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Use of 1-bromopropane (N-propyl bromide) in dry cleaning is rare and rapidly declining toward obsolescence

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Abstract

Ten years ago, the Halogenated Solvents Industry Alliance (HSIA) and the New York State Department of Environmental Conservation petitioned the US Environmental Protection Agency (USEPA) to classify 1-bromopropane (1-BP) as a hazardous air pollutant (HAP), the first such classification of a chemical since 1990. The USEPA plans to classify 1-BP as a HAP. One of the putative exposures supporting HAP classification is 1-BP-based dry cleaning solvents. Only two 1-BP-based dry cleaning solvents have ever been marketed domestically, i.e. the dominant market share product DrySolv® (DrySolv) and less commonly used Fabrisolv™ XL (Fabrisolv). The use of 1-BP-based dry cleaning solvents has been declining for several years. Fabrisolv is no longer marketed as a dry cleaning agent. In the first half of 2020, less than 1,600 pounds of DrySolv have been sold for the remaining six dedicated dry cleaning machines still in operation in the United States. It is expected that the number of dedicated DrySolv dry cleaning machines in operation will be reduced to three by the end of 2020. In addition, no 1-BP-based spot cleaner has ever been marketed in the United States. USEPA currently classifies 187 chemicals as HAPs, with a subset of 30 HAPS classified as urban air toxics. Dry cleaning is considered to be one of the 68 "area sources" that contribute to sub-classification of 1-BP as an urban air toxic. In the near future, 1-BP-based products will not be employed in the dry cleaning industry.

Keywords

1-Bromopropane, dry cleaning, declining use, dry cleaning machines, spot cleaners

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Introduction

The Clean Air Act has identified 187 chemicals or mixtures as Hazardous Air Pollutants (HAPs).[1] Recently, the United States Environmental Protection Agency (EPA) granted petitions to add 1-bromopropane to the Hazardous Air Pollutants list.[2] This recent action by EPA represents the first such addition to the HAP list since 1990.[3] A chemical is added to the HAP list based upon the petition providing "adequate data for EPA to determine that emissions, ambient concentrations, bioaccumulation, or deposition of the substance are known to cause or may reasonably be anticipated to cause adverse effects to human health or the environment." In contrast with industrial uses considered as non-emissive, e.g. vapor degreasing machines for the cleaning of metal parts,[4] the historical use of 1-bromopropane in selected dry cleaning operations provided an opportunity for small levels of exposure to the general public. In this paper, we demonstrate that 1-bromopropane exposures from dry cleaning have declined to regulatory insignificance and are headed toward extinction. The decline in 1-bromopropane exposure from dry cleaning has been driven by economic considerations with little to no expectation of a reversal in incentives. Therefore, the consideration of dry cleaning as a rationale for classification of 1-bromopropane as a HAP is unnecessary for the

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Table 1. Properties and uses of 1-bromopropane.

Synonym	n-Propyl bromide (1-BP)	Reference(s)
Chemical Abstracts Service Registry Number	106-94-5	4
Formula	C_3H_7Br	4
Molecular Weight	122.99 g/mol	4
Solubility in Water	0.25 g/100 mL @20°C	4
Octanol-water Partition Coefficient	log $P_{ow} = 2.1$	4, 10
Vapor Pressure	143 mmHg	4, 9
Globally Harmonized System Hazard Classification	H225 (Category 2)—flammable liquids	
	H315 (Category 2)—skin irritation	
	H319 (Category 2A)—eye irritation	
	H335/H336 (Category 3)—specific target organ toxicity/single exposure to respiratory system or central nervous system	4
	H360FD (Category 1B)—fertility (F) and developmental toxicities (D)	
	H373 (Category 2)—specific target organ toxicity via prolonged or repeated exposure	
Emissive Uses	Solvent for aerosol-applied adhesives used in foam cushion manufacturing	
	Dry cleaning	4–8
Non-Emissive Uses	Cleaning optics, electronics and metals	
	Solvent sprays for aircraft maintenance	4–8
	Asphalt production	
	Synthetic fiber manufacturing	

Table 2. Results from NTP 2-year inhalation study on 1-bromopropane.

