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Evaluation of Occupational Exposures at Drycleaning Shops Using SolvonK4 and DF-2000

Diana Ceballos, PhD, MS, CIH[1]
Jennifer Roberts[1]
Stephen Whittaker, PhD[2]
Eun Gyung Lee, PhD, CIH[1]
Wei Gong, MS[1]

[1]National Institute for Occupational Safety and Health
[2]Local Hazardous Waste Management Program, Public Health—Seattle & King County

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The cover photo is a close-up image of sorbent tubes, which are used by the HHE Program to measure airborne exposures. This photo is an artistic representation that may not be related to this Health Hazard Evaluation. Photo by NIOSH.

Highlights of this Evaluation

The Health Hazard Evaluation Program received a technical assistance request from a government program that provides technical assistance to drycleaning shops. The program manager was concerned about occupational exposures to two new drycleaning solvents: SolvonK4 and DF-2000.

What We Did

- We developed air and skin patch sampling methods for SolvonK4 and DF-2000.
- In May 2013, we evaluated one drycleaning shop that used SolvonK4 and two that used DF-2000.
- In the SolvonK4 shop we took air samples for butylal, the main ingredient in SolvonK4. We also took air samples for formaldehyde and butanol, possible byproducts from using SolvonK4.
- In the DF-2000 shops we took air samples for DF-2000.
- We tested employees' skin under their protective gloves for butylal or DF-2000.
- We checked to see if any ventilation systems were present in the shops.
- We measured temperature and relative humidity levels.

We evaluated drycleaning shops that used SolvonK4 and DF-2000 because a local government program was concerned about occupational exposures to these alternative drycleaning solvents. We found air and skin exposures to butylal, the main ingredient of SolvonK4, although no occupational exposure limits exist for this chemical. We measured air concentrations of DF-2000 that were well below occupational exposure limits. We provided recommendations on work practices, housekeeping, equipment maintenance, and the appropriate selection and use of personal protective equipment.

What We Found

- We found the highest air concentrations of butylal and DF-2000 on employees when they loaded and unloaded the drycleaning machine and pressed fabrics.
- We found low concentrations of formaldehyde and butanol in the SolvonK4 shop.
- We saw employees without personal protective equipment mixing SolvonK4 with a pretreatment product and spraying the mixture onto fabrics.
- We saw employees without adequate personal protective equipment cleaning the stills in the SolvonK4 and DF-2000 drycleaning machines.
- We saw dust and lint in the shops. The dust and lint can be a source of fuel if there is a fire.

What the Drycleaning Shops Can Do

- Brush pretreatments onto fabrics instead of spraying.
- Regularly inspect and maintain the drycleaning machine according to the manufacturers' recommendations.
- Clean the shop regularly with a high efficiency particulate air filter vacuum cleaner or wet methods.
- Provide eye protection and chemical resistant gloves to employees.

What the Drycleaning Shop Employees Can Do

- Wear eye protection and chemical resistant gloves while prespotting.
- Wear chemical resistant gloves and eye protection when removing still bottoms and handling the waste material.
- Wash hands or any exposed skin with soap and water after contact with chemicals.
- Wash hands after removing gloves.

Abbreviations

µg	Microgram
µg/sample	Microgram per sample
ACGIH®	American Conference of Governmental Industrial Hygienists
CAS	Chemical abstract service
CFR	Code of Federal Regulations
COSHH	Control of substances hazardous to health
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
LHWMP	Local Hazardous Waste Management Program in King County, Washington
m	Meter
mg/m^3	Milligrams per cubic meter
mL	Milliliter
mL/min	Milliliter per minute
mm	Millimeter
MDC	Minimum detectable concentration
MQC	Minimum quantifiable concentration
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational exposure limit
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
PERC	Perchloroethylene
PPE	Personal protective equipment
ppm	Parts per million
REL	Recommended exposure limit
SDS	Safety data sheet
TLV®	Threshold limit value
TWA	Time-weighted average
WEEL™	Workplace environmental exposure level

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Introduction

The Health Hazard Evaluation Program received a technical assistance request from a local government program to evaluate occupational exposures to the drycleaning solvents SolvonK4™ and DF-2000™. The government program facilitated health hazard evaluation requests at three drycleaning shops. We visited the drycleaning shops in May 2013. We observed work practices, collected air samples for drycleaning solvents and other chemicals produced or used during drycleaning, and evaluated potential skin exposures to these chemicals. We sent the owners and employees at each shop a letter with the results for their workplace and shared these letters with the local government program in July 2013, March 2014, and April 2014. Letters were translated to the first language of the employees at each of the shops.

Alternative Drycleaning Solvents

The drycleaning industry has adopted new solvents over the last decade to replace perchloroethylene (PERC). A survey conducted in King County, Washington, in 2010 revealed that while most dry cleaners (69%) were still using PERC, 21% were using a high flashpoint hydrocarbon solvent for drycleaning [LWHMP 2011; Whittaker and Johanson 2013]. Most shops (96%) had only one machine at their location. Consequently, most dry cleaners who adopted solvent alternatives to PERC had replaced their single drycleaning machine with a newer model that was compatible with the new solvents. Subsequent field observations in 2012 by King County found that the most frequently used high flashpoint hydrocarbon solvent was Exxon Mobil's DF-2000, a product similar to odorless mineral spirits. Another drycleaning chemical, SolvonK4, a diether acetal manufactured by Kreussler, began to be used in the United States after the King County survey [LWHMP 2013a].

SolvonK4

The drycleaning SystemK4 developed by Kreussler GmbH uses SolvonK4, a chemical that contains primarily butylal (> 99%), with small amounts of n-butanol (< 0.5%) and formaldehyde (< 0.05%) [Kreussler USA 2011]. Synonyms for butylal include dibutoxymethane, 1-(butoxymethoxy)butane, and formaldehyde dibutyl acetal. The Chemical Abstract Service (CAS) number is 2568-90-3. With a flash point of 143.6°F, SolvonK4 is a National Fire Protection Association Class IIIA solvent (i.e., flash point at or above 140°F and below 200°F).

DF-2000

DF-2000 is a nearly odorless mixture of hydrocarbons (chemicals that contain hydrogen and carbon). The CAS number of DF-2000 (64742-48-9) represents hydrotreated heavy naphtha (petroleum) or isoparaffinic hydrocarbon [Exxon Mobil Chemical 2014a]. This product is also referred to as synthetic hydrocarbon fluid [Exxon Mobil Chemical 2014b]. DF-2000 contains C_{11} to C_{15} aliphatic-branched hydrocarbons (boiling point range approximately 174°C–234°C) and does not, according to the manufacturer, contain more toxic aromatic hydrocarbons like benzene. These naphthas are more flammable than PERC and are generally classified as National Fire Protection Association Class IIIA solvents.

Drycleaning Process

All three shops evaluated had one alternative solvent drycleaning machine that was used principally by the shop owner. All shops also had a commercial washing machine that used water and detergent for laundering fabrics that did not require drycleaning.

The drycleaning process is similar for PERC, SolvonK4, and DF-2000. Fabrics, including clothes, drapes, and other textiles, are received from customers, labeled, and sorted for cleaning. Prior to drycleaning, stained fabrics may be precleaned or prespotted.

In the shops that we evaluated, the drycleaning machines had enclosed drums where the fabrics being cleaned were saturated with the drycleaning chemical. In all the alternative solvent drycleaning machines we observed in this evaluation, any cleaning additives (e.g., detergent, stain repellant) were injected into the solvent flow line or into the drum of the drycleaning machine (in contrast to an older method that involved predissolving the detergent in the solvent). When the cleaning cycle was complete, the solvent was drained, and the cleaned fabrics were placed under vacuum, heated, and tumbled to remove any remaining solvent. Employees could manually spot-clean fabrics that were still stained or soiled after drycleaning, using the same products used in precleaning. The cleaned fabrics were pressed (Figure 1) and ironed as needed, then hung on hangers and covered with plastic wrapping awaiting customer pick-up.

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

Modern drycleaning machines prevent the release of solvent vapors to ambient air by recycling the solvent in a closed loop system and automatically 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 [LHWMP 2014a]. 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 process also 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 drycleaning 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 drycleaning processed in a shop, the still bottoms are removed every 1–2 weeks.

Figure 2. An owner/operator removing still bottoms from the DF-2000 drycleaning machine. Photo by NIOSH.

Methods

The objectives for this evaluation were the following:

1. Assess occupational exposures to SolvonK4, DF-2000, and other substances that may be released such as formaldehyde and butanol.
2. Determine potential routes of exposure to the solvents.
3. Identify workplace conditions and practices that may contribute to exposures.
4. Identify strategies to minimize exposures and safety hazards at the shops.
5. Determine the efficacy of the protective gloves used at the shops.

