Evaluation of Exposure to Chemicals at a Polymer Additive Manufacturing Facility

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Contents

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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 request from the union at a polymer additive manufacturing facility. Employees were concerned about developing chronic health problems including lung disease, kidney disease, and cancer, from exposure to workplace chemicals.

What We Did

- We visited the facility in October 2012 and July 2013.
- We interviewed 10 current employees about health and workplace concerns.
- We observed work practices and reviewed safety data sheets.
- We sampled the air for several chemicals and dust.
- We took wipe samples on surfaces to look for aniline.
- We reviewed injury and illness logs, employee medical records, workers' compensation claims, prior sampling results, and facility policies and procedures.

What We Found

- Employees were overexposed to N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide when compared to the manufacturer's occupational exposure limit.
- Employees were not overexposed to chemicals we measured during the manufacture of N-tert-butylbenzothiazole-2-sulphenamide.
- Some employees had eye, nose, throat, and skin irritation at work that is consistent with exposure to workplace chemical irritants.
- Two former employees had chronic kidney disease. Medical records showed they had different types of disease affecting different parts of the kidney. Their kidney diseases were unlikely to be related to work exposures.
- Employees work with chemicals that are known or suspected causes of cancer.

We measured exposures to chemicals at a polymer additive manufacturing facility. Employees were overexposed to N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide compared to the manufacturer's occupational exposure limit. Employees worked with chemicals and agents known or suspected to cause cancer. Some employees had eye, nose, throat and skin irritation that was consistent with exposures to chemicals in the workplace. We recommended improving the local exhaust ventilation for packaging polymer additives, improving communication with employees, and training employees on the hazards of workplace chemical exposures.

What the Employer Can Do

- Improve local exhaust ventilation for bagging N'-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide and the primary polymer additive product.

- Follow the OSHA respiratory protection standard.
- Train employees on the use and care of gloves and other personal protective equipment.
- Encourage employees to report possible work-related symptoms to their supervisors and to seek medical follow-up.
- Improve communication between managers and employees regarding responses to employee safety and health concerns.
- Notify employees of the potential danger to their health if they are working with known or suspected cancer causing chemicals.

What Employees Can Do

- Follow all health and safety guidance. Learn about the chemicals you work with and how to handle and use them safely.
- Avoid getting chemicals on your skin. Wear gloves and protective clothing.
- Report health and safety concerns to your supervisor or health and safety manager.
- Wash your hands before eating, drinking, and smoking, and before and after using the bathroom.

Abbreviations

ACGIH®	American Conference of Governmental Industrial Hygienists
BEI®	Biological exposure index
BBTS	N-tert-Butylbenzothiazole-2-sulphenamide
CFR	Code of Federal Regulations
IARC	International Agency for Research on Cancer
mg/m^3	Milligrams per cubic meter
NaSH	Sodium and hydrogen sulfide
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational exposure limit
OSHA	Occupational Safety and Health Administration
OTOS	N-oxydiethylenethiocarbamyl-N’-oxydiethylenesulfenamide
PEL	Permissible exposure limit
ppb	Parts per billion
ppm	Parts per million
REL	Recommended exposure limit
STEL	Short-term exposure limit
TLV®	Threshold limit value
TWA	Time-weighted average
VOC	Volatile organic compound
WEEL™	Workplace environmental exposure level

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Introduction

The Health Hazard Evaluation Program received a request from the union at a polymer additive manufacturing facility. Employees were concerned about developing chronic health problems including lung disease, kidney disease, and cancer from exposure to chemicals at work. We visited the manufacturing facility in October 2012 and July 2013 to learn more about the health concerns and to assess potential exposures to toluene, benzene, methylene chloride, hydrogen sulfide, aniline, and dusts containing N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide (OTOS). We sent letters to union and management representatives in October 2012, March 2013, and September 2013 with preliminary findings and recommendations. In March 2013 and September 2013, we notified the employees by mail about their measured exposures.

Background

At the time of our visits, this facility produced polymer additives to improve the strength, flexibility, and heat resistance of rubber. The polymer additive and was also used as a corrosion inhibitor. The facility also generated hydrogen sulfide and a benzothiazole tar waste product used in asphalt manufacturing.

