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Investigation of d-Limonene Use During Aircraft Maintenance Degreasing Operations

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Reported by Max Kiefer, Faye Bresler, Stan Salisbury, and Stephanie Pendergrass

Introduction

d-Limonene is a naturally occurring monoterpene with a lemonlike odor that is found in a variety of foods and beverages, especially fruits. d-Limonene has received widespread interest as an alternative industrial chemical for a variety of applications, including metal degreasing. Toxicological studies indicate that d-limonene may be a skin irritant, and there have been reports of allergic contact dermatitis resulting from exposure to d-limonene–containing materials. The National Toxicology Program determined there was clear evidence of carcinogenic activity (kidney) in male rats under the conditions of a 2-year gavage study. The carcinogenic activity, however, is unique to a species- and sex-specific protein in male rats and should not be extrapolated to humans.

In response to a health hazard evaluation request, the National Institute for Occupational Safety and Health (NIOSH) conducted an industrial hygiene and medical assessment at aircraft maintenance facilities where d-limonene–based degreasing solvents were used. An air sampling method for d-limonene was determined, and personal and area air sampling for d-limonene and other constituents of the degreasing solvent (butyl carbitol, diethanolamine, ethanolamine) was conducted. Personal protective equipment (PPE) and other controls were evaluated. Potential adverse health effects were assessed by reviewing employee records and conducting confidential medical interviews with workers using the d-limonene–based products.

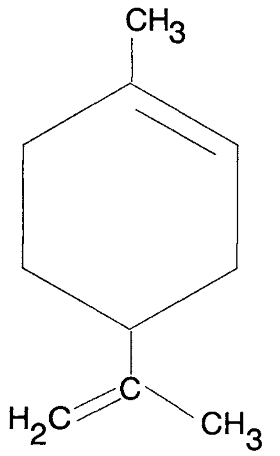
Personal exposure levels to d-limonene ranged from 0.1 ppm to 114.3 ppm, depending on the activity assessed. A 35-minute sample obtained from a worker using a d-limonene–based aerosol cleaner showed a concentration of 5.2 ppm. All butyl carbitol concentrations were below the analytical limit of quantification, and 7 out of 13 samples were below the limit of detection. Ethanolamine was detected in one area sample; a concentration of 0.1 ppm was found adjacent to one of the degreasing tanks. The medical evaluation identified 2 of 14 employees with potential allergic contact dermatitis (self-reported) associated with the use of the d-limonene–based degreasing solvent. Recommendations regarding personal protective equipment practices, targeting surveillance efforts to skin disorders, and activity-specific controls were made.

Background: d-Limonene

d-Limonene (Figure 1) (CAS #: 5989-27-5) is one of two chemical forms (stereoisomer) of limonene and is a member of a large class of natural hydrocarbons referred to as terpenes (d-limonene is a monoterpene).[1] The other form of limonene is called l-limonene and a mixture of the two isomers is known as dipentene. d-Limonene is listed on the Food and Drug Administration's Generally Recognized as Safe list, is widely used as a flavor and fragrance additive in perfumes, soaps, foods, chewing gum, and beverages, and is the most widely distributed monoterpene.[2-6]

The use of d-limonene, and other terpene-based materials, is increasing as stratospheric ozone depleting chemicals such as chlorofluorocarbons (CFCs) are phased out, and pressure is increased to reduce occupational exposure and environmental re-

d-LIMONENE



CAS#: 5989-27-5

MW: 136

Formula: $C_{10}H_{16}$

VP: 1.6 mm Hg

BP: 175-176° C

Synonyms: Cyclohexene, 4-isopropenyl-1-methyl; cinene; carvene

FIGURE 1. Structural formula for d-limonene.

leases of chlorinated solvents.[7,8] In 1990–1991, Florida produced over 15 million tons of d-limonene.[9] The principal use is not as a solvent, however, as the majority of d-limonene produced is used in the flavor and fragrance industry.[10] The bulk of naturally derived d-limonene is obtained from the high-vacuum fractional distillation and/or extraction of citrus oils (citrus oils are obtained from discarded lemon and orange pulp and peels) and there are an estimated 20 to 30 manufacturers of d-limonene.[3,8,10,11]