Bulk Analysis

We took a bulk sample of SolvonK4 from the drycleaning machine at the SolvonK4 shop to evaluate its chemical composition and help us select the appropriate analytical methods. The bulk sample was stored in a 40-milliliter (mL) glass vial and transported on ice. Because of the machine design it was not possible to remove a sample of DF-2000 from the drycleaning machines. Consequently, we obtained a sample from the local government program, which had purchased 5 gallons of DF-2000 from a local vendor. The bulk samples for DF-2000 and SolvonK4 were analyzed by gas chromatography with mass spectrometry (GC-MS) or a flame ionization detector (GC-FID) and compared to available standards. We used a commercial butylal standard (TCI America, Lot# FIE01, purity 98%). A commercial DF-2000 standard was not available.

Air Sampling

We collected personal and area air samples for butylal, formaldehyde, butanol, and DF-2000 using the methods listed in Table 1. Personal air samples were collected from most production employees and the owner/operators. We also collected area samples using thermal desorption tubes to identify other volatile contaminants in the shops. These tubes were analyzed with National Institute for Occupational Safety and Health (NIOSH) Method 2549 [NIOSH 2014a].

Table 1. Air sampling methods used during the evaluation

Substance	Rationale for sampling	Sampling method
Butylal	Main ingredient in SolvonK4	Custom method, described in Appendix A
Formaldehyde	Potential breakdown product when SolvonK4 is in use	OSHA 52*†
Butanol	Potential breakdown product when SolvonK4 is in use	NIOSH 1401‡
DF-2000	Main ingredient in DF-2000	Modified NIOSH 1550, described in Appendix A

*Following Occupational Safety and Health Administration (OSHA) sampling and analytical method [OSHA 2014a].

†Formaldehyde was not sampled with NIOSH Method 2016 because laboratory testing determined that formaldehyde was potentially generated using this method. More details are included in Appendix B.

‡Following NIOSH Manual of Analytical Methods [NIOSH 2014a].

The results from personal sampling were compared to occupational exposure limits (OELs), when available (Table 2). Detailed descriptions of the available OELs and the health effects of butylal and DF-2000, formaldehyde, and butanol are provided in Appendix C.

Table 2. Occupational exposure limits for measured substances

Substance	Concentration
Butylal	No OEL
DF-2000	300 mg/m^3 (DFG MAKs) (See also Table C1, Appendix C)
Formaldehyde*	0.016 ppm (NIOSH REL); 0.75 ppm (OSHA PEL)
Butanol	20 ppm (ACGIH TLV); 50 ppm (NIOSH REL); 100 ppm (OSHA PEL)

ACGIH = American Conference of Governmental Industrial Hygienists
DFG = Deutsche Forschungsgemeinschaft
MAK = Maximum concentrations at the workplace
mg/m^3 = Milligrams per cubic meter
OSHA = Occupational Safety and Health Administration
PEL = Permissible exposure limit
ppm = Parts per million
REL = Recommended exposure limit
TLV = Threshold limit value
*Formaldehyde is considered an occupational carcinogen.

Patch Sampling

We used patches (PERMEA-TEC™ Sensors for solvents) to determine whether butylal or DF-2000 contacted the hands of employees and owner/operators when they used protective gloves. While wearing nitrile gloves to avoid contamination, we placed four patches on the skin, beneath the protective gloves that were worn during a task (Figure 3). A patch was placed on the palm and one finger of each hand. The patch sample analysis methods for butylal and DF-2000 are described in Appendix D.

Figure 3. Patch samplers being placed on the owner/operator's hands before he donned protective gloves. Photo by NIOSH.

Other Measurements and Observations

We toured the drycleaning shops and observed work processes and practices, and personal protective equipment (PPE) use. We also spot-measured air temperature and relative humidity in the shops and checked the shops' ventilation with smoke tubes or fine powder puffs.

Results and Discussion

Bulk Analysis

Our bulk analysis of SolvonK4 revealed that this solvent contained primarily butylal, as described by the manufacturer. SolvonK4 also contained 0.06% of butanol and 0.007% of formaldehyde, consistent with the information reported by the manufacturer of < 0.5% butanol and < 0.05% formaldehyde [Kreussler USA 2011]. A GC-MS chromatogram of the bulk sample is shown in Figure 4.

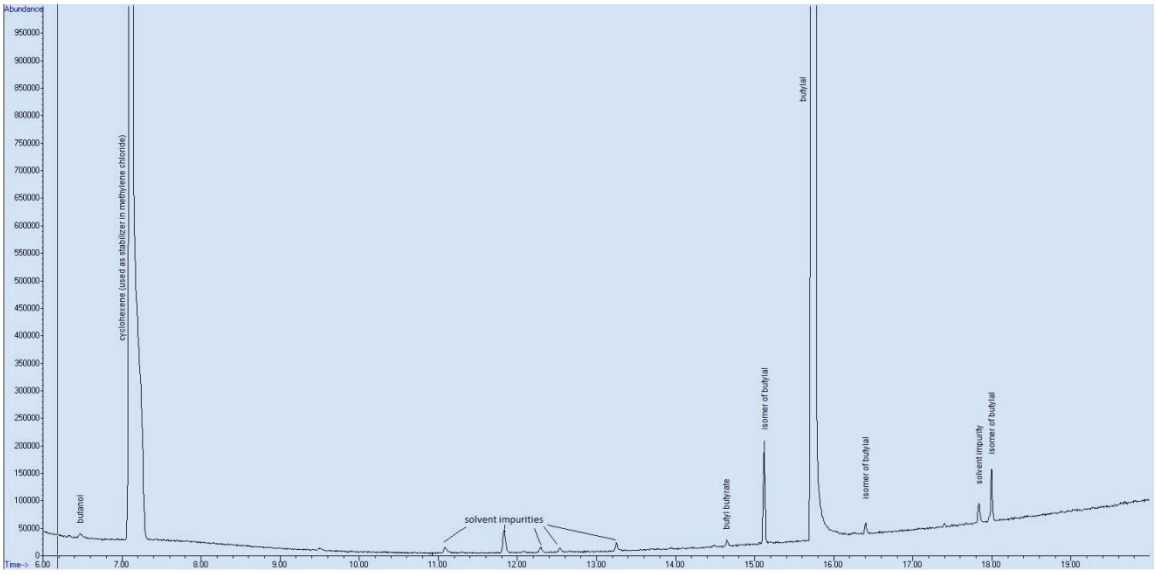

Figure 4. GC-MS chromatogram of SolvonK4 diluted in methylene chloride.

Bulk analysis of the DF-2000 (Figure 5) confirmed the presence of C_{11} to C_{15} aliphatic-branched hydrocarbons, with boiling points ranging from approximately 174°C–234°C, similar to that of the n-C_{10} to n-C_{13} straight-chained hydrocarbons. These results supported the manufacturers report that benzene was not present [Exxon Mobil Chemical 2014a] and the NIOSH international chemical safety card for CAS number 64742-48-9 [NIOSH 2014b]. The chromatogram presented in Figure 5 also shows that in this analysis the branched hydrocarbons eluted earlier than the straight-chained hydrocarbons.