This facility was formerly a tire and rubber manufacturing facility. Some of the buildings were at least 75 years old. In 2006, a change in ownership resulted in management changes and employee turnover. The company employed about 60 people at the time of our site visits and manufactured polymer additives 24 hours per day, 7 days per week. We observed processes in the crude building (one of the oldest buildings at the site) and in the expansion building. Employees in these two buildings worked 12-hour shifts. Each shift worked as a team and generally consisted of five employees, three working in the crude building and two working in the expansion building. Over the course of a month each team's work schedule rotated between day shift and night shift.

Employees at this facility could be exposed to many chemicals throughout their workday. We collected samples for the most frequently used or produced chemicals (i.e., aniline, hydrogen sulfide, volatile organic compounds [VOCs]) and those of most concern to the employees (i.e., methylene chloride, OTOS).

Management personnel reported that employees were given an annual health assessment which included hearing, lung function, and blood and urine testing. The blood and urine testing looked for red and white blood cell and platelet levels, and chemical and metabolic changes in the body. The testing results can be an indicator of certain chemical effects such as abnormal liver and kidney function, gout, and anemia, among others.

Process Descriptions

Crude Production

In the crude building, liquid aniline, carbon disulfide, and molten sulfur were heated in reactors to produce a precursor material. Hydrogen sulfide, a byproduct, was passed through a scrubber, and then the cleaned air was vented to the outdoors. The precursor material was transferred to another reactor where sodium hydroxide was added, producing a liquid referred to as “crude.” The crude was purified with toluene, which was recovered and recycled. Crude was stored in tanks either to be sold as crude or further processed in the next stage. Twice per shift, employees pumped benzothiazole tars, byproducts of crude production, from storage tanks to heated containers for shipping by truck. One to two operators were responsible for the production of crude and spent the majority of their shift in the crude building or in the sodium and hydrogen sulfide (NaSH) control room.

Polymer Additive Production

In the expansion building, one of the final products was made in an enclosed reactor by mixing crude with sodium hypochlorite and tert-butyl amine. The liquid product from this reaction was filtered and dried in a fluidized bed dryer. The dried product, N-tert-butylbenzothiazole-2-sulphenamide (BBTS), was packaged as either a powder or, more commonly, as pellets. Employees packaged the pellets in 50-pound bags or large bulk super sacks. Any dust or pellets that were not the correct size were recovered and reprocessed. Liquid waste was processed in the on-site water treatment facility. Most of this operation was controlled remotely and therefore the expansion operator spent the majority of the workday in the control room. The bagger spent the majority of the workday on the first floor of the expansion building bagging the product.

N-Oxydiethylenethiocarbamyl-N’-oxydiethylenesulfenamide Production

The other product manufactured in the expansion building was OTOS, which was processed by combining methylene chloride, morpholine, bleach, and carbon disulfide in a reactor. The methylene chloride was recovered and reused for production of OTOS for the remainder of the OTOS production run. The liquid OTOS was dried and packaged either as a powder or pellets. The facility only produced this product two or three times per year. This operation was also controlled remotely by the expansion operator and bagged manually by one employee.

Methods

Our objectives for this evaluation were to:

1. Assess work-related health problems and concerns of employees.
2. Evaluate employees’ exposures to VOCs, aniline, and OTOS.

Our evaluation included (1) confidential employee interviews; (2) reviewing records and facility policies and procedures, (3) air sampling for VOCs, aniline, and OTOS, and (4) surface wipe sampling for aniline.

Employee Interviews

We interviewed all 10 of the employees who worked day shift in the crude (six employees) and expansion (four employees) buildings on October 23 and 24, 2012, five from one team and five from another. Some employees were trained to work in both buildings. We asked employees about demographic information, work exposure history, medical history, and history of work-related health problems. We also asked whether they had experienced eye, nose, throat, or skin symptoms related to irritant exposures during work in the month prior to our site visit and if they had any concerns about their work. We also spoke to two former employees.

Records Review

We reviewed Occupational Safety and Health Administration's (OSHA) Form 300 Logs of Work-Related Injuries and Illnesses and workers' compensation claims for years 2010, 2011, and 2012. We also reviewed air sampling records and the facility respiratory protection program, hazard communication program, weekly safety check sheets, and accident reporting procedures. We reviewed medical records of one current employee and two former employees. We reviewed medical surveillance records for the blood, urine, and lung function testing results of 1 former and 10 current employees, comparing their baseline results at hire with test results from years 2008–2013. We performed an extensive literature search for information regarding the predominant chemicals employees could be exposed to at work.