Terpene compounds, including d-limonene, are noncorrosive, low-foaming, relatively nonreactive, and low temperature-effective materials with a high solvency of greases and oils.[8] However, they are not water soluble, and surfactant must be added prior to addition to water. Although d-limonene is an attractive potential substitute for many degreasing operations, some process changes do require significant capital investments to make the necessary equipment modifications. A major reason for the equipment changes is because terpenes are combustible and have low odor thresholds; the odor threshold of d-limonene is reported to be as low as 1 part per billion (ppb).[8,12]

Occupational Exposure/Health Hazard Information

Occupational exposure recommendations or limits have not been established for d-limonene by NIOSH, the Occupational Safety and Health Administration (OSHA) or the American Conference of Governmental Industrial Hygienists (ACGIH). Recently, however, the American Industrial Hygiene Association (AIHA) Workplace Environment Exposure Level Committee recommended a time-weighted average (TWA) exposure limit of 30 parts per million (ppm) for d-limonene.[13] This limit was established to protect against potential adverse liver affects. Occupational exposure monitoring data during both the manufacturing and use of this chemical are lacking. Additionally, although numerous toxicological investigations of this chemical have been conducted, health effect studies concerning the industrial use of d-limonene are not available. However, Environmental Protection Agency (EPA)-sponsored studies have been conducted to provide qualitative and engineering estimates of the potential for exposure (dermal and inhalation) to d-limonene in industrial operations. These assessments were conducted as part of an extensive evaluation of terpene-based cleaners as potential replacements of CFCs and other stratospheric ozone-depleting chemicals.[7,8] Inhalation exposures were estimated based on monitoring data from similar processes with different chemicals (e.g., chlorinated solvents) and adjusting for vapor pressure differences. Another technique used a vapor generation rate and box dispersion model to estimate d-limonene concentrations. Dermal exposures were estimated based on the skin surface area exposed and the length of exposure.

These estimates suggest that employees handling parts during cold immersion cleaning (tank at ambient temperature) with a 20 percent d-limonene–based solvent would experience TWA inhalation exposures of 0.07–0.79 ppm.[8] The modeling also showed that workers formulating a 90 percent d-limonene solution would be exposed to TWA concentrations of 13–144 ppm during dedrumming or sampling. The range is wide because of the assumptions and uncertainty associated with estimating exposures using surrogate chemicals or modeling.

The human health effects most commonly reported in association with limonene use are dermal drying and allergic contact sensitization. d-Limonene is an irritant that causes both irritation and drying of the skin.[14] Limonene is also a well-known sensitizer, causing allergic contact dermatitis among several occupational groups, including food handlers (citrus peel oil), painters (turpentine), and carpenters (lemon wood).[14–18] There is conflicting evidence that limonene functions as a sensitizing quencher. Cinnamic aldehyde, a derivative of cinnamon oil and a compound used extensively by the perfume industry, is a contact sensitizer. Reports that limonene inhibits cinnamic aldehyde sensitization have led to the use of "prequenched" compounds—cinnamic aldehyde to which limonene has been added.[19] The ability of limonene to breach the dermal barrier is also recognized. Limonene was reported to be well absorbed dermally in animals, with maximal blood concentrations reached in 10 minutes.[20,21]