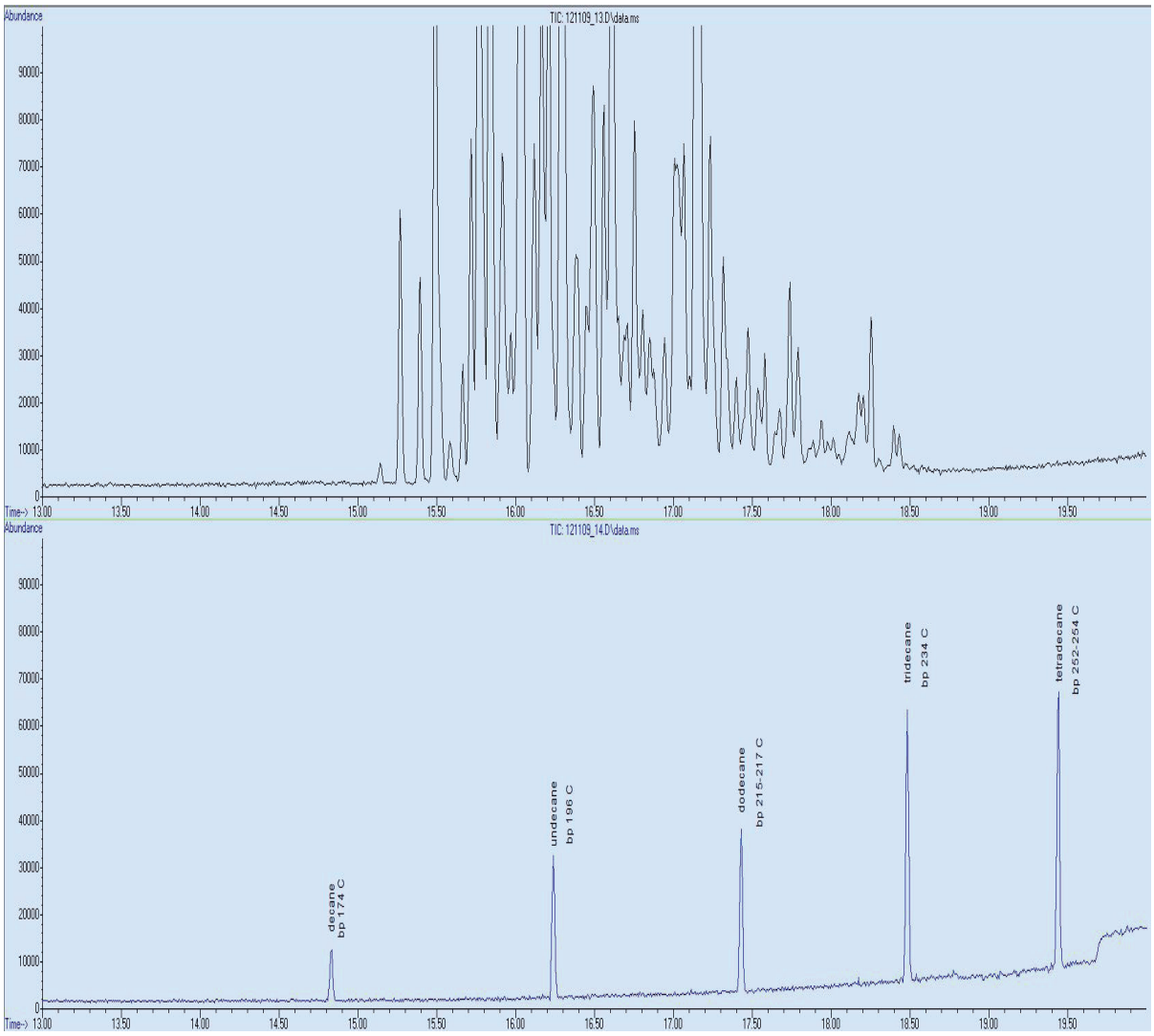

Figure 5. GC-MS chromatogram of DF-2000 diluted in methylene chloride.

SolvonK4 Drycleaning Shop

Shop Description

The shop was staffed by two full-time employees and an owner/operator. The first language of the employees and the owner was Cantonese. The business hours were 7 a.m. to 7 p.m. Monday through Saturday. The size of the store was 35 feet × 33 feet × 18 feet. The shop did not have a heating or air-conditioning system to filter or condition the air. Employees or the owner could open the front and back doors in the shop and turn on a ceiling-mounted exhaust fan to provide general dilution ventilation, as needed. The shop had a 50-pound capacity drycleaning machine (Multimatic MultiStar+, Frankford Machinery, Inc.) installed more than a year before our visit. Each drycleaning cycle took 70–80 minutes. The drycleaning machine was mainly operated by the owner. The shop cleaned an average of 20–25 loads per week. Five loads of fabrics were cleaned in the drycleaning machine during the first day of our visit and four loads on the second day. The owner removed the still bottoms every 3 days. The shop also had six pressing stations.

Air Sampling

The personal air sample results are presented in Appendix E, Table E1. The results from the analysis of thermal tubes revealed the absence of other major air contaminants (data not presented). The highest airborne exposures to butylal were measured in the employee who worked closest to the drycleaning machine. This employee pressed fabrics near the drycleaning machine and loaded/unloaded fabrics. Except for one formaldehyde concentration on employee A on day 2 we did not detect formaldehyde (< 0.008 ppm) or butanol (< 0.001 ppm) in personal samples. The detected concentration was below the NIOSH REL for formaldehyde.

The area air sample results are shown in Appendix E, Table E2. The highest butylal concentrations were detected next to the drycleaning machine. Butanol was detected in two area air samples at 0.0079 ppm; results for two other samples were below the minimum quantifiable concentration (MQC). Formaldehyde was present in two area air samples at concentrations below the MQC.

The results of short-term area air samples collected near the employees are shown in Appendix E, Table E3. The highest concentrations of butylal (1.9 ppm and 1.6 ppm) were measured during unloading and loading of fabrics. Formaldehyde was detected at the drycleaning machine when fabrics were loaded, washed, and unloaded. Area air samples taken near the drycleaning machine after it was shut down for the day revealed butylal concentrations of 0.052 ppm during 102 minutes of the first day and 0.082 ppm during 141 minutes of the second day (data not shown in table).

Kreussler reports that SolvonK4 is chemically stable in conditions ranging from very acidic (pH 4) to very basic (pH 14). However, this solvent may hydrolyze in the presence of water, heat, and acid to yield formaldehyde and butanol [Kreussler USA 2011]. The shop added an acid neutralizer to the still after the waste (still bottoms) had been removed. This neutralizer likely helped prevent the hydrolysis of SolvonK4. As noted above, formaldehyde was present at low concentrations in a few samples. However, low concentrations of formaldehyde exist in many indoor environments because of off gassing from furnishings, clothing, and other materials. Consequently, the presence of formaldehyde may not have originated from the use of SolvonK4. Butanol concentrations were well below OELs. The results of preliminary laboratory experiments designed to evaluate the extent of decomposition of SolvonK4 in extreme conditions typically encountered in the drycleaning process are presented in Appendix F.

Patch Sampling

We observed the owner/operator removing the still bottoms from the drycleaning machine. This operation lasted only a few minutes. He wore reusable leather gloves while transferring the still bottoms to a waste drum, and did not wash his hands after performing this task. We detected butylal on all four patch samples that had been placed on his hands. This contamination may have resulted from butylal penetrating the gloves or from previous contamination on the interior of the reusable leather gloves. The manufacturer's safety data sheet (SDS) for SolvonK4 recommends against the use of leather gloves [Kreussler USA 2011].

Other Measurements and Observations

We observed the owner/operator spraying a custom mixture of 40% SolvonK4, 40% PrenettK4, and water from an unlabeled spray bottle. PrenettK4 is a commercially available spot cleaning product that contains alcohols and a detergent. The owner sprayed this mixture onto fabrics without wearing gloves and safety glasses. According to the SDS for SolvonK4, eye protection and polyvinyl chloride or polyethylene protective gloves should be worn [Kreussler USA 2010, 2011]. This spray application may also create a fire hazard by aerosolizing the SolvonK4, a combustible liquid [Kreussler USA 2011]. The owner did not wash hands after performing this task. The shop was not equipped with an emergency eyewash station.

Several additional spot cleaners were also stored in the shop, although they were reportedly used infrequently. Although we did not see it being used, a spot cleaner called RustGo® (A.L. Wilson Chemical Company) was occasionally used at the shop. The SDS for RustGo states that this product contains hydrofluoric acid and ammonium bifluoride, substances that can cause chemical burns and permanent damage to unprotected eyes and skin. Accidental ingestion of this product may cause throat burns and swelling that may restrict breathing.

We noted the strong odor of SolvonK4 especially near the operating drycleaning machine. Employees told us that they preferred the odor of SolvonK4 to that of PERC.

The shop was not equipped with a mechanical heating or air-conditioning system to filter or condition the air. Employees mentioned that a ceiling-mounted exhaust fan was available for general dilution ventilation, but because it was noisy when it operated they only used it sporadically. On the day of our evaluation the outdoor weather conditions were mild (temperatures ranged from 55°F–65°F, with about 60% relative humidity). In the shop the temperatures ranged from 70°F–80°F, and the relative humidity was about 60%. Employees mentioned that indoor temperatures became uncomfortable during the hotter summer months.

We also observed that some of the accumulated dust in the shop may be fabric lint that contains organic material. Lint can be a source of fuel if a fire is present [OSHA 2014b].

In addition to air sampling, use of a chemical like butylal for drycleaning can also be evaluated by control banding, a technique used to guide the assessment and management of workplace risks to chemicals. Control banding may help employers select an appropriate control method (e.g., dilution ventilation, engineering controls, containment) on the basis of a range or "band" of hazards (skin/eye irritant, very toxic, carcinogenic, etc.) and exposures (low, medium, large exposure). Details on the use of control banding for SolvonK4 in a drycleaning shop are presented in Appendix G. The control banding methods confirmed that general ventilation was recommended in the SolvonK4 drycleaning shop for tasks such as loading and unloading fabrics into and from the drycleaning machine and spraying spot cleaners. The control banding methods also recommended avoiding direct contact with SolvonK4 (e.g., wearing protective gloves and a long-sleeve shirt) while spraying spot cleaners.

DF-2000 Drycleaning Shop A

Shop Description

The shop was staffed by two part-time employees and two owner/operators. The first language of the employees and the owners was Korean. The business hours were 7 a.m. to 7 p.m. Monday through Saturday. The size of the store was 18 feet × 36 feet × 20 feet. The mechanical heating and air-conditioning system in the shop was not operating during our evaluation but employees and the owner opened the front, side, and back doors to the shop throughout the work day to provide natural ventilation. The shop had a 40-pound capacity drycleaning machine (Union HL840, UNION Dry Cleaning Products USA) installed approximately 6 months before our visit. Typically, the shop cleaned an average of 10 loads per week. Each drycleaning cycle took 70–80 minutes. The drycleaning machine was operated exclusively by the owner. One load of fabrics was cleaned in the drycleaning machine during the first day of our visit and four loads on the second day. The owner removed the still bottoms every 1–3 weeks. The shop also had three pressing stations.

