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TECHLAB REPORT

FACTS ON HAZARDOUS CLEANING SOLVENTS AND RECOMMENDED REPLACEMENTS

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N-Propyl Bromide (nPB), Trichloroethylene (TCE), Perchloroethylene (Perc) and methylene chloride (MeCl) are toxic chemicals commonly used in industrial applications as aerosol cleaners, in vapor degreasers, ultrasonic cleaning equipment, and immersion cleaning. They are commonly used as cleaners because they are non-flammable, have high solvency, and are relatively inexpensive.

The onus is on the organizations using solvents to select products carefully, and equip the users to safely handle the chemicals. The lack of such knowledge and control can lead to employee ill health, downtime, and potential liability, no matter what the legal standing of a particular chemical.

Techspray has engineered the PWR-4™ cleaning solvents to be a safer replacement for n-propyl bromide and other toxic solvents. P WR-4™ is formulated with trans 1,2-dichloroethylene (trans-DCE) and does not contain nPB, TCE, Perc, MeCl, or any other hazardous air pollutants (HAP). The following is an overview, history and likely trends for the currently available toxic industrial cleaners, and the data that supports PWR-4™ as a viable, safer alternative.

IDENTIFYING TOXIC SOLVENTS IN YOUR FACILITY

The first step to replacing these toxic solvents is identification. Ingredients are referenced either by a variety of chemical identifiers, trade names, or CAS numbers. The Global Harmonized System (GHS) provides a pictogram to help quickly identify potential carcinogens, reproductive toxicity, acute toxicity and other serious health hazards (see pictogram to the right). The definitive way to identify the solvent in questions is the CAS number, which is stated on the product label and Safety Data Sheet (SDS). Below is a list of common chemical names for the toxic industrial solvents, and CAS numbers:

CHEMICAL NAME	ALTERNATIVE NAMES	CAS #
n-propyl bromide	nPB, bromopropane, 1-propyl bromide, 1-bromopropane	106-94-5
Trichloroethylene	TCE, 1,1,2-trichloroethene, 1,1-dichloro-2-chloroethylene, 1-chloro-2,2-dichloroethylene, acetylene trichloride, trethylene	79-01-6
Perchloroethylene	Perc, perchloroethene, tetrachloroethylene, PCE	127-18-4
Methylene chloride	MeCl, DCM, dichloromethane, methylene dichloride	75-09-2

EXPOSURE CONTROL METHODS

Whether these exposure limits are acceptable or not depends on the ability to control fumes and atomized solvents. The use of solvents in spray applications poses much greater concern to worker safety than batch, vapor degreasing as workers are directly exposed to the solvent.

The EPA commissioned ICF Consulting to perform a risk study on the issue of nPB, which was released at the May 2002 CleanTech exposition. In evaluating spray adhesive applications, the ICF found, “Before installation of the spray booths, the overall mean concentration of nPB was 168.9 ppm, with main exposures in each work area ranging from 117.1 ppm in the Saw area to 197.0 ppm in the covers area. Following installation of the spray booths, the overall main nPB exposure concentration was 19 ppm, with individual measurements ranging from 1.2 to 58 ppm.”[1]

Note that even with proper engineering controls, some workers outside the booth had exposure as high as 58 ppm. A spray booth is above-and-beyond typical ventilation control in a cleaning application, so open air spraying, or even spraying under a ventilation hood will most likely cause exposure well over the limits for nPB, TCE, Perc, and MeCl. The harm caused by excessive exposure depends on the material. The specifics are not generally covered in detail in MSDS, so facilities considering a particular chemical should do additional research if safety is in question.

TCE, PERC AND MeCl

Use of TCE, Perc, and MeCl has decreased significantly from the time they were approved as substitutes for the ozone depleting substances (ODS), because of concerns with toxic exposure and ground water contamination. In a study of Perc exposure on rats and mice conducted by the US National Toxicology Program (NTP), exposure from 200 ppm and above resulted in hepatic congestion, liver lesions, and mitotic alterations (changes in how cells divide), while some in the high-dose groups died before the study was completed.[2]

There are also reported incidents of workers being hurt from exposure to these chemicals with some resulting in death. OSHA has linked 50 worker fatalities related to methylene chloride exposure. Two successive deaths, one in September 2011 and the other in February 2012, have prompted OSHA/NIOSH to issue a hazard alert. In both cases "a worker using a product containing methylene chloride" to refinish a bathtub succumbed to the toxic levels associated with an enclosed space and a poorly ventilated work area.[3]

In response, state and federal agencies set exposure limits to protect workers. OSHA has set the permissible exposure limit (PEL) to 100 ppm for Perc and TCE and 25 ppm MeCl.[4] An agency of CDC, the National Institute for Occupational Safety and Health (NIOSH) lists Perc as a potential occupational carcinogen and MeCl as an occupational carcinogen. It advises the "lowest feasible exposure" for both and recommends an exposure limit (REL) of 25 ppm for TCE.[5] California Occupational Safety and Health Standards Board (OSHSB) has regulated the workplace PEL to 25 ppm for Perc, TCE, and MeCl.[6] The professional association for industrial hygienists known as the American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) of 10 ppm for TCE, 25 ppm for Perc, and 50 ppm for MeCl.[7]

Without exception, the NTP classifies TCE, Perc, and MeCl as "reasonably anticipated to be human carcinogen."[8] TCE, Perc, and MeCl are listed as carcinogens under California Prop 65.[9] Perc is also an animal carcinogen by ACGIH.[10] Under the Safe Drinking Water Act, EPA restricted the maximum contaminant level (MCL) to 0.005 mg/L (5ppb) for TCE, PCE and MeCl.[11]

While these toxic solvents are still being used in industrial environments, the trend has been to move to alternatives, of which nPB was commonly considered a viable alternative.