Animal studies with male rats raised concerns that limonene was carcinogenic. Male F344/N rats which were orally dosed had an increased occurrence of uncommon tubular cell adenomas and adenocarcinomas of the kidney. However, the biological relevance of these findings to humans has not been established. Similar dosing of female F344/N rats, and B6C3F$_1$ mice of both sexes, did not result in an analogous increase in kidney lesions.[3] The male rat-specific urinary protein ($\alpha_{2\mu}$-globulin) is not produced in the unique strain of rats known as NCI-Black-Reiter (NBR) rats. In an experiment, male F344 and male NBR rats were orally dosed with d-limonene. The F344 male rats developed an increase in hyaline droplets, as well as renal adenomas. No increase in tumors or preneoplastic lesions were observed in the male NBR rats. It was concluded that the species- and sex-specific protein ($\alpha_{2\mu}$-globulin) was necessary for the development of these cytotoxic and carcinogenic responses.[22] Given the species- and sex-specificity of $\alpha_{2\mu}$-globulin to the male rat kidney, the extrapolation of d-limonene rat toxicity data to humans and other species is not appropriate.[22–24]

Materials Evaluated

The degreasing agent evaluated was a water soluble solvent containing 20 percent–30 percent d-limonene, 1 percent–5 percent monoethanolamine and diethanolamine, and 5 percent–10 percent butyl carbitol. The material was a clear amber liquid with a citrus odor and a pH of 11.2. The spray cleaner evaluated was purchased and dispensed from hand-held aerosol spray cans. The spray cleaner, intended for industrial use only as a general purpose cleaner, contains 70 percent–80 percent d-limonene and uses a propane propellant.

Facility Descriptions

Shop 1

Shop 1 fabricates aluminum, stainless steel, and titanium tube assemblies from $\frac{1}{8}$ to $4\frac{1}{2}$ inches in diameter. The shop is located within a very large warehouse adjacent to other maintenance, fabrication, and painting shops. Tubing is cleaned, by soaking only, with the d-limonene–based cleaner at ambient temperature in an open and unvented 100-gallon tank for 10–30 minutes and then rinsed in an adjacent tank of hot water. Chemical usage is about 55 gallons per month. A pneumatic pump is used to transfer solvent from the drum to the degreasing tank. Chemical loss is through evaporation, dragout during removal of parts, or residual loss from a rotating skimmer that is mounted in the top of the tank to remove grease and other impurities from the surface of the tank. There is no lid or cover for the tank and it is open to the shop environment at all times. Twelve employees work in the shop and the tank is used about 5 hours/day, although the majority of this time is unattended soaking of parts. PPE consists of rubber gloves and safety glasses. Neoprene gloves are also occasionally used. The aerosol cleaner is used approximately 10 minutes per day to clean table tops, equipment, and tubing. Gloves are not typically worn when using the aerosol spray cleaner. No other chemicals are used in this shop.

Shop 2

Shop 2 is a small (3500 ft^2), single story (sloped roof 12′–20′) building that provides aircraft tire and wheel maintenance services. The d-limonene–based cleaner has been used in the shop to clean aircraft wheel hubs (magnesium/aluminum) since 1988. A 60-gallon unvented tank with a lid contains the cleaning solvent. The wheel hubs are soaked for approximately 5 minutes in a degreasing solvent/water mixture (1:1) at ambient temperature. Cleaning is very labor intensive and, after soaking, the hubs are vigorously brushed while still in the tank. The hubs are then manually lifted out of the tank where they are further polished and dried by a co-worker. Cleaning wheel hubs requires two workers and is typically conducted in a batch process; that is, cleaning is not conducted until at least five or six hubs accumulate, and then they are all completed at one time. Cleaning wheel hubs with the d-limonene degreasing agent entails approximately 1–2 hours/week.