Air Sampling

The air sampling results are shown in Appendix E, Tables E4–E7. The results from the sampling with thermal tubes did not identify any other major air contaminants, so these results are not presented. The personal air samples results are in Appendix E, Table E4. The concentrations of DF-2000 (1.4 mg/m^3 and 0.99 mg/m^3) were well below the most protective OEL for naphtha of 300 mg/m^3 for an 8-hour time-weighted average (TWA) exposure. The results of personal air samples taken during short-term work tasks are presented in Appendix E, Table E5. The highest exposure to DF-2000 (7.9 mg/m^3) was measured on an employee who was pressing shirts near the drycleaning machine and using two shirt presses simultaneously. The measured exposures were well below the most protective OEL.

The results of area air samples taken over the work shift are presented in Appendix E, Table E6. DF-2000 was detected throughout the shop in low concentrations (< 1 mg/m^3). The results of area air samples taken during various tasks are in Appendix E, Table E7. The highest concentrations of DF-2000 (10 mg/m^3 and 21 mg/m^3) occurred during unloading and loading of fabrics from and into the drycleaning machine and pressing shirts. We also collected air samples near the press area and at the front desk after the drycleaning machine was shut down for the day (data at the front desk not presented in tables). We sampled for 140 minutes and we did not detect DF-2000 in either location.

Patch Sampling

Because of the design of the drycleaning equipment, direct contact with DF-2000 was limited to cleaning the still. We observed the owner wearing nitrile gloves during the still cleaning operation, which lasted only a few minutes. The owner washed his hands after removing the still bottoms and before donning another pair of nitrile gloves (3 to 5 mil thickness). The NIOSH investigator placed the patches on the owner's hands before the gloves were donned, and the patches were present only while the waste was handled for disposal. We detected low levels of DF-2000 on two of the six patch samples. We inspected the gloves after removal

and found no visible holes or tears. DF-2000 may have passed through the nitrile glove material or entered through a small opening in the gloves. It is also possible that DF-2000 may have remained on the owner's skin after washing his hands and before donning a new pair of gloves. According to the manufacturer's SDS, eye protection and chemical resistant gloves are recommended when handling DF-2000 [Exxon Mobil Chemical 2014a]. Further, nitrile glove material is recommended for protection against products similar to DF-2000 in commercial glove compatibility charts.

Other Measurements and Observations

The owner wore a surgical mask, prescription glasses, and nitrile gloves when cleaning the still and washed his hands after removing the gloves. Although surgical masks do not provide protection from gases or vapors, including those from DF-2000, our measurements indicated that a respirator is not needed. Prescription glasses provide only limited eye protection; safety glasses or safety goggles would provide better eye protection.

We did not observe any direct contact with liquid DF-2000. No new solvent had been added since the machine was installed. Supplementary solvent was typically added by a distributor/vendor.

On the days of our evaluation the outdoor weather conditions were mild (temperatures ranged from 42°F–65°F, with about 54% relative humidity), and the shop temperature was approximately 75°F.

We also noted several unlabeled bottles of spot cleaner and accumulated dust throughout the shop. The shop was not equipped with an emergency eyewash station.

DF-2000 Drycleaning Shop B

Shop Description

The shop was staffed by two full-time employees, one part-time employee, and two owner/operators. The first language of the two owners was Korean, whereas that of the three employees was Spanish. The business hours were from 7 a.m. to 7 p.m. Monday to Saturday. The size of the store was 18 feet × 39 feet × 20 feet. The mechanical heating and air-conditioning system in the shop was not operating during our evaluation but employees and the owner opened the front door to the shop throughout the work day to provide natural ventilation. The shop had a 40-pound capacity drycleaning machine (Union HL840) that was installed approximately 6 months before our visit. Typically, the shop cleaned an average of 15–18 loads per week. Each drycleaning cycle took 70–80 minutes. The drycleaning machine was mainly operated by the owner. Four loads of fabrics were cleaned in the drycleaning machine during the first day of our visit and three loads on the second day. The owner removed the still bottoms every week. The shop also had five pressing stations.

Air Sampling

The air sampling results are presented in Appendix E, Tables E8–E10. Thermal tube results did not reveal any other major air contaminants, so these results are not included. The results of personal air samples are presented in Appendix E, Table E8. The DF-2000 concentrations (2.0–5.4 mg/m^3) were well below the most protective OEL. The results of area air samples taken over the work shift are presented in Appendix E, Table E9. DF-2000 was detected throughout the shop at low concentrations ranging from 0.24–5.6 mg/m^3. The lowest concentration was measured near the front desk, and the highest concentration measured near where the owner/operator unloaded fabrics. The results of short-term area air samples taken in the vicinity of work tasks are presented in Appendix E, Table E10. The short-term concentrations ranged up to 37 mg/m^3.

Other Measurements and Observations

The mechanical heating and air-conditioning system in the shop was not operating during our evaluation and had reportedly not been operational for several years. During our evaluation the temperature in the shop ranged from 94°F–109°F with 13% relative humidity, despite the front doors remaining open and two pedestal fans operating. The outdoor temperature reached 87°F. OSHA suggests starting a heat stress management program when workplace temperatures exceed 90°F [OSHA 2014c]. Such a program can help prevent heat stress and strain among employees.

We also noted the use of RustGo as a spot cleaner and accumulated dust throughout the shop. The shop was not equipped with an emergency eyewash station.

SolvonK4 and DF-2000 as "Safer Alternatives" to Perchloroethylene

A key step in the assessment of alternatives is to determine the intrinsic hazard associated with the chemical of concern. While the hazardous properties of PERC are well documented, this is not the case for the new drycleaning solvents DF-2000 and SolvonK4. In many respects, both SolvonK4 and DF-2000 are likely preferable to PERC, because they are not chlorinated hydrocarbons. More information on the toxicological properties of SolvonK4 and DF-2000 is presented in Appendix C. 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. Consequently, insufficient data are currently available to determine definitively whether these new solvent alternatives to PERC potentially represent "regrettable substitutions," which are defined as substitutions for hazardous chemicals that are later also found to be hazardous. Independent evaluation of the toxicological properties to these alternative drycleaning solvents is needed.

The SolvonK4 shop evaluated in this report was using a new drycleaning machine, and the process included the use of an acid stabilizer. It would be important to periodically monitor

solvent exposures in shops that use SolvonK4, particularly if changes in work practices are made that may affect emissions (i.e., not using an acid stabilizer or using insufficient amounts of an acid neutralizer) and if maintenance problems may arise, acidic conditions may be harder to control, and formaldehyde could become a hazard.

Conclusions

The highest air concentrations of alternative drycleaning solvents were measured during loading and unloading of the drycleaning machines and when pressing fabrics. We documented inhalation and dermal exposures to butylal (the main component of SolvonK4); however, no OELs exist and the long-term human health effects of SolvonK4 are unknown. Low concentrations of formaldehyde were measured in the SolvonK4 shop, but it is not known if the formaldehyde originated from the alternative drycleaning solvent or from other sources such as furnishings and clothing. We measured airborne concentrations of DF-2000 that were well below OELs for petroleum naphthas.

Recommendations

On the basis of our findings, we recommend the actions listed below. We encourage the shops to use a labor-management health and safety committee or working group to discuss our recommendations and develop an action plan. Those involved in the work can best set priorities and assess the feasibility of our recommendations for the specific situation. We encourage the shops to contact the state's occupational safety and health consultation group (http://lni.wa.gov/Safety/Consultation/About.asp) if assistance is needed in implementing these recommendations.

Our recommendations are based on an approach known as the hierarchy of controls. This approach groups actions by their likely effectiveness in reducing or removing hazards. In most cases, the preferred approach is to eliminate hazardous materials or processes and install engineering controls to reduce exposure or shield employees. Until such controls are in place, or if they are not effective or feasible, administrative measures and PPE may be needed.

Elimination and Substitution

Eliminating or substituting hazardous processes or materials reduces hazards and protects employees more effectively than other approaches. Prevention through design, considering elimination or substitution when designing or developing a project, reduces the need for additional controls in the future.

1. Replace RustGo (used at SolvonK4 drycleaning shop and DF-2000 drycleaning shop B) with a safer spot cleaner to remove rust. Consumer-grade detergents and other aqueous products can frequently accomplish spot cleaning successfully [LWHMP 2013a,b].

Engineering Controls

Engineering controls reduce employees' exposures by removing the hazard from the process or by placing a barrier between the hazard and the employee. Engineering controls protect employees effectively without placing primary responsibility of implementation on the employee.

1. Install an emergency eyewash station.
2. Brush the prespotting mixture onto fabrics, rather than spraying.
3. Improve mechanical ventilation to reduce the SolvonK4 odor and improve thermal comfort.
4. Ask the building owner to hire a qualified ventilation engineer to evaluate the design and operation of the ventilation system. This recommendation applies to the DF-2000 drycleaning shop B where the heating, ventilation, and air-conditioning system was not functioning and there was not good natural ventilation.