Air Sampling

Volatile Organic Compounds

In October 2012, we took area air samples on thermal desorption tubes to screen for VOCs. After sampling, the thermal desorption tubes were stored in a cooler and then qualitatively analyzed in the laboratory for VOCs according to the National Institute for Occupational Safety and Health (NIOSH) Method 2549 [NIOSH 2014]. We collected these samples in the crude building, at the crude and expansion operators' desks, and on each of the three floors of the expansion building near the pipeline and fluidized bed dryer. We identified tasks of greatest concern to the employees and collected the air samples for approximately 1 hour during those tasks. In the crude building these tasks included filling the reactors to manufacture crude, heating a batch of crude, pushing the batch of crude from the reactors to the holding tank, and dumping benzothiazole tars to a truck. In the expansion building these tasks included cleaning out the pipeline, running the fluidized bed dryer, and bagging BBTS. We also collected one background sample in the conference room. At the same time, we collected area air samples on charcoal tubes to quantitate for specific VOCs of interest found in the qualitative thermal tube results. On the basis of those results, we had the charcoal tubes quantitatively analyzed for benzene, toluene, ethyl benzene, and xylene by NIOSH Method 1501 [NIOSH 2014].

Aniline, Hydrogen Sulfide, Methylene Chloride, Total Dust, and N'-Oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide

In July 2013, we observed the production of crude and OTOS. In the crude building, we took full-shift breathing zone air samples on the two crude/NaSH operators over two 12-hour day-shifts to be analyzed for aniline. We also collected area air samples on the expansion and crude operators' desks. Samples were analyzed according to NIOSH Method 2002 [NIOSH 2014]. In addition, we took breathing zone air samples from the two operators using BW Technologies Gas Alert Extreme single gas meters. We collected samples over the entire 12-hour dayshift on two consecutive days. These direct reading instruments continuously logged hydrogen sulfide concentrations.

In the expansion building during the manufacture of OTOS, we took full-shift breathing zone air samples on the OTOS bagger and expansion operator over two 12-hour day shifts to be analyzed for methylene chloride according to NIOSH Method 1005 and total dust by NIOSH Method 0500 [NIOSH 2014]. We then analyzed the dust samples for OTOS using a method developed by Bureau Veritas North America.

We also collected two area samples for OTOS dust over two shifts on each side of the bagging operation, and area air samples for methylene chloride on the second and third floor of the expansion building. These sample were taken near where the OTOS was dried in the fluidized bed dryer and where methylene chloride was added to the process.

Surface Sampling

We collected eight surface wipe samples for aniline in the crude building, the NaSH building, and the main building where the employee locker rooms were located. One operator indicated that there had been an aniline spill on the expansion operator's desk a few weeks prior to our visit and therefore we selected that location to take a surface wipe sample. The handle to the aniline valve was sampled because there appeared to be a liquid on the valve handle. We selected other locations (e.g., sink in the women's locker room, and NaSH control room) to assess possible contamination in areas where we would not expect to find aniline. Surface wipe samples were collected on premoistened Ghost Wipes and analyzed according to NIOSH Method 2017 [NIOSH 2014], modified for the Ghost Wipe media.

Workplace Observations

We looked at the local exhaust ventilation system in the expansion building and observed work practices, procedures, and personal protective equipment use in the crude and expansion buildings.

Results and Discussion

Employee Interviews

Of the ten employees interviewed, all were male, their average age was 44 years (range: 27–56 years), and their average number of years worked at the facility was 4 (range: 1 month–19 years). Four of the employees had been hired in the year prior to our visit. Employees reported that they had an annual health assessment provided by the company that included routine blood and urine screening, hearing, vision, lung function, and lifting ability testing. The more recently hired employees reported having 4 days of training comprised of 2 days of computer-based training, and 2 days of on-the-job training.

When we asked the employees if they had a health problem related to working at the facility in the past year, we found one employee reporting headaches and one reporting sinusitis. These conditions, although nonspecific and common in the general public, were consistent with exposure to irritant chemicals and gases. A third employee reported back strain/sprain from opening stuck production process valves in the crude building. No current employees reported a history of lung or kidney disease or cancer.

We asked employees whether they had experienced certain symptoms in the past month at work. Five employees reported having throat irritation, and four of the ten reported having eye irritation, nose irritation, or headaches. These employees thought that exposures from cleaning the pipeline that transferred OTOS or BBTS through the expansion building, pushing benzothiazole tars out of the system, and chemical releases such as toluene and hydrogen sulfide were responsible for their symptoms. None of the interviewed employees reported cough, wheezing, or chest tightness. Eight of the ten employees interviewed reported occasionally getting chemicals on their skin. Two employees reported a recent history of skin irritation and felt that the OTOS product caused their skin symptoms.