TABLE I. Shops 1 and 2 Air Sampling Results: Limonene, MEK, Other VOCs

Task Monitored and Location	Sample #	Sample Time (min)	Contaminants Sampled	Concentration ppm[A]	Concentration mg/m³ [B]
Area sample adjacent degreasing tank, Shop 1	L-A1	07:43-11:34 (231)	Limonene	0.45	2.51
			MEK[C]	2.15	6.33
			Other VOCs		0.48
	L-A1A	11:37-15:15 (218)	Limonene	3.56	19.79
			MEK	0.91	2.69
			Other VOCs		0.27
Area sample behind hot-water rinse tank, Shop 1	L-A2	07:48-11:43 (235)	Limonene	2.85	15.85
			MEK	1.85	4.66
			Other VOCs		0.93
	L-A2A	11:45-15:16 (211)	Limonene	5.82	32.35
			MEK	0.72	2.11
			Other VOCs		1.05
Area sample center of Shop 1, 25 ft from degreasing tank	L-A3	07:53-15:15 (442)	Limonene	0.14	0.77
			MEK	0.98	2.89
			Other VOCs		0.33
Area sample left side of Shop 1, 25 ft from degreasing tank	L-A4	07:54-15:15 (441)	Limonene	0.10	0.53
			MEK	0.93	2.73
			Other VOCs		0.27
Personal sample metal tube maker, Shop 1	L-P1	08:09-15:24 (435)	Limonene	0.26	1.43
			MEK	0.77	2.28
			Other VOCs		0.18
Personal sample metal tube maker, Shop 1	L-P2	08:47-11:30 11:48-15:24 (379)	Limonene	0.14	0.78
			MEK	0.82	2.43
			Other VOCs		0.49
Personal sample metal tube maker, Shop 1	L-P3	08:53-15:24 (391)	Limonene	0.15	0.85
			MEK	0.76	2.25
			Other VOCs		0.45
Personal sample sheet metal mechanic Shop 1	L-P4	08:39-11:29 12:11-15:24 (363)	Limonene	0.77	4.28
			MEK	0.85	2.50
			Other VOCs		0.50
Personal sample cleaning with limonene-based aerosol, Shop 1	L-P5	08:32-09:07 (35)	Limonene	5.20	29.00
			MEK	1.47	4.33
			Other VOCs		0.58
Personal sample transfer of solvent from drum to tank, Shop 1	L-ST1	13:09-13:32 (23)	Limonene	0.63	3.52
			MEK	0.77	2.26
			Other VOCs		ND[D]
Area sample adjacent degreasing tank, Shop 2	L-A5	09:54-11:05 (70)	Limonene	11.58	64.4
			MEK	ND	ND
			Other VOCs		4.43
Personal sample cleaning wheel hubs (four total) in degreasing tank, Shop 2	L-P6	09:57-10:56 (59)	Limonene	114.30	635.70
			MEK	ND	ND
			Other VOCs		37.56
Personal sample final polish and dry of wheel hubs, Shop 2	L-P7	09:59-10:59 (60)	Limonene	14.63	81.39
			MEK	ND	ND
			Other VOCs		4.35

[A]ppm = parts of gas or vapor per million parts of air.
[B]mg/m³ = milligrams of contaminent per cubic meter of air.
[C]Reported results for MEK should be considered estimated minimum concentrations.
[D]ND = none detected (level of detection = 0.5 μg per sample for VOCs, 1 μg for MEK, and 0.5 μg for limonene).

The shop is air-conditioned and has a comfort fan for employees to use at their discretion. Workers wear rubber gloves, rubber aprons, and face-shields when the tank is in use. Respirators are not required or used when working at the degreasing tank. The tank is emptied two or three times a year by manually pumping the waste solvent into a drum.

Industrial Hygiene Methodology

Bulk Sampling (Liquid and Air)