Administrative Controls

The term administrative controls refer to employer-dictated work practices and policies to reduce or prevent hazardous exposures. Their effectiveness depends on employer commitment and employee acceptance. Regular monitoring and reinforcement are necessary to ensure that policies and procedures are followed consistently.

1. Label any containers such as spray bottles and spot cleaning containers used for storing chemicals.
2. Take the precautions listed in the OSHA Fact Sheet: Protecting Employees from the Effects of Heat when temperatures are uncomfortably hot. http://www.osha.gov/OshDoc/data_Hurricane_Facts/heat_stress.pdf.
3. Start a heat stress management program for shops with limited ventilation. This program should include making sure that employees drink enough fluids, use the buddy system, and take breaks in cool areas throughout the work day and during lunch. More information on heat stress and heat strain can be found at the websites listed below.
   English: http://www.cdc.gov/niosh/docs/2010-114/pdfs/2010-114.pdf
   and http://www.osha.gov/SLTC/heatillness/index.html
   Spanish: http://www.cdc.gov/spanish/niosh/docs/2010-114_sp/
   and http://www.osha.gov/SLTC/heatillness/spanish/index_sp.html
4. Wash hands or any exposed skin with soap and water after contact with chemicals and before and after removing gloves.
5. Clean the shop regularly using a high efficiency particulate air filter vacuum cleaner or wet methods. This will prevent dust from becoming a potential fuel source in the case of a fire. Avoid dry sweeping.
6. Inspect and maintain the drycleaning machine regularly per the manufacturers' recommendations.
7. Dispose of the separator water and still bottoms according to local regulatory requirements.

Personal Protective Equipment

PPE is the least effective means for controlling hazardous exposures. Proper use of PPE requires a comprehensive program and a high level of employee involvement and commitment. The right PPE must be chosen for each hazard. Supporting programs such as training, change-out schedules, and medical assessment may be needed. PPE should not be the sole method for controlling hazardous exposures. PPE should be used until effective engineering and administrative controls are in place.

1. Wear gloves and eye protection (safety glasses or safety goggles) when using spot cleaners. Review the manufacturers' SDS for further information on each chemical. If spot cleaners contain SolvonK4, wear a long sleeve shirt and polyvinyl chloride or polyethylene protective gloves.
2. Wear eye protection and chemical protective gloves when cleaning the still bottoms. Thick (12 mil) nitrile gloves should be worn for the DF-2000 machine and neoprene or butyl rubber for the SolvonK4 machine.
3. Do not use a surgical mask to protect against inhaling solvents in the air. A surgical mask is not effective for this use.

Appendix A: Sampling and Analysis Methods for Butylal and DF-2000 in Air

Sampling and Analysis Method for Butylal in Air

We collected air samples on 150-mg charcoal tubes at a flow rate of 200 milliliters per minute (mL/min). We developed an analysis method because none was available. After sample collection, the front and back sections of each sorbent tube were placed in separate vials. The front glass wool was included with the front sorbent section. The samples were chemically desorbed with 1 mL of carbon disulfide. The samples were allowed to desorb for 60 minutes with continuous agitation before being analyzed by GC-FID, using a Hewlett Packard 5890A with a Nukol 30 meters (m) × 0.32 millimeter (mm) internal diameter (or similar) column.

The butylal analysis had a limit of detection (LOD) of 0.5 microgram per sample (µg/sample) and limit of quantitation (LOQ) of 1.7 µg/sample. The analytical range was 0.5–5040 µg/sample. Two media and two field blanks were associated with each sample set. Two laboratory control spikes were associated with each set. One blind spike was prepared and analyzed in replicate with the samples in each set. A sample in each set was analyzed in replicate. Butylal was recovered within the quality control recovery limits of 80%–120%. The replicate analysis was within the 20% relative percent difference limit.

During the method development phase, we found adequate recoveries from charcoal tubes (> 90%) at approximately 25, 125, 250, and 500 micrograms (µg) of butylal. Each level was tested in six replicate spikes. Spikes were placed into the front section charcoal bed of the charcoal tube with a microliter syringe. Tubes were allowed to sit refrigerated overnight before being prepared for analysis. Butylal (125 µg spike) was stable during storage of the charcoal tube for 30 days at ambient temperature (average recovery of 92%). We also found adequate recoveries (≥ 88%) at varying loadings of butylal on charcoal tubes and varying relative humidity levels. Approximately 25 µg and 500 µg of butylal in carbon disulfide were spiked on the front glass wool of the sorbent tube, using a microliter syringe, while laboratory air was being drawn through the tube at approximately 80% and ambient (3%–11%) relative humidity. Each level was tested in six replicates.

Sampling and Analysis Method for DF-2000 in Air

We collected air samples on 150-mg charcoal sorbent tubes. The analysis method was adapted from NIOSH Method 1550 to optimize the identification of the chemicals in DF-2000. The front and back sections of each sorbent tube were placed into separate vials, with the front glass wool included with the front sorbent section. The samples were chemically desorbed with 1 mL of carbon disulfide for at least 30 minutes with occasional agitation before being analyzed using NIOSH Method 1550, modified to include DF-2000. The analysis was performed by GC-FID, with a Hewlett Packard 5890 Series II with a Phenomenex ZB-1, 30 m, 0.32 mm internal diameter with a 1-micrometer film thickness or similarly appropriate column.

The DF-2000 analysis had an LOD of 6 µg/sample and LOQ of 19 µg/sample. The analytical range was 6 to 770 µg/sample. Two media and two field blanks were associated with each sample set. Two laboratory control spikes were associated with each set. Two blind spikes were prepared and analyzed in replicate with the samples in each set. Two samples in each set were analyzed in replicate. DF-2000 was recovered above 100%. The replicate analysis was within the 20% relative percent difference limit.

During the method development phase, we found adequate recoveries from charcoal tubes (> 85%) at approximately 25, 250, and 500 µg of DF-2000. Each level was tested in six replicate spikes. Spikes were placed into the front section charcoal bed of the charcoal tube with a microliter syringe. Tubes were refrigerated overnight before being prepared for analysis. DF-2000 (134 µg spike) was stable during storage of the charcoal tube for at least 21 days at both ambient and 39°F temperature (recoveries of > 89%).

Appendix B: Analyzing Formaldehyde in the Presence of SolvonK4

Testing NIOSH Method 2016 for the Analysis of Formaldehyde in the Presence of Butylal

We found that NIOSH Method 2016 provided false positives when sampling and analyzing for formaldehyde in the presence of butylal. The front glass wool section of six 2,4-dintrophenylhydrazine-coated silica gel tubes (SKC 226-119) were spiked with approximately 500 µg of SolvonK4 per tube. Four tubes were similarly spiked with pure acetonitrile as blanks. The tubes were connected to sampling pumps calibrated at 200 mL/min for 75 minutes to collect 15 liters of ambient air. After 1 day of refrigerated storage, the blank corrected results showed an average 26% conversion of butylal to formaldehyde. After 4 days of refrigerated storage, there was a 54% conversion. These results indicate that 2,4-dintrophenylhydrazine-coated silica gel tubes should not be used to sample for formaldehyde in an environment in which SolvonK4 is used.

Testing OSHA Method 52 for the Analysis of Formaldehyde in the Presence of Butylal

We found that OSHA Method 52 was appropriate for the sampling of formaldehyde in SolvonK4 drycleaning shops. The front glass wool section of six XAD-2 tubes coated with 2-hydroxymethyl piperidine (SKC 226-117, lot 7787) were spiked with 501 µg of SolvonK4. In addition, four blanks were spiked with 3 µL of methanol. These tubes were then placed on the sampling manifold for 75 minutes and had ambient air pulled through them at a rate of 200 mL/min. After 1 day and 4 days of refrigerated storage no formaldehyde was detected above the LOD of 0.9 µg of formaldehyde on any of the butylal spiked samples or any of the blanks.

Appendix C: Occupational Exposure Limits and Health Effects

NIOSH investigators refer to mandatory (legally enforceable) and recommended OELs for chemical, physical, and biological agents when evaluating workplace hazards. OELs have been developed by federal agencies and safety and health organizations to prevent adverse health effects from workplace exposures. Generally, OELs suggest levels of exposure that most employees may be exposed to for up to 10 hours per day, 40 hours per week, for a working lifetime, without experiencing adverse health effects. However, not all employees will be protected if their exposures are maintained below these levels. Some may have adverse health effects because of individual susceptibility, a pre-existing medical condition, or a hypersensitivity (allergy). In addition, some hazardous substances act in combination with other exposures, with the general environment, or with medications or personal habits of the employee to produce adverse health effects. Most OELs address airborne exposures, but some substances can be absorbed directly through the skin and mucous membranes.