Employee eye, nose, throat, and skin irritation symptoms at work, although nonspecific and common in the general public, were consistent with exposures to chemicals known to have irritant properties. Many of the chemicals at the facility, including carbon disulfide, aniline, hydrogen sulfide, benzothiazole, OTOS, and tert-butylamine can irritate the skin, eyes, and upper respiratory tract. Exposure to toluene and other VOCs can produce neurologic symptoms, such as headache and dizziness. Some chemicals can be absorbed into the body through skin and cause health problems similar to those caused by inhaling the chemical. These effects can become more severe with repeated or prolonged skin contact. Low levels of exposure to a mixture of irritants and volatile organic compounds can have an additive effect and result in irritant symptoms even when the individual chemical levels are below exposure limits [Hudnell et al. 1992; Hempel-Jorgensen et al. 1999]. Exposure to certain irritants in high concentrations or over a long period of time can also lead to occupational asthma [Balmes and Scannell 1997]. Effects of high-dose exposure to certain chemicals and gases, such as hydrogen sulfide, OTOS, benzothiazole, and morpholine, can range from transient, mild irritation of the mucous membranes to fatal adult respiratory distress syndrome [Balmes and Scannell 1997].

We asked the employees if they had any concerns about their health from workplace exposures. Four of the ten employees were concerned about the risk of developing lung disease, kidney disease, or cancer from long term chemical exposures. Some employees' concerns stemmed from reports of former employees who had developed chronic kidney disease.

Expansion building employees were most concerned about OTOS exposure. They reported that the OTOS bags were labeled as possible carcinogens and they had heard that this product was no longer produced in Europe or Canada because "it was too hazardous." These employees said they wore half-mask elastomeric respirators (some reported their use as mandatory) and gloves when bagging OTOS powder; however, they were concerned about inhaling the OTOS dust that accumulated on their clothing.

According to the manufacturer, OTOS can cause eye irritation, acute and chronic skin irritation, and chronic respiratory irritation. It is classified as a presumed human carcinogen (category 1B) under the Globally Harmonized System. One animal study found higher rates of benign and cancerous tumors of the urinary tract in rats fed high doses of OTOS for over 2 years [Hinderer et al. 1986]; however, it is unknown whether the results from the animal studies are relevant for the concentrations and routes of exposure found in the workplace. To date, there have not been adequate studies in humans regarding health effects from OTOS exposure.

Crude building employees were most concerned about long-term exposure to benzothiazole tars. Benzothiazole has no occupational exposure limits (OEL). Studies show benzothiazole can cause respiratory irritation and allergic contact dermatitis [Bogert and Husted 1931; Ginsberg et al. 2011]. The acute toxicity of benzothiazole includes central nervous system and respiratory depression as well as liver and kidney toxicity [Bogert and Husted 1931; Zapór 2005]. There is some evidence of this substance causing cancer in animals and humans, but the evidence is not consistent [NTP 1988; Sorahan 2009; Ginsberg et al. 2011].

Several other chemicals in this workplace, including morpholine and carbon disulfide, have been found to cause damage to the kidneys or urinary tract in experimental animal studies. Morpholine exposure in animals was found to damage the liver and kidneys, but human effects have not been reported, and it has not been classified as a carcinogen [European Commission 1999; NIOSH 2010]. Animal studies have found exposure to carbon disulfide caused liver toxicity, kidney disease, and chronic interstitial nephritis [ATSDR 1996; EPA 2013] but no published scientific studies have shown convincing evidence for kidney damage in humans. Additional information on chemical exposures in this workplace and their OELs is in Appendix A, Table A1.