Two bulk liquid samples (spent and unused solvent) were obtained from

TABLE II. Shops 1 and 2 Air Sampling Results: Butyl Carbitol

Task Monitored and Location	Sample #	Sample Time (min)	Concentration ppm[A]	Concentration mg/m³ [B]
Area sample adjacent degreasing tank, Shop 1	BC-A1	07:43-11:34 (231)	(0.06)[C]	(0.43)
	BC-A1A	11:37-15:15 (218)	(0.04)	(0.23)
Area sample behind hot-water rinse tank, Shop 1	BC-A2	07:48-11:43 (235)	<0.06[D]	<0.41
	BC-A2A	11:45-15:16 (211)	(0.14)	(0.92)
Area sample center of Shop 1, 25 ft from degreasing tank	BC-A3	07:53-15:15 (442)	<0.02	<0.11
Area sample left side of Shop 1, 25 ft from degreasing tank	BC-A4	07:54-15:15 (441)	<0.03	<0.22
Personal sample metal tube maker, Shop 1	BC-P1	08:09-15:24 (435)	(0.07)	(0.47)
Personal sample metal tube maker, Shop 1	BC-P2	08:47-11:30 11:48-15:24 (379)	<0.02	<0.12
Personal sample metal tube maker, Shop 1	BC-P3	08:53-15:24 (391)	<0.02	<0.15
Personal sample sheet metal mechanic Shop 1	BC-P4	08:39-11:29 12:11-15:24 (363)	<0.01	<0.07
Area sample adjacent degreasing tank, Shop 2	BC-A5	09:54-11:05 (70)	<0.14	<0.90
Personal sample cleaning wheel hubs (four total) in degreasing tank, Shop 2	BC-P6	09:57-10:56 (59)	(0.27)	(1.76)
Personal sample final polish and dry of wheel hubs, Shop 2	BC-P7	09:59-10:59 (60)	(0.12)	(0.79)

[A]ppm = parts of gas or vapor per million parts of air.
[B]mg/m³ = milligrams of contaminent per cubic meter of air.
[C]() = concentration detected was between the analytical level of detection and the level of quantification.
[D]< = less than (the contaminent detected); the concentration listed is the analytical level of detection. The analytical level of detection for butyl carbitol was 5 μg per sample and the level of quantification was 20 μg per sample.

Shop 1 for qualitative analysis by gas chromatography with mass spectrometry detection (GC-MSD). The samples were collected to verify major components, determine if any unexpected compounds were present that may impact the air sampling, and compare the results of the two samples. The samples, collected in glass vials with Teflon liners, were shipped separate from the air samples to the NIOSH laboratory for analysis.

Two bulk air samples were collected directly over the degreasing tanks in Shops 1 and 2 and submitted to the NIOSH laboratory for qualitative analysis of volatile organic compounds (VOCs). The samples were collected using constant-volume low-flow sampling pumps with standard charcoal tubes as the collection media. The samples were desorbed in 1 ml of carbon disulfide and screened by gas chromatography with a flame-ionization detector (GC-FID). Both samples were further analyzed by GC-MSD to identify contaminants.

The samples collected for d-limonene and butyl carbitol were placed on hold pending the results of the bulk sample analyses. This was done to allow for the possible quantitation of unexpected compounds which may be identified in the bulk samples, as well as allow for necessary analytical adjustments if potentially interfering compounds were detected.

d-Limonene Air Sampling

Fifteen integrated air samples for d-limonene were collected using constant-volume low-flow sampling pumps. Flow rates of 50–200 cc/min were used to collect the samples. Sampling time ranged from 15 minutes to 7 hours. Standard charcoal tubes (100 mg front section/50 mg backup) were used to collect the d-limonene. Two field blanks were submitted with the samples. After sample collection, each charcoal tube section was desorbed in 1 ml of carbon disulfide (CS_2) for a minimum of 30 minutes. Following desorption, each section was analyzed by GC-FID using a 30-m Stabilwax fused silica capillary column. Using the splitless mode, 1-μl sample aliquots were analyzed.

The analytical method used for d-limonene sampling and analysis was determined by the NIOSH Measurement Research Support Branch. The method is not specific to d-limonene but determines total limonene (both the d and l isomer). Analytical recovery and storage stability studies were conducted to verify the validity of the method. Charcoal tubes were spiked at three levels (20 μg, 60 μg, 100 μg), six tubes per level, and desorption efficiency was greater than 92 percent at each level, with a standard deviation of less than 2 percent. Tubes were analyzed at 7, 14, and 30 days to assess storage stability. Analysis after 30 days showed a desorption efficiency of 93 percent, indicating stability at these levels for at least 30 days. Mass spectrometry was used to confirm that none of the terpene analytes decomposed during storage on the charcoal tubes or in CS_2.

