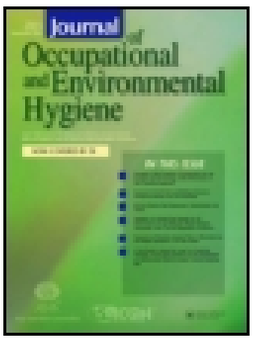

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Occupational Exposures to New Drycleaning Solvents: High-flashpoint Hydrocarbons and Butylal

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ABSTRACT

The drycleaning industry is moving away from using perchloroethylene. Occupational exposures to two alternative drycleaning solvents, butylal and high-flashpoint hydrocarbons, have not been well-characterized. We evaluated four drycleaning 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 drycleaning machines and pressed drycleaned 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 the safety of butylal in occupational settings. Independent evaluation of the toxicological properties of these alternative drycleaning solvents, especially butylal, is urgently needed.

INTRODUCTION

There are about 36,000 commercial drycleaning shops in the United States.[1] Most are owner-operated small businesses with fewer than 10 employees.[2,3] In addition, some drycleaning 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]

Drycleaning Solvent Alternatives to Perchloroethylene

Increasing environmental regulations and awareness of the potential occupational hazards from the drycleaning chemical perchloroethylene (PERC) has resulted in some drycleaners 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 drycleaners (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 drycleaning solvent called SolvonK4™ was introduced in the United States.[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°C–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] However, data are available for similar petroleum naphthas.[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 hours). 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 hour 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 (8 mil) 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 drycleaning machines, and some had low workloads during the days of our visit. These shops are not representative of all drycleaning 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 drycleaning shops using retrofitted drycleaning

machines. For example, drycleaning 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 drycleaning 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.

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FIGURES

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

FIGURE 2. An owner/operator removing still bottoms from the DF-2000™ drycleaning machine.

FIGURE 3. Employee spraying shirts with a solution containing SolvonK4™ to pretreat fabrics before drycleaning cycle.

TABLES

TABLE I. Summary characteristics of the drycleaning 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	18ft × 36ft × 20ft	18ft × 36ft × 20ft	35ft × 33ft × 18ft	24ft × 99ft × 10ft
Ventilation used during	Natural (HVAC not operational)	Natural (HVAC not operational)	Natural (HVAC not operational)	Natural and HVAC*

visit[A]				
Doors[B]	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 day 4 loads on 2nd day	4 loads on 1st day 3 loads on 2nd day	5 loads on 1st day 4 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 drycleaning 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. *The SolvonK4™ Shop B turned on HVAC system after turning-off the drycleaning machine and our sampling time includes with and without HVAC operation. [B]Doors were opened when needed for natural ventilation.

TABLE II. Personal full-shift air samples from drycleaning 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 III. Personal full-shift air sample results from drycleaning shops using SolvonK4™

Location	Main tasks	Sample Time (minutes)	Concentration (ppm)		
			Butylal	Butanol	Formaldehyde
Shop A	Pressing fabrics, unloading and loading fabrics from drycleaning 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 IV. Results of personal task-based air samples from drycleaning 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 V. Results of personal task-based air samples from drycleaning shop using SolvonK4™

Worker	Main tasks	Sample Time (minutes)	Concentration (ppm)		
			Butyl al	Butanol	Formaldehyde
Shop B Owner/operator	Loading, unloading, and spot cleaning with SolvonK4™ containing mixture	23	0.57	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 VI. Results of full-shift and short-term area air samples collected from drycleaning shops using DF-2000™

Shop	Location	Sample Time (minutes)	DF-2000™ concentration (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 drycleaning machine	554	0.90
		545	0.63
		15	(5.3)[A]
		15	10
		102	1.4
		15	21
	Next to drycleaning machine, cleaning stills	8	ND[C]
	Next to drycleaning 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 drycleaning 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 MDC was 2.0 mg/m^3.

TABLE VII. Results of full-shift and short-term area air samples from drycleaning 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 Drycleaning 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 Drycleaning 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 VIII. 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
Task 1	Loading, unloading, and hanging fabrics	Inhalation	COSHH Essentials	A	1	CS1-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	CS1-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 Systemic effec[D]

	Hands	Local effect: Moderate Systemic effect: no	High for local and systemic effects	Local effect: 4 Systemic effec [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 reference 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.