “Evaluation of DF-2000™ Dry cleaning Solvent in an Acute Fish Toxicity Test.” by S. G. Whittaker. Final report LHWMP_0203 Local Hazardous Waste Management Program in King County, Seattle, Washington. 2014
9. NIOSH. [accessed January 2016] Criteria for a Recommended Standard: Occupational Exposure to Refined Petroleum Solvents. Available at http://www.cdc.gov/niosh/docs/1970/77-192.html
10. Environmental Protection Agency (EPA). [accessed: January 2016] Hazard Characterization Document. Screening-Level Hazard Characterization: Low Benzene Naphthas Category. Available athttp://www.epa.gov/chemrtk/hpvis/hazchar/Category_%20Low%20Benzene%20Naphthas_December_2010.pdf
11. Office of Environmental Health Hazard Assessment. Memo from George Alexeeff to Peter Venturini regarding health effects of exposure to alternative dry cleaning solvents. California Environmental Protection Agency; Dec 2. 2003
12. GESTIS. [accessed January 2016] GESTIS Substance Database - GESTIS is the Information System on Hazardous Substances of the German Social Accident Insurance. Available athttp://gestis-en.itrust.de/nxt/gateway.dll/gestis_en/000000.xml?f=templates$fn=default.htm$vid=gestiseng:sdbeng$3.0

13. ACGIH. 2015 TLVs® and BEIs®: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists;
14. Kreussler USA. Material Safety Data Sheet PrenettK4. Tampa, FL: Kreussler; 2010.
15. Kreussler USA. What Landlords Need to Know about SystemK4. Tampa, FL: Kreussler USA; 2011.
16. New York State Department of Environmental Conservation. Memorandum to Tom Gentile, Chief, Air Toxics Section (ATS) from Donald Ward Jr., Ph.D., Research Scientist, ATS, Toxic Contaminant Review of the Butylal Dry Cleaning Solvent (currently marketed under the trade name SolvonK4 by Kreussler Inc.). Feb 23.2011
17. Toxics Use Reduction Institute (TURI). Assessment of alternatives to perchloroethylene for the dry cleaning industry. Methods and policy report No 27. 2012
18. Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). [accessed January 2016] 1,1′- [methylenebis(oxy)] dibutane. Available at http://apps.echa.europa.eu/registered/data/dossiers/DISS-dffb4072-e3fe-47ae-e044-00144f67d031/AGGR-b43af097-dc94-4c92-ac59-957369d550fa_DISS-dffb4072-e3fe-47ae-e044-00144f67d031.html#L-283d8d46-26d3-4496-b81c-743fc9c1583b
19. LHWMP. Evaluation of SolvonK4™ in an Acute Fish Toxicity Test, by S. G. Whittaker. Final report LHWMP_0185 Local Hazardous Waste Management Program in King County, Seattle, Washington. 2013
20. European Chemicals Agency (ECHA). [accessed January 2016] C&L Inventory Database. Available at http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database
21. LHWMP. Evaluation of Still Bottom Wastes from “Alternative Solvent” Dry Cleaning, by S. G. Whittaker. Final Report LHWMP_0190 Local hazardous waste management program in King County, Washington. 2014
22. NIOSH. Evaluation of Occupational Exposures at Dry Cleaning Shops Using SolvonK4 and DF-2000, by D Ceballos, J Roberts, S G Whittaker, E Lee, and W Gong. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2015. NIOSH HHE Report No. 2012-0084-3227
23. NIOSH. Evaluation of Occupational Exposures at a Dry cleaning Shop using SolvonK4, by D Ceballos, and K Broadwater. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2015. NIOSH HHE Report No. 2014-0081-3231
24. NIOSH. [accessed January 2016] NIOSH Manual of Analytical Methods. Available at http://www.cdc.gov/niosh/docs/2003-154/
25. OSHA. [accessed January 2016] OSHA “Sampling and Analytical Methods.”. Available at http://www.osha.gov/dts/sltc/methods/index.html
26. NIOSH. [accessed January 2016] NIOSH Pocket Guide to Chemical Hazards. Available at http://www.cdc.gov/niosh/npg/
27. NIOSH. [accessed January 2016] International Chemical Safety Cards - Naphtha (Petroleum), Hydrotreated Heavy, CAS# 64742-48-9. Available at http://www.cdc.gov/niosh/ipcsneng/neng1380.html
28. Kreussler Textile Care. [accessed January 2016] Peramon. Available at http://en.kreussler-chemie.com/products/product/infos-heet.html?type=7474&tx_krproducts_products%5Bproduct%5D=131&tx_krproducts_products%5Baction%5D=infoSheet&tx_krproducts_products%5Bcontroller%5D=Product&cHash=9bebb7ec3c9a8f0a72dafcd63dc3df92
29. Forsberg, K., Mansdorf, SZ. Quick Selection Guide to Chemical Protective Clothing. 5th. Hoboken, NJ: Wiley-Interscience, John Wiley & Sons, Inc;
30. NIOSH. Evaluation of 1-bromopropane Use in Four NJ Commercial Dry Cleaning Facilities, Various Locations, NJ, by J Eisenberg, and J Ramsey. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2010. NIOSH HETA No. 2008-0175-3111