Butyl Carbitol Air Sampling

Thirteen integrated air samples for butyl carbitol were collected by the same monitoring methodology used for the d-limonene samples. Standard charcoal tubes (100 mg front section/50 mg backup) were used to collect the butyl carbitol. Two field blanks were submitted with the samples. Although no specific NIOSH analytical method exists for butyl carbitol, this chemical had previously been determined using NIOSH Method 1403 (Alcohols IV), and this method was followed to collect the samples.[25] After sample collection, each charcoal tube section was desorbed in 1 ml of 5 percent methanol in dichloromethane for a minimum of 30 minutes and then analyzed by GC-FID. A method validation check was conducted and desorption efficiency determined at three levels, six samples per level. An average desorption efficiency of 86.3 percent (range: 84.4%–87.8%) was obtained and applied to all results. Six spiked tubes were analyzed over 30 days with a desorption efficiency of 88.4 percent, indicating stability for at least 30 days at this level.

Monoethanolamine, Diethanolamine Air Sampling

Five integrated area air samples were collected for monoethanolamine and diethanolamine in Shops 1 and 2 using constant-flow air sampling pumps. Flow rates of 0.7 to 1.0 L/min were used to collect the samples. Sample times ranged from 1 to 6 hours. Sampling and analysis was conducted according to NIOSH Method 3509.[25] Standard impingers containing 15 ml of 2 mM hexanesulfonic acid were used as the collection medium. After the samples were collected, deionized water was added to adjust the volume back to 15 ml. The samples were transferred to polyethylene scintillation vials and shipped to the NIOSH contract laboratory for analysis by ion chromatography. Two blanks were submitted with the samples.

Medical Evaluation Methodology

Fourteen employees with direct, discrete, limonene exposure were identified through the industrial hygiene investigation. Of these, 12 employees work in Shop 1, and 2 employees work in Shop 2. Records of work-related injuries and illness are maintained in employee medical charts and are also summarized in a log system similar to the OSHA 200 log. When an employee presents to a medical clinic for care of a work-related illness or injury, the employee completes a form describing the nature of the illness or injury. Information from these forms is abstracted and computerized, allowing chronologic and shop-specific review. Additionally, the form prompts follow-up by the Safety and/or Medical departments. The computer logs from Shops 1 and 2 for the previous 2 years were reviewed.

Medical records are located at the facility occupational health clinic. A chart review of all 14 employee medical records was conducted to identify work-related dermal symptoms, as well as work-related problems in general.

Confidential health interviews were conducted with all 14 employees. Information concerning the frequency and usage of limonene, and any associated dermal symptoms, was elicited. Additional information regarding workplace injuries was collected.

Results: Industrial Hygiene

Bulk Sampling

The two liquid solvent samples contained similar components and were consistent with the manufacturer's material safety data sheets. This analysis confirmed the compounds suspected to be present and did not identify any unforeseen contaminants in the degreasing solvent.

Bulk air sample LB-A5, obtained directly over the degreasing tank in Shop 1, showed that limonene and an unexpected compound, methyl ethyl ketone (MEK), were the major constituents. Other terpenes, butyl carbitol, toluene, and hexane were also detected on the sample. MEK was an unexpected contaminant, the samples collected for limonene quantitation were also analyzed for MEK. Because charcoal tubes are not the media of choice for MEK, and MEK will sometimes react on charcoal to produce a hydrolysis product, the MEK results should be considered minimum concentrations. The source of the MEK was thought to be from solvent use in an adjacent shop where maintenance is conducted on airplane bay doors.

Bulk air sample LB-A6 was obtained directly over the degreasing tank in Shop 2. This sample showed that limonene was the major constituent detected. Additionally, other terpenes, terpene derivatives, and alkyl benzenes were detected. No MEK was found on this sample.

d-Limonene/MEK Air Sampling

The results of the air samples collected for d-limonene are shown in Table I. As noted above, these samples were also analyzed for MEK. Because minor amounts of other VOCs were detected on all samples except one (sample #L-ST1), total VOCs were also quantitated using limonene as the standard. None of the compounds of interest were detected on the field blanks. All personnel sampled stated that their activities during the sampling period were consistent with those of a normal work day.