Most OELs are expressed as a TWA exposure. A TWA refers to the average exposure during a normal 8- to 10-hour workday. Some chemical substances and physical agents have recommended short-term exposure limit or ceiling values. Unless otherwise noted, the short-term exposure limit is a 15-minute TWA exposure. It should not be exceeded at any time during a workday. The ceiling limit should not be exceeded at any time.

In the United States, OELs have been established by federal agencies, professional organizations, state and local governments, and other entities. Some OELs are legally enforceable limits; others are recommendations.

- The U.S. Department of Labor OSHA PELs (29 CFR 1910 [general industry]; 29 CFR 1926 [construction industry]; and 29 CFR 1917 [maritime industry]) are legal limits. These limits are enforceable in workplaces covered under the Occupational Safety and Health Act of 1970.
- NIOSH recommended exposure limits are recommendations based on a critical review of the scientific and technical information and the adequacy of methods to identify and control the hazard. NIOSH recommended exposure limits are published in the *NIOSH Pocket Guide to Chemical Hazards* [NIOSH 2014c]. NIOSH also recommends risk management practices (e.g., engineering controls, safe work practices, employee education/training, PPE, and exposure and medical monitoring) to minimize the risk of exposure and adverse health effects.
- Other OELs commonly used and cited in the United States include the TLVs, which are recommended by ACGIH, a professional organization, and the workplace environmental exposure levels (WEELs), which are recommended by the American Industrial Hygiene Association, another professional organization. The TLVs and WEELs are developed by committee members of these associations from a review of the published, peer-reviewed literature. These OELs are not consensus standards. TLVs are considered voluntary exposure guidelines for use by industrial hygienists and others

trained in this discipline "to assist in the control of health hazards" [ACGIH 2014]. WEELs have been established for some chemicals "when no other legal or authoritative limits exist" [AIHA 2014].

Outside the United States, OELs have been established by various agencies and organizations and include legal and recommended limits. The Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (Institute for Occupational Safety and Health of the German Social Accident Insurance) maintains a database of international OELs from European Union member states, Canada (Québec), Japan, Switzerland, and the United States. The database, available at http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-Internationale-Grenzwerte-für-chemische-Substanzen-limit-values-for-chemical-agents/index-2.jsp, contains international limits for more than 1,500 hazardous substances and is updated periodically.

OSHA requires an employer to furnish employees a place of employment free from recognized hazards that cause or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970 (Public Law 91–596, sec. 5(a)(1))]. This is true in the absence of a specific OEL. It also is important to keep in mind that OELs may not reflect current health-based information.

When multiple OELs exist for a substance or agent, NIOSH investigators generally encourage employers to use the lowest OEL when making risk assessment and risk management decisions. NIOSH investigators also encourage use of the hierarchy of controls approach to eliminate or minimize workplace hazards. This includes, in order of preference, the use of (1) substitution or elimination of the hazardous agent, (2) engineering controls (e.g., local exhaust ventilation, process enclosure, dilution ventilation), (3) administrative controls (e.g., limiting time of exposure, employee training, work practice changes, medical surveillance), and (4) PPE (e.g., respiratory protection, gloves, eye protection, hearing protection). Control banding, a qualitative risk assessment and risk management tool, is a complementary approach to protecting employee health. Control banding focuses on how broad categories of risk should be managed. Information on control banding is available at http://www.cdc.gov/niosh/topics/ctrlbanding/. This approach can be applied in situations where OELs have not been established or can be used to supplement existing OELs.

SolvonK4

Little toxicity information is available for butylal [NYSDEC 2011], the main ingredient in SolvonK4. Only acute toxicity studies focused on dermal and oral exposures have been published [NYSDEC 2011]. In an assessment of safer alternatives to PERC in drycleaning, the Toxics Use Reduction Institute concluded that toxicological data are lacking for some of the alternatives — particularly the new acetal-based system like SolvonK4 — making the human health assessment incomplete [TURI 2012].

Kreussler GmbH reported low toxicity of butylal on the basis of studies in which animals were exposed via ingestion and through the skin [Kreussler USA 2011]. Kreussler suggests that the risk for airborne exposure to butylal at drycleaning shops should be low because this solvent has a low vapor pressure, meaning that it does not quickly evaporate at room temperature [Kreussler USA 2011]. In a long-term inhalation study researchers observed no

adverse effects in rats after exposing them to 478 ppm butylal over 13 weeks [REACH 2014]. 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 butylal is not a skin sensitizer or skin or eye irritant from short-term exposures [Kreussler USA 2011]. We are not aware of any studies that have evaluated longer duration exposures from ingestion or through skin contact. The Local Hazardous Waste Management Program in King County, Washington (LHWMP) determined that SolvonK4 exhibited lower toxicity to fish than PERC [LHWMP 2013b]. The European Union has not classified butylal in the Registration, Evaluation, Authorization and Restriction of Chemicals program. However, the European Chemical Agency has listed butylal as causing skin irritation [ECHA 2013].

DF-2000

Little specific health information is available for DF-2000 [LHWMP 2014b]. However, information is available for similar petroleum naphthas, and this information is consistent with the information provided in the manufacturer's SDS for DF-2000 [NIOSH 1977]. The manufacturer [Exxon Mobil Chemical 2014a] reports that repeated skin exposure to DF-2000 may cause skin dryness or cracking. When swallowed, it can be aspirated and damage the lungs. It can also irritate the eyes, nose, throat, and lungs, but at concentrations much higher than what we measured in the shops. Exposures to concentrations much higher than those measured during these evaluations for long time periods can cause headaches, dizziness, drowsiness, unconsciousness, and other central nervous system effects including death [Exxon Mobil Chemical 2014a]. A review by the California Environmental Protection Agency, Office of Environmental Health Hazard Assessment [2003] of animal studies involving hydrocarbons similar to DF-2000 suggests the absence of aromatic hydrocarbons like benzene make DF-2000 a safer solvent than Stoddard solvent, which can contain aromatic hydrocarbons like benzene [OEHHA 2003]. The German Social Accident Insurance Information System lists substances in the CAS category that includes DF-2000 and indicates these substances are harmful and may cause lung damage if swallowed [GESTIS 2014].

The composition and physical properties of substances with the DF-2000 CAS number can vary [EPA 2014; LWHMP 2014b; NIOSH 2014b]. Consequently, substances with this CAS number may exhibit different toxic and environmental properties [LWHMP 2014b]. A search of the Pharos Project database using the CAS number for DF-2000 revealed that this substance is regarded as a mutagen and a carcinogen in a European Union classification system [The Healthy Building Network 2014]. However, the supporting documentation states that the classification as a carcinogen need not apply if it can be shown that the substance contains less than 0.1% weight by weight benzene [European Union 2006]. Chemical analysis of the DF-2000 solvent in this report and that by LWMHP [2014b] confirmed that benzene was not detected. Therefore, DF-2000 would not be classified as a carcinogen according to these criteria.

The OELs related to chemicals similar to DF-2000 are shown in Table C1 and include the Federal Republic of Germany, which has an occupational exposure limit for a naphtha mixture with the same CAS number as DF-2000.

Table C1. Occupational exposure limits related to DF-2000 in air

Substance	NIOSH* OEL (mg/m^3)	ACGIH† OEL (mg/m^3)	OSHA OEL (mg/m^3)	Other OEL (mg/m^3)
DF-2000 (CAS 64742-48-9), as naphtha, petroleum, hydrotreated, heavy		1142–1200 (8 hours)		Exxon Mobile Chemical 1,200 (8 hours) DFG MAKs‡ 300 (8 hours)
Petroleum distillate naphtha, VM & P naphtha§	350 (8 hours) 1800 (15 minutes)			CAL OSHA 1,350 (8 hours) 1800 (15 minutes)
Petroleum distillates naphtha (rubber solvent)§	350 (8 hours) 1800 (15 minutes)		2000 (8 hours)	CAL OSHA 1,600 (8 hours)
Stoddard solvent§	350 (8 hours) 1800 (15 minutes)	525 (8 hours)	2900 (8 hours)	CAL OSHA 525 (8 hours)

*NIOSH action level is 200 mg/m^3 during 8 hours.

†ACGIH TLV was calculated using the reciprocal calculation mixture formula with two different group guidance values [ACGIH 2013] and assuming 10% cycloparaffins and 90% paraffins [OEHHA 2003].

‡Deutsche Forschungsgemeinschaft (DFG), Federal Republic of Germany, maximum concentrations at the workplace (MAK) [GESTIS 2014].

§Because DF-2000 is considered a refined petroleum product, we also compared the personal air sampling results to the occupational exposure limit for petroleum distillates (naphtha) and Stoddard solvent (white spirits), similar refined petroleum products.