Species/Sex	Skin Neoplasms	Large Intestine Neoplasms	Lung Neoplasms	Reference
Male Mice	Negative	Negative	Negative	6
Female Mice	Negative	Negative	Positive	6
Male Rats	Positive	Positive	Negative	6
Female Rats	Negative	Positive	Negative	6

Negative = Non-significant vs. control.
Positive = Significant increase vs. control.

protection of public health, and falsely implies a level of community exposure no longer extant.

1-Bromopropane (1-BP) is an important industrial chemical with a wide variety of industrial applications including cleaning optics, electronics, and metal parts.[5–8] The chemical is volatile with a vapor pressure of 143 mmHg[4,9] and somewhat hydrophobic with a log P = 2.1. The solubility of 1-BP in water is 0.25 g/100 mL at 20°C.[4,10] 1-BP displays a number of toxicities to mammals including eye and skin irritation, reproductive toxicity, neurotoxicity, and tumorigenicity.[11]

A summary of the physical properties, globally harmonized system hazards and open (emissive) and closed (non-emissive) uses of 1-BP is shown in Table 1. The National Toxicology Program (NTP) has classified 1-BP as "reasonably anticipated to be a human carcinogen" based on induction of tumors in rats and mice in a 2-year inhalation study[6,7] (Table 2). In the NTP inhalation study, lung neoplasms were only seen in female mice and were not found in male mice, female rats, or male rats. This pattern of lung tumor induction in a rodent inhalation bioassay has been challenged as not relevant to the risk of development of lung tumors in humans.[12,13]

As noted above, EPA plans to add 1-BP to its list of HAPs at a time not yet clarified. The uniqueness of this intention is demonstrated by 1-BP being the first chemical added to the HAP list since the Clean Air Act (CAA) was amended in 1990.[3] HAPs, also known as toxic air pollutants or air toxics, are known or suspected carcinogens, reproductive or developmental toxicants, or cause harm to the environment.[3] The impetus behind this upcoming EPA action was a petition filed almost 10 years ago by the Halogenated Solvents Industry Alliance (HSIA), a trade group representing manufacturers and distributors of chlorinated solvents (including tetrachloroethylene (PERC) and trichloroethylene (TCE)) which are direct business competitors of the 1-BP solvent manufacturers, and the New York State Department of Environmental Conservation. [The filing by a New York agency is notable in that the major 1-BP-based dry cleaning solvent, i.e. DrySolv, was never used in New York. In

addition, it is also unlikely that the only other 1-BP-based dry cleaning solvent, i.e. Fabrisolv, was ever used either, as New York requires pre-approval of dry cleaning solvents, and no 1-BP-based dry cleaning solvent was ever approved.] The two petitioners alleged that air emissions of 1-BP cause adverse effects to human health. In addition, HSIA argued that 1-BP is marketed as an alternative to the solvent trichloroethylene.[3] [Note: Fabrisolv is no longer marketed as a dry cleaning agent].

The allegation regarding adverse human health effects from state-of-the-art dry cleaning machines has recently been addressed in an exposure study conducted by Enviro Tech International (ETI). Renzacci dry cleaning machines were found to be run, at most, three to four times per week. At the end of a run cycle, the highest amount of 1-bromopropane found remaining in the drum was 300 ppm. Given the air volume of the small dry cleaning store where the exposure study was conducted, volatilization of the entire 300 ppm 1-bromopropane residue only resulted in a transient room air concentration of 1 ppm or less. This maximal exposure level of 1 ppm was quickly dissipated to below the 0.1 ppm American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV) from normal room ventilation.[4]