In Shop 1, the highest concentration of limonene detected was 5.82 ppm (#L-A2A) in an afternoon sample collected from behind the hot-water rinse tank adjacent to the d-limonene–containing degreasing tank. The highest concentration detected on a personal sample in Shop 1 was 5.20 ppm (#L-P5) from a 35-minute sample obtained during the use of the d-limonene–containing aerosol cleaner. A 23-minute personal sample obtained during the transfer of solvent from a drum to the tank, using an automatic pump with a hand-held hose, showed a concentration of 0.63 ppm (#L-ST1).

The highest MEK concentration detected in Shop 1 was 2.15 ppm (#L-A1A) in a morning sample collected from behind the hot-water rinse tank. The range of MEK concentrations detected (both personal and area) was 0.72 to 2.15. Although MEK can be readily detected by the sense of smell at low concentrations, and workers in Shop 169 were familiar with the odor of MEK from the adjacent shop, no MEK odors were detected during the sampling period. It is likely that the characteristic citrus odor of the limonene masked the MEK.

At two of the locations sampled in Shop 1, the charcoal tubes were changed during the lunch break to assess relative differences between morning and afternoon samples. The results suggest that MEK concentrations were relatively higher in the morning than the afternoon and that the converse was true for the limonene samples. One possible explanation is that MEK may have only been used in the adjacent shop in the morning and that the limonene levels increased in the afternoon as parts soaked with the d-limonene – based degreasing solvent were placed in the hot-water rinse tank, thus enhancing volatilization of the limonene.

In Shop 2, a limonene concentration of 114.30 ppm was measured on a 1-hour personal sample obtained from an employee cleaning aircraft hubs in the degreasing tank. As noted in the process description, this activity entails vigorous scrubbing of the wheel hubs while they are submerged in the degreasing solvent. The worker must lean over the tank to conduct this task, often within the envelope of the tank freeboard space. This close contact, continuous use, agitation of the solution, and lack of ventilation contributed to the higher concentration of limonene, relative to Shop 1. A 1-hour sample obtained from the worker assisting the employee cleaning the aircraft hubs showed a limonene concentration of 14.63 ppm. This worker would assist with the removal of wheel hubs from the degreasing tank and then use cloth rags to dry and polish the hubs. The worker conducted this task at a station approximately 6 feet away from the degreasing tank. The cloth rags were frequently changed and were disposed of in a 55-gallon drum that had been converted into a waste container.

No MEK was detected in the samples collected in Shop 2. Other VOCs were detected on both samples but were well below the concentration of limonene (e.g., 637.5 mg/m^3 limonene, 37.56 mg/m^3 other VOCs).

Butyl Carbitol Air Sampling (See Table II)

None of the samples detected butyl carbitol at a quantifiable level. On 6 of the 13 samples, the concentration of butyl carbitol was between the analytical level of detection and the level of quantification. This was not an unexpected result, as butyl carbitol comprises only 5 percent – 10 percent of the degreasing solvent and has a low vapor pressure (0.02 mm Hg).

Diethanolamine/Ethanolamine Air Sampling

Ethanolamine was only detected in one of the five area samples collected. A concentration of 0.10 ppm was found in the sample obtained from behind the degreasing tank in Shop 1. No diethanolamine was detected.

Personal Protective Equipment/ Workplace Observations

Safety glasses are required to be worn at all times in Shop 1, and some employees were observed to wear natural rubber gloves when working at the degreasing tank. Face shields and aprons are not worn by employees when working at the degreasing tank. Housekeeping throughout the shop was good. Quick drenching facilities (emergency eye wash) are located in the center of the shop. Comfort fans were operational during the monitoring. Smoking is not allowed in Shop 1.