Figure 1.
Employee pressing shirts by using two pressing machines in series.

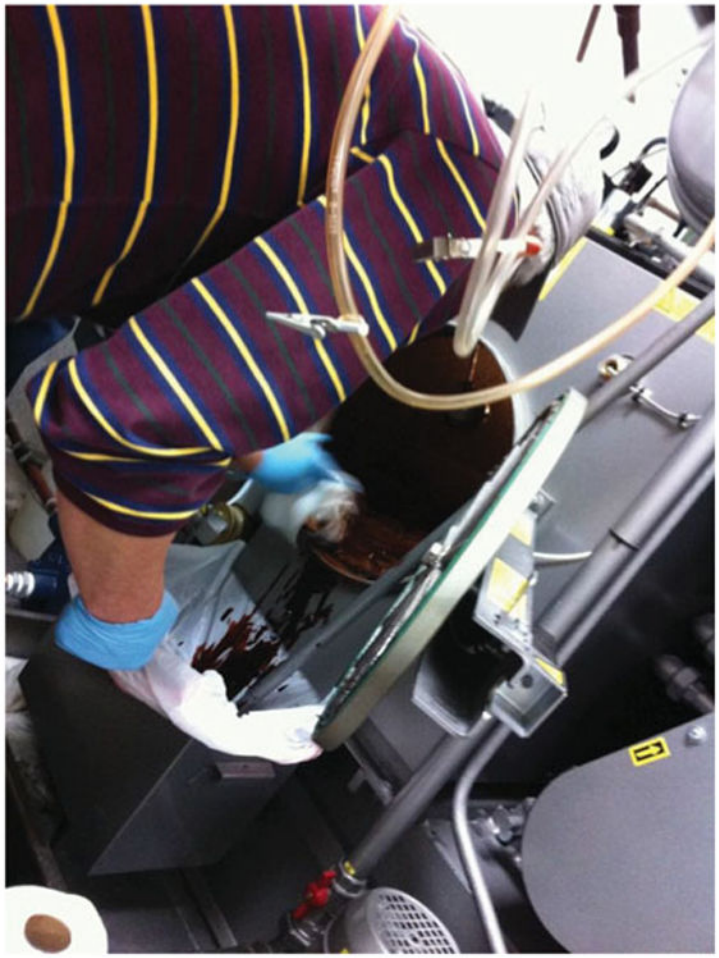

Figure 2.
An owner/operator removing still bottoms from the DF-2000 dry cleaning machine.

Figure 3.
Employee spraying shirts with a solution containing SolvonK4 to pretreat fabrics before dry cleaning cycle.

Table 1

Summary characteristics of the dry cleaning shops.

	DF-2000		SolvonK4	
	Shop A	**Shop B**	**Shop A**	**Shop B**
Previous solvent	PERC	PERC	PERC	Water
Date changed to new solvent	November 2012	November 2012	February 2013	October 2012
Shop size	18 ft × 36 ft × 20 ft	18 ft × 36 ft × 20 ft	35 ft × 33 ft × 18 ft	24 ft × 99 ft × 10 ft
Ventilation used during visit[a]	Natural (HVAC not operational)	Natural (HVAC not operational)	Natural (HVAC not operational)	Natural and HVAC[b]
Doors[c]	Front, side, and rear	Front	Front and side	Front and rear
Language spoken (n)	Korean (3)	Korean (2) Spanish (3)	Cantonese (3)	Korean (6) Spanish (4)
Still bottom cleaning schedule	Every 1–3 weeks	Every week	Every 2–3 days	Every week
Machine capacity & manufacturer	45-lb Union HLH40	40-lb Union HL840	50-lb Multimatic MultiStar+, Frankford Machinery, Inc.	60-lb Firbimatic, Italy
Loads run per week	10	15–18	20–25	20–40
Loads ran during evaluation	1 load on 1st day4 loads 2nd day	on 4 loads on 1st day3 loads on 2nd day	5 loads on 1st day4 loads on 2nd day	5 load on both days
Number of garment pressing stations	3	5	6	6

PERC = perchloroethylene. HVAC = Heating, ventilation, and air conditioning system. The shop turned off the HVAC fan during the day while shop doors were opened. The shop turned on the air conditioning and closed shop doors once the dry cleaning machine was no longer operating. n = number of employees including owner(s).