According to the International Agency for Research on Cancer (IARC), occupational exposures to some chemicals in the rubber-manufacturing industry have been found to be carcinogenic to humans, and have been associated with leukemia, lymphoma, and cancers of the urinary bladder, lung, and stomach [IARC 2012]. Coming into contact with a carcinogen does not mean that a person will get cancer. Getting cancer from chemical exposure depends on (1) the type of chemical, (2) the amount of the chemical, (3) how long the exposure lasted, (4) how often the exposure occurred, (5) how long ago the exposure started, (6) whether the exposure was by inhalation, ingestion, or skin absorption, and (7) a person's general health. It is not possible to determine the risk of developing cancer in an individual worker. In the

United States tobacco smoke is the primary cause of lung cancer. Exposures to a combination of tobacco smoke and certain workplace substances can lead to a much greater risk of lung disease and cancer [American Lung Association 2010]. The complex nature of developing cancer from workplace exposures shows us that aggressively reducing exposures is important. The CDC informative brochure titled *Chemicals, Cancer, and You*, contains more information about these issues. It can be found at http://www.atsdr.cdc.gov/emes/public/docs/Chemicals,%20Cancer,%20and%20You%20FS.pdf.

Some employees had concerns about required overtime, shift scheduling, and what they perceived as the company's lack of interest in the well-being of their employees. Although we did not evaluate these concerns, we note that they can affect work performance and cause employee stress. Effective communication between management personnel and employees and having employee involvement in health and safety decisions often results in more employee satisfaction, increased productivity, and less overall workplace stress [Pincus 1986; Spector 1986; Brown and Leigh 1996].

Records Review

Medical Record Review

We reviewed medical records of one current employee and two former employees. The current employee's record did not indicate a work-related condition. The two former employees had been medically evaluated and diagnosed with two different types of autoimmune disorders that involved the kidneys, but were unrelated to each other. One was a condition that involved all the blood vessels in the body (a systemic vasculitis) and the other involved the filtration system of the kidney (a glomerulonephritis). We do not have evidence that these two conditions were related to workplace exposures. Additional information about chronic kidney disease can be found on the National Kidney Foundation website: http://www.kidney.org/kidneydisease/aboutckd.cfm [National Kidney Foundation 2013].

Medical Surveillance Records

We reviewed urine, blood, and lung function test results of 11 employees from medical surveillance records. No specific pattern of abnormality in the urine or blood was found to make us suspect adverse biological effects from exposures in the workplace. One individual had non-specific changes over time in their kidney function that would benefit from physician follow-up. (We contacted this employee to make this suggestion.) The lung function tests did not show an abnormal decrease in lung function over time.

Workers' Compensation Claims Review

We reviewed the company's workers' compensation claims for years 2010, 2011, and 2012. During that time period, 19 claims were processed. Twelve of the claims were still open at the time of our review. Four of the 19 claims were for chemical overexposures. Three of these four claims were for cumulative chemical exposures and were still open; one was for a single incident of aluminum chloride overexposure and was closed. No detailed information about these claims was available. The other claims were not pertinent to this evaluation.

Occupational Safety and Health Administration Log Review

There were sixteen entries on the 2010, 2011, and 2012 OSHA Logs. Only one entry related to a chemical exposure; it was for respiratory difficulty and shortness of breath due to smoke inhalation from putting out a fire in the crude building.

Air Sampling Records Review

We reviewed the results of industrial hygiene sampling done by the company in 2010. The company had a quarterly air sampling program to evaluate employee exposures to aniline, carbon disulfide, hydrogen sulfide, methylene chloride, morpholine, tert-butylamine, toluene, and OTOS dust, among others. This quarterly air sampling was discontinued in 2010. The only reported overexposures were to OTOS dust when compared to the manufacturer's exposure limit of 0.1 milligrams OTOS dust per cubic meter of air (mg/m^3) as an 8-hour time-weighted average (TWA) [Manufacturer's name withheld 2013].

Health and Safety Policy Review

The written respiratory protection program specified that all employees who were required to wear a respirator receive a physical examination and participate in initial and annual training and respirator fit testing. Employees confirmed that they had been receiving these examinations and training. The program specified that "cartridge-type filter masks, equipped with high-efficiency particulate air cartridges could be used for asbestos removal." "Single use dust respirators" were mentioned in the program for protection against nuisance dusts; however, no specific type was described. We noticed that critical elements of the respiratory protection program were missing. The program required worksite-specific procedures for required respirator use, including when and how a respirator would be used in routine work activities, maintenance activities, and emergencies such as spill response or personnel rescue. Although the program listed the available respirators, it did not specify how to select the proper respirator for a particular hazard. Some employees indicated that the use of respirators was mandatory while bagging OTOS, however OTOS was not listed in the program. The program stated that employees must be fit tested and undergo a physical examination; however, it did not describe how medical evaluations were provided, or how fit testing should be carried out. Although the employees were permitted to wear filtering facepiece respirators voluntarily, the written program did not contain provisions for voluntary use of a respirator.