Specific written procedures regarding the use of the degreasing tank, including personal protective equipment requirements, have been developed for Shop 2. The employee cleaning the wheel hubs at the degreasing tank wore heavy duty rubber gloves, rubber apron, and face shield. Eye protection was not worn. The employee wiping down the cleaned wheel hubs wore rubber gloves and eye protection. The shop has comfort fans and an air-conditioner. Smoking is not allowed in the shop, and an emergency eye wash station has been installed.

Results: Medical Evaluation

Record Review

Review of the illness and injury log maintained by the safety department did not uncover any symptomatology related to limonene use. Review of individual employee medical records confirmed the absence of reported limonene-related symptomatology.

Employee Interviews

All 14 employees confirmed that they currently or recently used the limonene dip tanks in their respective shops. Shop 1 workers reported 1–2 hours of direct exposure per week. In this shop, there was a maximal direct weekly exposure of 2 hours, with reported use of the dip tank varying from "rarely" to "daily." Indirect exposure due to time spent in the vicinity of the dip tanks was not quantified. In both shops, a pair of communal gloves was available for use with the dip tanks; all employees reported using them. Additionally, a face shield and splash apron were used in Shop 2.

Eleven employees in Shop 1 used a limonene-based spray-can cleanser to clean stationary equipment. Frequency of use ranged from once per month to three times per week. Gloves for this task were not specifically available and were never used.

Two workers (14%, 2/14) reported experiencing an allergic contact dermatitis response to limonene (a rash similar to that of poison ivy). One worker had used the dip tank without the benefit of gloves when the tank was newly installed and subsequently developed dermatitis. Since that time, he used the dip tank infrequently, always with gloves, and has not had a recurrence. The other worker experienced repeated episodes of dermatitis until his job rotation removed him from limonene exposure. Neither of these workers had reported for medical care.

Half of the workers (7/14) described an increase in skin dryness since limonene began to be used. None had reported this as a work-related symptom, and only a few used skin lotions to alleviate the dryness.

One individual in Shop 2 reported superficial skin sloughing on one hand after an hour of exposure to limonene due to a hole in his glove. He denied local itching or redness, or other skin or systemic symptoms.

In Shop 1, where the limonene tank is not covered, four workers (33%, 4/12) reported an increase in nasal or throat irritation since tank installation. Several noted an increase in symptoms when in the vicinity of the tank.

Conclusions

A limited industrial hygiene and medical evaluation was conducted to assess the industrial use of a d-limonene-based cleaning solvent at an aircraft maintenance facility. The environmental sampling results indicate relatively higher d-limonene concentrations than those predicted by previous modeling studies of cold-cleaning of parts.[8] However, neither tank was provided with local exhaust ventilation, and there was no cover for the degreasing tank in Shop 1. The potential health hazard associated with exposure to these levels of d-limonene, however, is not clear. From a general industry standpoint, additional industrial hygiene and medical data, as well as vigilant surveillance, is necessary as the use of d-limonene-based cleaning agents increases.

Personal exposures to d-limonene in Shop 2 were considerably greater than those found in Shop 1. This is an understandable finding as the work tasks are very different at the two shops. Again, the health implications of these exposure levels is not known.

Airborne concentrations of butyl carbitol, ethanolamine, and diethanolamine were very low and were often below the analytical level of detection. As both the vapor pressures and relative percentages of these materials in the degreasing solvent are low, this was not an unexpected result.

The potential exists for dermal exposure to d-limonene at both maintenance shops. The activities entailed close contact with the degreasing solvent, particularly at Shop 2. This is of particular concern as d-limonene is a skin irritant and sensitizer.[3]

Industrial surveillance programs may not identify issues such as d-limonene-related allergic contact dermatitis. This is because these problems may not be reported to supervisors for subsequent investigation, or workers may not associate these problems with the d-limonene-based materials. The potential for increasing use of d-limonene-based materials warrants the need to target surveillance at early identification of skin problems.

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