[a] During the sampling time, all shops except for SolvonK4 Shop B were dependent upon natural ventilation.

[b] The SolvonK4 Shop B turned on HVAC system after turning-off the dry cleaning machine and our sampling time includes with and without HVAC operation.

[c] Doors were opened when needed for natural ventilation.

Table 2

Personal full-shift air samples from dry cleaning shops using DF-2000.

Worker	Main tasks	Duration (minutes)	DF-2000 concentration (mg/m$^{[3]}$)
Shop A Owner/Operator	Unloading and loading	492	1.4
		555	0.99
Shop B Owner/Operator	Attending customers and unloading and loading	518	5.4
		576	2.0
Shop B Employee 1	Pressing and ironing	643	Sampling pump failure
		586	2.8
Occupational exposure limit (mg/m$^{[3]}$)			300 (DFG MAKs) 1200 (Exxon Mobil Chemical) 1142–1200 (ACGIH® TLV®)

DFG MAKs = Deutsche Forschungsgemeinschaft, maximum concentrations at the workplace.

Table 3

Personal full-shift air sample results from dry cleaning shops using SolvonK4.

Location	Main tasks	Sample Time (minutes)	Concentration (ppm)		
			Butylal	Butanol	Formaldehyde
Shop A	Pressing fabrics, unloading and loading fabrics from dry cleaning machine	491	0.30	NS	ND[a]
		471	0.18	NS	(0.0087)[b]
	Pressing	499	0.017	ND	NS[c]
		458	0.017	ND	NS
Shop B	Loading, unloading, and spot cleaning with SolvonK4 mixture	464	0.67	ND	ND
		615	0.83	ND	ND
	Pressing	418	0.23	ND	ND
	Spot cleaning with degreaser, pressing and hanging	426	0.32	ND	ND
	Pressing	408	0.14	ND	ND
		528	0.15	ND	ND
	Pressing	346	0.14	ND	ND
	Pressing	330	0.34	ND	ND
		411	0.15	ND	ND
NIOSH recommended exposure limit (ppm)			None	50	0.016
OSHA permissible exposure limit (ppm)			None	100	0.75
ACGIH Threshold Limit Value (ppm)			None	20	0.3

[a] ND = not detected, below the minimum detectable concentration. For butanol this was below 0.001 ppm; for formaldehyde this was below 0.008 ppm.

[b] Concentration shown in parenthesis is between the minimum detectable and minimum quantifiable concentration. This means there is more uncertainty associated with this value.

[c] NS = no sample collected.

Table 4

Results of personal task-based air samples from dry cleaning shop using DF-2000.

Worker	Main tasks	Sample Time (minutes)	DF-2000 concentration (mg/m[3])
Shop A Owner/Operator	Cleaning still	8	ND
	Loading, washing cycle, and unloading	235	2.8
Shop A Employee 1	Pressing and ironing shirts	133	7.9

ND = Not detected.

Table 5

Results of personal task-based air samples from dry cleaning shop using SolvonK4.

Worker	Main tasks	Sample Time (minutes)	Concentration (ppm)		
			Butylal	Butanol	Formaldehyde
Shop B Owner/operator	Loading, unloading, and spot cleaning with SolvonK4 containing mixture	23	057	NS	NS
		21	1.9	NS	NS
		21	1.1	NS	NS
	Pouring solvent from storage container into bulk container, and loading and unloading	21	0.81	NS	NS
Shop B Employee 1	Hanging and pressing	23	1.8	NS	NS
		20	0.42	NS	NS

NS = Not sampled

Table 6

Results of full-shift and short-term area air samples collected from dry cleaning shops using DF-2000.