Currently, there are 187 HAPs on the USEPA's list.[14] From the list of 187 HAPs, the USEPA has identified a subset of 30 chemicals posing the greatest potential health threat in urban areas. The USEPA refers to this subset of HAPs as the 30 urban air toxics. These 30 chemicals are emitted from what the USEPA terms an "area source." In contrast with ambient air pollution emitted by ubiquitous moving sources like automobiles, area sources include smaller stationary sources of air pollution emitting less than 10 tons per year of a single air toxic, or <25 tons per year of a combination of air toxics.[14] The USEPA has identified 68 area source categories representing 90% of the combined emissions from the 30 urban air toxics.[14] Dry cleaning facilities are listed among the 68 source categories for urban air toxics.[14]

History of the use of 1-bromopropane in the dry cleaning industry

The first 1-BP-based dry cleaning solvent to achieve commercial product status was "DrySolv," which Enviro Tech International, Inc. (Melrose Park, Illinois) (ETI) entered into the USA market in 2006. Several years later, a second 1-BP-based dry cleaning solvent called Fabrisolv was also marketed by Polysystems USA (Bayonne, New Jersey). DrySolv and Fabrisolv were the only 1-BP-based solvents ever used in the domestic dry cleaning industry. The major supplier of 1-BP-based dry cleaning solvents was ETI.[15,16]

Drysolv contains at least 87% 1-BP and a stabilizer package that is composed of <0.6% nitromethane, 1.2% 1,2-butylene oxide and other specific components and amounts of components considered trade secret.[17]

DrySolv was conceived and marketed as a relatively small volume niche product intended to serve as a transition away from perchloroethylene (PERC) as a solvent while still using existing dry cleaning machines. Only third-generation PERC machines were converted; second-generation machines were already well beyond their useful life and no cost effective benefit was to be had with newer fourth-generation PERC machines.[15,16]

The direct cost of converting a third-generation PERC dry cleaning machine to Drysolv was 5 to 10 thousand dollars. However, required modifications of boilers and pipes raised the actual cost considerably higher. Nonetheless, the cost of converting a PERC dry cleaning machine to a 1-BP-based solvent was normally less than one-third the purchase price of a new machine regardless of solvent type. In many cases, converting an existing third-generation PERC machine represented the only option that allowed small, individual dry cleaners to stay in business until a new dry cleaning machine was affordable.[15,16]

Between 2006 and 2011, ETI converted 47 third-generation PERC machines in the USA to using DrySolv. During that same 6-year time period, less than half as many PERC machines were converted to using Fabrisolv. In total, not more than 75 PERC dry cleaning machines in the USA were known to have been converted to using any available 1-BP-based solvent.[15,16]

The third-generation PERC dry cleaning machines that were modified were already well into their expected 15-year lifespans. Most of the approximately 75 PERC machines converted to 1-BP solvents only remained in use for an average of 2 years following conversion. The majority of the operators went out of business, with the remainder purchasing new dry cleaning machines. In 2011, ETI ceased converting PERC machines to Drysolv, and no additional PERC machines were converted after 2012.[15,16]

In 2010, equipment manufacturers introduced new dry cleaning machines specifically designed to use 1-BP-based solvents, and DrySolv in particular. High cost of the machine ($40,000–$52,000) and additional installation costs ($5,000–$15,0000) resulted in less than 25 dedicated 1-BP dry cleaning machines being put into service in the entire dry cleaning industry from 2010–2015. In 2015, ETI no longer accepted new DrySolv customers regardless of the equipment type employed. Since June of 2015, no new dedicated dry cleaning machines of any kind using 1-BP were put into service.[15,16]

By 2016, only 9 converted PERC, and 19 dedicated 1-BP dry cleaning machines were known to be in service. After September 1, 2016, ETI stopped selling DrySolv to dry cleaners using converted PERC machines. By this time, all converted PERC dry cleaning machines in the USA had aged beyond their working lifespans, with only a limited number of machines still using stockpiled DrySolv. By mid-2017, no converted PERC dry cleaning machines were thought to be in service leaving all DrySolv customers using machines specifically manufactured for 1-BP solvent use which met strict EU machine regulations.[16] Contemporaneous with the decline in the number of active converted PERC machines, the number of dedicated DrySolv machines was also