Appendix D: Sampling and Analysis Method for Butylal and DF-2000 on Patch Samplers

Analysis Method for Butylal on Patch Samplers

The samples were collected on PERMEA-TEC patches. The patch was separated from the bandage backing, placed into a 4-mL vial, and the bandage backing was discarded. The samples were chemically desorbed by using 1.5 mL of carbon disulfide. The samples were desorbed for a minimum of 1 hour, and during desorption the samples were shaken several times. After desorption, the samples were transferred to amber-colored autosampler vials and analyzed by GC-FID, using a Hewlett Packard 5890A with a Zebron Wax plus 60 m × 0.32 mm internal diameter (or similar) column. The results obtained from the butylal analysis of patch samples had a higher LOD (1 µg/sample) and LOQ (4.7 µg/sample) compared to the air analysis results.

During the method development phase, we found adequate recoveries from patches (> 85%) at approximately 25, 125, 250, and 500 µg of butylal. Each level was tested in six replicate spikes. Butylal (125 µg spike) was stable during storage of the patches for 30 days at ambient and 39°F temperatures (recovery of > 82%).

Analysis Method for DF-2000 on Patch Samplers

The patch was separated from the bandage backing, placed into a 4-mL vial, and the bandage backing was discarded. The samples were chemically desorbed by using 3 mL of carbon disulfide and placed on a mechanical flatbed shaker for a minimum of 45 minutes. After desorption, the samples were transferred to amber autosampler vials and analyzed using NIOSH Method 1550, modified for DF-2000 on patches. The analysis was performed by GC-FID, with a Hewlett Packard 5890 Series II with a Phenomenex ZB-1 60 m × 0.32 mm internal diameter (or similarly appropriate) column. The results obtained from the DF-2000 analysis of patch samples had a higher LOD (40 µg/sample) and LOQ (190 µg/sample) compared to the air analysis results.

During the method development phase, we found adequate recoveries from patches (> 98%) at approximately 25, 125, 250, and 500 µg of DF-2000. Each level was tested in six replicate spikes. Spikes were placed on the charcoal surface of the patch, using a microliter syringe. The patches were removed from the adhesive bandage prior to spiking. Spiked patches were allowed to sit overnight before being prepared for analysis. DF-2000 was recovered within the quality control recovery limits of 80%–120%. However, variability was high in the lowest spike level (25 µg). This level is below the calculated media LOD.

DF-2000 (130 µg spike) was stable during storage of the patches for 21 days at ambient and 39°F temperature (recoveries of > 87%). DF-2000 (130 µg spike) in the patches had unacceptable storage stability at 35 days at ambient or 39°F temperature (recoveries of < 74%).

Appendix E: Tables

Table E1. Results of personal air samples collected over the work shift, SolvonK4 drycleaning shop, May 8–9, 2013

	Main tasks		Formaldehyde (ppm)	Butanol (ppm)	Butylal (ppm)
Employee A	Pressing fabrics and unloading and loading fabrics from drycleaning machine	Day 1	Not detected*	Not sampled	0.30
		Day 2	(0.0087)†	Not sampled	0.18
Employee B	Pressing shirts	Day 1	Not sampled	Not detected*	0.017
		Day 2	Not sampled	Not detected*	0.017

*For these samples, the minimum detectable concentration (MDC) was 0.008 ppm of formaldehyde and 0.001 ppm of butanol.

†This concentration was above the MDC but below the minimum quantifiable concentration (MQC). This means that there is more uncertainty associated with this value.

Table E2. Results of area air samples collected over the work shift, SolvonK4 dry cleaning shop, May 8–9, 2013

Sample location		Formaldehyde (ppm)	Butanol (ppm)	Butylal (ppm)
Front desk	Day 1	(0.0084)*	Not detected†	0.0039
	Day 2	Not detected†	Not detected†	0.010
Next to press machine	Day 1	Not detected†	(0.0028)*	0.056
	Day 2	(0.012)*	(0.0024)*	Not sampled
Next to drycleaning machine	Day 1	Not detected†	0.0079	0.31
	Day 2	Not sampled	0.0079	0.29

*This concentration was above the MDC but below the MQC. This means that there is more uncertainty associated with this value.

†For these samples, the MDC was 0.008 ppm of formaldehyde and 0.001 ppm of butanol.

Table E3. Results of short-term area air samples collected near employees near the drycleaning machine, SolvonK4 drycleaning shop, May 8–9, 2013

	Work task	Duration of sampling (minutes)	Formaldehyde (ppm)	Butanol (ppm)	Butylal (ppm)
Day 1	1st unloading, 2nd loading	16	Not detected*	(0.079)†	1.9
	2nd unloading, 3rd loading	15	Not detected*	(0.052)†	1.6
	3rd unloading, 4th loading	84	Not detected*	(0.018)†	0.72
Day 2	Cleaning still	19	Not detected*	(0.054)†	0.17
	Loading, washing cycle, and unloading	114	0.043†	Not detected‡	0.52

*For these air samples, the MDC was in the range of 0.04 to 0.2 ppm of formaldehyde.

†This concentration was above the MDC but below the MQC. This means that there is more uncertainty associated with this value.

‡For this air sample, the MDC was 0.006 ppm of butanol.

Table E4. Results of personal air samples collected over the work shift, DF-2000 drycleaning shop A, May 2–3, 2013

	Main tasks		DF-2000 concentration (mg/m^3)
Owner/Operator	Unloading and loading	Day 1	1.4
		Day 2	0.99

Table E5. Results of personal air samples collected during short-term work tasks, DF-2000 drycleaning Shop A, May 2–3, 2013

	Main tasks		Duration of task (minutes)	DF-2000 concentration (mg/m^3)
Owner/Operator	Loading, washing cycle, and unloading	Day 1	235	2.8
	Cleaning still	Day 2	8	Not detected*
Employee A	Pressing and ironing shirts	Day 1	133	7.9

*For this sample, the MDC was 3.8 mg/m^3.

Table E6. Results of area air samples collected over the work shift, DF-2000 drycleaning shop A, May 2–3, 2013

Sample location		DF-2000 concentration (mg/m^3)
Front desk	Day 1	(0.16)*
	Day 2	0.74†
Table in the back of the shop	Day 1	0.65
Next to drycleaning machine	Day 1	0.90
	Day 2	0.63

*This concentration was above the MDC but below the MQC. This means that there is more uncertainty associated with this value.

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

Table E7. Results of area air samples collected during short-term work tasks near the drycleaning machine, DF-2000 drycleaning shop A, May 2–3, 2013

	Work task sampled	Duration of task (minutes)	DF-2000 concentration (mg/m^3)
Day 1	Unloading, loading, and pressing	15	(5.3)*
	Unloading, loading, and pressing	15	10
	Pressing	53	Not detected†
	Pressing	133	(0.38)*
Day 2	Cleaning still	8	Not detected‡
	Loading, washing, and unloading	102	1.4
	Unloading	15	21
	Drycleaning machine turned off	140	Not detected§

*This concentration was above the MDC but below the MQC. This means that there is more uncertainty associated with this value.

†For this sample, the MDC was 2.0 mg/m^3.

‡For this sample, the MDC was 3.8 mg/m^3.

§For this sample, the MDC was 0.21 mg/m^3.

Table E8. Results of personal air samples collected over the work shift, DF-2000 drycleaning shop B, May 6–7, 2013

	Main tasks		DF-2000 concentration (mg/m^3)
Owner/Operator	Attending customers and unloading and loading	Day 1	5.4
		Day 2	2.0
Employee A	Pressing and ironing	Day 1	Sample pump failure
		Day 2	2.8

Table E9. Results of area air samples collected over the work shift, DF-2000 drycleaning shop B, May 6–7, 2013

Sample location		DF-2000 concentration, (mg/m^3)
Front desk	Day 1	0.56
	Day 2	0.24
Next to shirt presses	Day 1	3.1
	Day 2	1.4
Next to drycleaning machine	Day 1	3.5
	Day 2	5.6

Table E10. Results of short-term area air samples (15 to 101 minutes) taken near the drycleaning machine, DF-2000 drycleaning shop B, May 6–7, 2013

	Work tasks nearby	Duration of task (minutes)	DF-2000 concentration (mg/m^3)
Day 1	Loading and washing cycle	86	5.2
	Unloading	15	37
	Pressing	75	5.4
Day 2	Loading	101	2.9
	Drycleaning machine turned off	65	0.65

Appendix F: SolvonK4 Stability in Typical Drycleaning Conditions

Butylal has the potential to decompose into formaldehyde and butanol in the presence of water and an acid catalyst. The purpose of this experiment was to determine how readily butylal decomposes into formaldehyde and butanol under conditions similar to those in the drycleaning environment of high temperature and humidity.

Procedure

Samples were prepared in either 20 or 40 mL vials, each with varying amounts of SolvonK4 (40–100 µL) and varying amounts of water (0–100 µL). Each vial was placed in a hot block and heated to approximately 266°F for 1 hour. These parameters were selected because they are roughly equivalent to the field conditions. According to the manufacturer of the drycleaning machine, each cleaning cycle runs for 60–65 minutes and the solvent is heated to 275°F. We removed the vial from the hot block and allowed it to reach room temperature for about 30 minutes. The above experiments were also conducted at 194°F to stay below the boiling point of water to potentially allow for more interaction between the water and butylal.