NPB

During the phase-out of class I ODS in the 1990's, nPB was relatively new to the US industry. nPB did not have a history of widespread use, so was not regulated. Its unregulated status made it an attractive alternative to the heavily regulated solvents like TCE, Perc and MeCl, with some formulators marketing it as a "safety solvent". Even now, there is no exposure limit set by OSHA or NIOSH.

However, there are cited examples in the industry where workers suffered major health effects when exposed to nPB. The following is a case reported to regional poison control centers in Pennsylvania (2007) by attending physicians who treated the affected workers, and later investigated by federal and state health agencies.
"In 2007, a male aged 50 years visited an emergency department in Pennsylvania with a history of confusion, dysarthria [unclear speech], dizziness, paresthesias [tingling], and ataxia [loss of full body control] for 24--48 hours. The patient had worked for 8 years at an electronics plant in Pennsylvania, where for 3 years 1-BP [nPB] had been used to clean circuit boards by vapor and immersion degreasing… One week after the patient went to the emergency department, the Occupational Safety and Health Administration (OSHA) evaluated his workplace and found a 1-BP concentration of 178 ppm by short-term area air sampling… His peripheral neuropathy and ataxia persisted 1 year after the initial visit. The patient also reported having trouble maintaining mental focus and stopped working at the electronic plant because of continuing medical problems."[12]

While federal agencies have been slow in regulating nPB, CA OSHSB has a PEL of 5ppm and listed it as a developmental/reproductive toxicant under Prop 65. Pennsylvania has included it on its hazardous substance list.[13] ACGIH has listed the TLV for nPB as 10 ppm, but there is a proposal to decrease it to 0.1 ppm.[14] Comparable to TCE, PCE, and MeCl in toxicity, nPB has been determined by NTP as "reasonably anticipated to be a human carcinogen."[15]

Though nPB is listed in Significant New Alternatives Policy (SNAP) under the Clean Air Act, it actually has an ozone depleting potential (ODP). It is also likely to be designated as an air toxin by the EPA. In October 2010 the Halogenated Solvents Industry Alliance petitioned EPA to list nPB as a HAP. New York State followed with its own petition in November 2011. The petitions must undergo a completeness review followed by a technical review. As of Feb. 6, 2015, the petitions passed the completeness review. NPB has taken the first step in joining TCE, Perc, and MeCl as HAPs and subject to regulation by the National Emission Standards for Hazardous Air Pollutants (NESHAPs).[16]

TECHSPRAY PWR-4™ CLEANING SOLVENTS

In contrast, PWR-4™ does not exhibit any of the health issues associated with nPB, TCE, Perc, and MeCl. A 14-week NTP study in which rats and mice were fed microcapsules with 45% trans-DCE (key active ingredient of PWR-4™) at a maximum concentration of 50,000 ppm did not result in deaths. More significantly, there were no adverse effects observed in the histopathology and clinical chemistry data.[17]

In another study, rats were exposed to air containing 200 ppm trans-DCE for 8 hours/day, 5 days/week for 16 weeks. Again, results of the study found no statistically significant changes in clinical chemistry, hematology, or histopathology of the animals.[18]

Because of these and other studies, PWR-4™ has a high exposure limit of 200 ppm based on standards from OSHA, NIOSH and ACGIH. Due to the overwhelming, negative environmental impact and health risks associated with the nPB, TCE, Perc, and MeCl, PWR-4™ offers a favorable contrast as an overall safer chemical. The positive impact on the atmosphere, environment, and workers' safety, in addition to comparable cleaning performance, positions PWR-4™ as a viable alternative for industrial solvent cleaning.

CHART 1: HEALTH & SAFETY COMPARISON OF CLEANING SOLVENTS

Atmospheric Effects	MeCl	TCE	Perc	nPB	Trans-DCE
ODP	NO	NO	NO	YES	NO
GWP*	8.7 years[19]	5 years[20]	12 years[21]	0.31 years[22]	12.7 years[23]
SNAP	YES	YES	YES	YES	YES
Environmental Effects					
VOC	NO	YES	NO	YES	YES
HAP (NESHAP)	YES	YES	YES	EVAL.	NO
EPA Safe Drinking Water Act	5 ppb	5 ppb	5 ppb	NONE	100 ppb
Fed. Toxicity Exposure Limit					
OSHA (PEL)	25 ppm	100 ppm	100 ppm	NONE	200 ppm
NIOSH (REL-TWA)	Lowest possible**	25 ppm	Lowest possible***	IN PROCESS	200 ppm
ACGIH	50 ppm	10 ppm	25 ppm	10 ppm****	200 ppm
NTP	†	†	†	†	Low toxicity
State Toxicity Exposure Limit					
California Prop 65	YES††	YES††	YES††	YES‡	N/A
CA OSHSB	25 ppm	25 ppm	25 ppm	5 ppm	N/A
Pennsylvania				YES‡‡	

* 100 year time horizon
** Listed as an occupational carcinogen
*** Listed as a potential occupational carcinogen.
**** Proposal to decrease to 0.1ppm.
† Reasonably anticipated as a human carcinogen.
†† Listed as a carcinogen
‡ Listed as developmental/reproductive toxicant
‡‡ Listed in its hazardous substance list

Techspray®, a division of Illinois Tool Works (ITW), is a leading manufacturer of chemical products and soldering tools for the electronics industry. Techspray formulates, blends, and packages a wide variety of chemicals and assorted support products for the electronics industry, heavy industry, and plant and equipment maintenance including degreasers, contact cleaners, flux removers, dusters, conformal coating, solder mask, water-based cleaners, desoldering wick, soldering tips, and the popular Plato shear cutters. More information can be found at www.techspray.com.

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