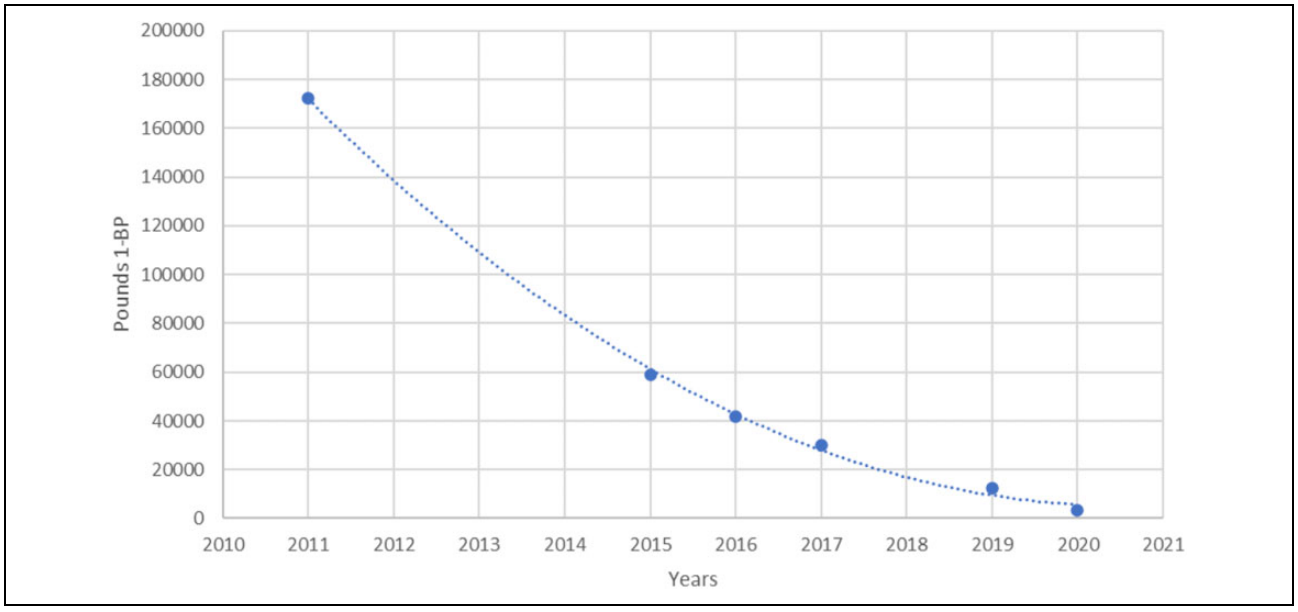

Figure 1. Estimated pounds of 1-BP used in dry cleaning by year (2011–2020). Data from References 15 and 16.

declining from its 2016 level of 19 active machines to 12 active dedicated DrySolv machines in mid-2017.

In 2015, less than 50,000 pounds of 1-BP-based solvents were used in the dry cleaning. By 2016, usage in dry cleaning had declined to just over 40,000 pounds. Usage in dry cleaning for 2017 was under 30,000 pounds and under 18,0000 pounds for 2018 (ETI 2019).[16] By the end of 2019, usage had fallen to under 12,500 pounds. Business records from ETI accrued after ETI filed its comments to USEPA indicated that, in the first half of 2020, less than 1,600 pounds have been sold for the remaining six dedicated DrySolv machines still in operation in the United States. It is expected that the number of dedicated machines in operation will be reduced by half by the end of 2020.[15,16]

Figure 1 illustrates the rapid decline in the use of 1-BP in the dry cleaning industry. The data used to construct this figure are from ETI sales data (described in the text) and the estimated number of dry cleaning machines using 1-BP per year (also described in text). The estimated amount of 1-BP used per year per dry cleaning machine is ~2300 pounds (~200 gallon 1-BP/machine/year * 11.3 pounds/gallon). This value is based on the amount of PERC normally used in third-generation PERC machines (and is assumed to be identical to amount of 1-BP used in converted third-generation PERC machines) and amount of 1-BP used in dedicated 1-BP dry cleaning machines.[18,19] It is obvious from the precipitous drop in 1-BP usage per year that by 2025, or sooner, the use of 1-BP as a solvent for dry cleaning will be over.