We collected a headspace sample two ways: using a thermal desorption tube and using a solid-phase micro-extraction fiber. The thermal desorption samples were collected by opening the vial and dangling a thermal desorption tube inside the vial while drawing air through the tube for 45 seconds at approximately 100 mL/min. The micro-extraction fiber samples were collected by puncturing the septum on the lid of the vial and sampling the static headspace in the vial (i.e., vial unopened so no shift in equilibrium) with a fiber for 5 seconds or 30 minutes.

Results

Butanol was monitored in these reactions as an indicator of the extent of butylal decomposition as the collection and recovery of formaldehyde was problematic with a sampler without a derivatizing reagent (formaldehyde is highly reactive and highly volatile). The amount of butanol did not vary from the background amount in any appreciable quantity, regardless of the parameter variations (amount of water, temperature, and dynamics of the headspace). If butylal decomposes, both butanol and formaldehyde are formed, and, because the butanol did not change considerably, we would not expect the formaldehyde quantities to change either. These results should be considered as preliminary because the butylal peak was off-scale, and the background amount of butanol in the bulk SolvonK4 made changes in the amount of butanol hard to evaluate.

Appendix G: Control Banding Methods Applied to SolvonK4

The traditional approach to protecting employee health measures employee exposures to potentially hazardous agents, compares them to occupational exposure limits, and then determines if existing control measures provide adequate protection. Reliance on this approach has become increasingly difficult because of the growing number of potentially hazardous materials in the workplace that do not have occupational exposure limits. Control banding is a technique used to guide the assessment and management of workplace risks. It uses the solutions that experts have developed previously to control occupational chemical exposures and suggest them for other tasks with similar exposure situations. Control banding methods are also called control banding tools or toolkits. More information on control banding is available at http://www.cdc.gov/niosh/topics/ctrlbanding/.

There are many fully developed control banding methods or toolkits. Although they may use different terminology, all of these methods have some things in common. The first step is to evaluate the health hazard of the material, then determine the potential exposure. These two steps are used to determine the control band for the task. These control banding methods have been developed for inhalation and dermal hazards and for specific industries such as nanotechnology.

We selected three commonly used control banding tools to evaluate inhalation and dermal exposure hazards associated with (1) loading/unloading/hanging clothes from the drycleaning machine and (2) spraying clothes with a prespotting solution containing SolvonK4. We limited our control banding evaluation to butylal, the main ingredient in SolvonK4.

The first control banding method we used is called control of substances hazardous to health (COSHH) Essentials and was developed by the Health and Safety Executive (http://www.hse.gov.uk/coshh/essentials/index.htm). To evaluate the health hazard of the material we selected an appropriate risk phrase (R-phrase), sometimes called a hazard statement (H-code). The R-phrase describes the special risks associated with chemical substances. These R-phrases are defined by the European Union and are found internationally in SDSs. With the implementation of the globally harmonized system of classification and labelling of chemicals, H-codes will eventually replace the R-phrases; however, at this time the control banding toolkits still use the R-phrases. On the basis of the R-phrase the control banding tool places the material into one of five groups labeled A–E, with A being the least hazardous group and E the most hazardous group. To determine the exposure potential of the task, we decide the volatility (how quickly it evaporates at room temperature) of the chemical, choosing from low, medium, or high levels of volatility. We also decide on the quantity used or generated (small, medium, or large quantity). The COSHH Essentials tool then combines the results from these two steps and assigns the task to one of four control strategies.

The second control banding method we used was the Stoffenmanager 5.1 model (referred to as Stoffenmanager in this report), developed by TNO (Netherlands Organization for Applied Scientific Research) and Arbo Unie (Work Safety Union) in the Netherlands. Unlike the COSHH Essentials model, the Stoffenmanager inhalation and dermal models do not recommend a control method. The web-based tool is available at http://www.stoffenmanager.nl/.

For the Stoffenmanager inhalation assessment, the health hazard of the material is obtained from R-phrases and required information on SDSs, and assigned to one of six health hazard classes: none, A-low, B-average, C-high, D-very high, and E-extreme. The exposure potential is assigned to one of four classes, ranging from 1 (low) to 4 (very high), on the basis of the tasks and workplace environment. The model then combines the outputs of health hazard and exposure potential to generate one of three risk classes, ranging from I (high) to III (low).

For the Stoffenmanager dermal assessment, the health hazard of the material is obtained and assigned in the same way as the Stoffenmanager inhalation model. Similarly, the exposure potential is assigned to one of six classes, ranging from 1 (negligible) to 6 (extreme) on the basis of answers to the task-related questions such as handling method of the material, amount of the material, duration of the activity, etc., and workplace environment-related questions. The model then combines the outputs of health hazard and exposure potential to generate one of three risk classes, ranging from I (high) to III (low). The dermal model generates two separate results, local effect upon contact and systemic effect after uptake through the skin.

The third control banding method we used was the RISKOFDERM toolkit, developed for the European Union RISKOFDERM project. A free version of the toolkit is available at http://www.eurofins.com/product-testing-services/services/research-development/projects-on-skin-exposure-and-protection/riskofderm-skin-exposure-and-risk-assessment.aspx.

On the basis of the R-phrases, the RISKOFDERM toolkit assigns the health hazard of the material to one of five classes: low, moderate, high, very high, and extreme hazard. The exposure potential class is determined only for a task assigned to one of six dermal operational units, handling contaminated objects, manual dispersion, hand tool dispersion, spray dispersion, immersion, and mechanical treatment. For each dermal operation unit, the exposure potential is assigned to one of six classes: negligible, low, moderate, high, very high, and extreme, based on the material characteristics and exposed body area. The RISKOFDERM toolkit then combines the outputs of health hazard and exposure potential to generate a risk score from 1 (no action required) to 10 (substitute, stop working). This toolkit generates two separate results: local effect upon contact and systemic effect after uptake through the skin. Each effect produces dermal risks of body and hands separately.

Using Control Banding for Two Tasks

We identified one R-phrase for butylal—R38-Irritating to skin—from the Classification and Labeling Inventory Database of the European Chemical Agency available at http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database.

Task One: Loading/Unloading/Hanging Clothes from the Drycleaning Machine

During our visit to the SolvonK4 drycleaning shop, four cycles were completed and each cycle took 70–80 minutes. Using this information, the COSHH Essentials suggested control level 1 (general ventilation) and provided the exposure potential class of 1 (low exposure). The Stoffenmanager generated a risk score of "III," meaning the employee had a low risk

while performing the task.

We did not perform a dermal risk assessment because of no direct contact of butylal occurred while performing this task.

Task Two: Spraying Clothes with a Prespotting Solution Containing SolvonK4

Inhalation

Using the same health hazard class "A" of butylal and assuming a small quantity of solution is sprayed for less than 30 minutes before each loading, the COSHH Essentials suggested control level 1 (general ventilation) and provided an exposure class of 2 (average exposure). The Stoffenmanager model generated a risk score of "III," meaning the employee had a low risk for performing this task.

Dermal

The Stoffenmanager model assigned R38-Irritating to skin to the hazard class of "B (average)" for the local effect, and "none" for the systemic effect. On the basis of how the spraying task was performed, the model generated the potential exposure class of "4 (high)" for local and systemic effects. The combined results of the hazard class "B" and potential exposure class "4" generated a dermal risk "II," meaning the employee had a medium risk level for the local effect. The combined result of the hazard class "none" and potential exposure class "4" generated a dermal risk "III," meaning the employee had a low risk level for the systemic effect.

The RISKOFDERM toolkit assigned a hazard score of "moderate" for the local effect and "no" for the systemic effect (for body and hands). To determine an exposure potential class, we selected the "spray dispersion" task. For the local effect, the toolkit produced "moderate" exposure for body and "high" exposure for hands. For the systemic effect, the toolkit produced "moderate" exposure for body and hands. The model then generated a local effect risk score of 3 for body and 4 for hands. For the systemic effect, the model generated a 2 for body and hands. The recommended controls for the risk scores are 2 (no special treatment), 3 (reduction of skin exposure to the chemical), and 4 (necessity of skin care requiring primarily exposure reduction to the chemical).

Conclusions

These control banding methods confirmed that general ventilation was recommended in the SolvonK4 drycleaning shop for tasks such as loading and unloading fabrics into and from the drycleaning machine and when spraying spot cleaners. The control banding methods did not recommend advanced control methods (e.g., local exhaust ventilation). The control banding methods also advised reduction of dermal exposures to butylal while spraying spot cleaners, especially when handling butylal with bare hands. Although the control banding recommendations did not require urgent skin care after contact with butylal, avoiding direct contact by wearing protective gloves and a long-sleeve shirt would be recommended.

The recommended controls from the control banding methods were similar to those recommended on the basis of exposure measurements in this report. Although these control banding methods have not been fully tested, the results provide helpful general information to health and safety professionals. As more toxicological information about butylal becomes available, these models could be further refined to provide more specific recommendations.

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