Shop	Location	Sample Time (minutes)	DF-2000concentration (mg/m[3])
Shop A	Front desk	545	(0.16)[a]
		542	0.74[b]
	Table in the back of the shop	558	0.65
	Near dry cleaning machine	554	0.90
		545	0.63
		15	(5.3)[a]
		15	10
		102	1.4
		15	21
	Next to dry cleaning machine, cleaning stills	8	ND[c]
	Next to dry cleaning machine, machine off	140	ND[c]
	Pressing	53	ND[c]
		133	(0.38)[a]
Shop B	Front desk	652	0.56
		626	0.24
	Next to shirt presses	650	3.1
		620	1.4
		75	5.4
	Next to dry cleaning machine	648	3.5
		622	5.6
		86	5.2
		15	37
		101	2.9

[a]Concentration shown in parenthesis is between the minimum detectable (MDC) and minimum quantifiable concentration. This means there is more uncertainty associated with this value.

[b]This should be considered a minimum concentration because we found DF-2000 on the back section of the sample tube.

[c]ND = Not detected. For these samples, the MDCwas2.0mg/m[3].

Table 7

Results of full-shift and short-term area air samples from dry cleaning shops using SolvonK4.

Sample location	Sample Time (minutes)	Concentration (ppm)		
		Butylal	Butanol	Formaldehyde
Shop A Front desk	535	0.0039	ND[a]	(0.0084)[b]
	444	0.010	ND[a]	ND[a]
Shop A Press area	502	0.056	(0.0028)[b]	ND[a]
	459	NS	(0.0024)[b]	(0.012)[b]
Shop A Dry cleaning area	521	0.31	0.0079	ND[a]
	482	0.29	0.0079	NS
	16	1.9	(0.079)[b]	ND[c]
	15	1.6	(0.052)[b]	ND[c]
	84	0.72	(0.018)[b]	ND[c]
Shop B Front desk	533	0.18	ND[d]	ND[d]
Shop B Press area	449	0.21	ND[d]	ND[d]
	528	0.12	ND[d]	ND[d]
Shop B Dry cleaning area	455	0.19	ND[d]	ND[d]
	525	0.19	ND[d]	ND[d]
	19	0.17	(0.054)[a]	ND[c]
	114	0.52	ND[c]	(0.043)[a]

[a] For these samples, the minimum detectable (MDC) was 0.008 ppm of formaldehyde and 0.001 ppm of butanol.

[b] Concentration shown in parenthesis is between the minimum detectable (MDC) and minimum quantifiable concentration. This means there is more uncertainty associated with this value.

[c] For these air samples, the MQC was in the range of 0.04 to 0.2 ppm of formaldehyde and 0.006 ppm of butanol.

[d] For these samples the MDC was 0.008 ppm of formaldehyde and 0.005 ppm of butanol.

Table 8

Summary of control banding tool outputs for shops using SolvonK4(butylal).

Task	Description	Exposure route	Tool		Hazard band[a]	Exposure band	Recommended control strategy or risk priority/score
Taskl	Loading, unloading, and hanging fabrics	Inhalation	COSHH Essentials		A	1	CSI-General ventilation
			Stoffenmanager		A-low	1-low, using VP = 79 Pa.2-average, using VP = 250 Pa[b]	III – low risk for both VPs
Task 2	Spraying and brushing fabrics with a spotting solution	Inhalation	COSHH Essentials		A	1	CSI-General ventilation
			Stoffenmanager		A-low	1-low for both VPs	III – low risk for both VPs
		Dermal	Stoffenmanager[b]		Local effect: B-average[c] Systemic effect: none	4-high for local effect and 5-very high for systemic effect (both VPs)	Local effect: II – medium risk Systemic effect: III – low risk
			RISKOFDERM[b]	Body	Local effect: Moderate Systemic effect: no	Moderate for local and systemic effects	Local effect: 3[d] Systemic effect: 2[d]
				Hands	Local effect: Moderate Systemic effect: no	High for local and systemic effects	Local effect: 4[d] Systemic effect: 2[d]

VP = vapor pressure. Pa = Pascal. CS = control strategy.

[a]Hazard band class was assigned based on R38-Irritating to skin.

[b]Due to various vapor pressures listed in the ECHA (European Chemicals Agency) at 20°C, 79 Pa, <138 Pa, and <250 Pa, we used the minimum and maximum values for this tool.

[c]Follow-up advice based on hazard class is “none.”

[d]According to Table 9 of Exxon Mobil Chemical (2016),[7] risk score 2 means “no special treatment,” 3 means “exposure reduction, if easily accomplished,” and 4 means “action necessary: primarily exposure reduction to be considered.