In addition to the use of 1-BP-based solvents in dry cleaning machines, the USEPA has expressed concern over the possible use of DrySolv as a spotting agent.[20] [Some of this concern probably resulted from EPA staff Google searching safety data sheets (SDSs) that are not dispositive of a product's actual availability in the marketplace.] Although DrySolv spotting agents were developed, these products were never commercialized.[15,16] One lot of spotting agent spray cans using 3,500 pounds of 1-BP was manufactured in 2008, but this stock was disposed of by 2012 and never distributed.[15,16] Most other DrySolv-based spotting agents were never commercialized, and test samples were sent for destructive recycling in 2010. In contrast with the exposure scenarios presented by the USEPA wherein workers at dry cleaning establishments are exposed to 1-BP via use of spot cleaners, 1-BP-based spot cleaning products were and are not actually marketed in the US.[20]

USEPA's concern regarding putative future use of 1-BP in dry cleaning applications

In 2020, ETI is in the latter stages of phasing out all uses of 1-BP-based products for the dry cleaning industry. To our knowledge, no other company is offering a 1-BP-based dry cleaning solvent in the US market. No PERC-based dry cleaning machine has been converted since 2012. No new dry cleaning customer has been accepted by ETI since 2016.[15,16] New machines meet strict European Union standards for solvent emissions from dry cleaning machines, as they are all manufactured in Italy.[19] By the third quarter of 2019, only eight machines remained using DrySolv in the US.[15,16] As of June 2020, there are six establishments using DrySolv in the United States. As these six businesses switch out their current dry cleaning machines or cease business operations, use of 1-BP as a dry cleaning solvent will come to an end. As the average lifespan of a dry cleaning machine is approximately 15 years, all dedicated

DrySolv machines are expected to be at or near the end of their usage by 2025.

In contrast with the currently stated plans of the US manufacturers and distributors to discontinue providing 1-BP into the dry cleaning sector, the USEPA has speculated that future exposures to 1-BP from dry cleaning will persist because PERC-based dry cleaning machines can easily be converted to use of 1-BP-based solvents.[20] In actuality, conversions from PERC-based to 1-BP-based solvents were done using third-generation PERC machines, all of which are now far beyond their useable life and unable to be modified.[15,16] Additionally, there is no benefit to modifying a fourth-generation PERC machine as it is likely that the expense of doing so would be significantly more than the conversion of older PERC machines, making such a conversion economically prohibitive. In summary, any further conversion of PERC-based dry cleaning machines to 1-BP-based solvents is highly unlikely.[15,16] Finally, there is no manufacturer or current importer of 1-BP who allows the use of 1-BP in the dry cleaning industry.

Conclusions

By 2025, the six remaining dry cleaners with machines using 1-BP-based solvents are expected be out of use, thereby eliminating all dry cleaning uses of 1-BP-based solvents in the United States. There is no benefit to converting the latest generation of PERC-based dry cleaning machines to 1-BP-based machines. Thus, no commercial entity in the United States is planning to use 1-BP-based dry cleaning solvents in the future. In addition, no spot cleaners containing 1-BP were ever or are currently in use in the domestic dry cleaning industry. Deliberations by USEPA regarding the classification of 1-BP as a HAP should not consider potential exposures from dry cleaning as current exposures from the six remaining later technology machines are miniscule, and there are no plans for further use of 1-BP after 2025.

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