The company's written hazard communication program provided employees with information on the workplace's chemical hazards and how to obtain safety data sheets. The plan also described proper container identification and labeling. The plan specified different levels of hazard communication training on the basis of what each individual would be doing in the facility, with the most basic level covering facility visitors.

Operators in the crude and expansion buildings used weekly safety check sheets to inspect important safety related equipment. These check sheets included inspection of personal protective equipment such as respirators and face shields, fire extinguishers, fire hoses, safety showers, exit signs, lighting, fall protection equipment, hydrogen sulfide testing kits, and nitrogen bottles.

The company's written procedure for accident reporting required injured or ill employees to notify their supervisor, if possible, and then proceed to the dispensary or obtain first aid. The supervisor then must notify the company's health and safety manager who makes the decision about additional medical treatment for the employee. The supervisor and the department head complete an occupational injury/illness report, which is then forwarded to the health and safety manager. The site of the accident would then be investigated, and steps would be taken to correct any contributing conditions.

Air Sampling

Volatile Organic Compounds

Toluene, tert-butylamine, benzothiazole, and n-tert-butyl-2-benzothiazole sulfonamide were the predominant VOCs present in the area air samples taken in the crude and expansion buildings. Other compounds identified were limonene, dichlorobenzene, methylbenzothiazole, aniline, benzene, and various hydrocarbons, but all were present in much lower amounts. The charcoal tube area air samples that were taken alongside the thermal desorption tubes were analyzed for benzene, toluene, ethylbenzene, and xylene. Concentrations of toluene and xylene were less than 2 parts per million (ppm). Benzene was detectable (0.003 ppm) but not reliably measurable, and ethylbenzene was not detected.

Aniline, Hydrogen Sulfide, Methylene Chloride, Total Dust, and N'-Oxydiethylenethiocarbamyl-N'-oxydiethylensulfenamide

Summary results of the aniline and hydrogen sulfide personal sampling are shown in Table 1. Detailed results, including the area air sampling data, are in Table B1 in Appendix B. The concentration of aniline in the crude operator's air sample was 4.0 parts per billion (ppb), while no aniline was detected in the NaSH operator's air sample. Due to the 12-hour work schedule we reduced the ACGIH threshold limit value to 1,000 ppb. See Appendix A for a description of the method used to adapt the TLVs to extended working hours. No hydrogen sulfide was detected in the personal air samples.

Table 1. Full shift breathing zone air sampling results for aniline and hydrogen sulfide, July 2013*

Job Title	Aniline concentration (ppb)	Hydrogen sulfide concentration (ppb)
Crude operator	ND and 4.0	ND
NaSH operator	ND	ND
NIOSH recommended exposure limit	Carcinogen	10,000 (ceiling limit)
OSHA permissible exposure limit	5,000	20,000 (ceiling limit)
ACGIH threshold limit value	1,000†	5,000 (short-term exposure limit)

ND = not detected; the minimum detectable concentration of aniline was 1 ppb based on a 127 liter air sample. The limit of detection for hydrogen sulfide was 1 ppb for the direct reading meter.

*Samples for aniline and hydrogen sulfide were collected on two days, July 16 and July 17, 2013.

†Adjusted for a 12-hour work shift.

During the July 2013 site visit, the indoor temperatures ranged from 74°F–92°F and relative humidity ranged from 62%–92%. Under these environmental conditions the collection capacity of the activated charcoal sample media used to sample for methylene chloride is greatly reduced. In addition, our air samples had total sample volumes ranging from 37–92 liters of air. The method used to sample for methylene chloride, NIOSH Method 1005 [NIOSH 2014], was validated for more moderate sample volumes, ambient temperatures, and relative humidity than were encountered during our evaluation. Due to these conditions "breakthrough" occurred on our sampling tubes and therefore we are not reporting these data. Breakthrough means that contaminants flowed through the sampler without being captured, or that they initially were captured but were driven off the media and no longer remained for analysis.

The polymer additive manufacturer recommends an exposure limit of 0.1 mg/m^3 for OTOS, as an 8-hour TWA [Manufacturer's name withheld 2013]. The breathing zone concentrations of OTOS ranged from 0.10–0.81 mg/m^3. As the manufacturer's exposure limit is based on an 8-hour workshift, it may need to be reduced to account for the longer shift. Although the employees wore a North® model 7700 half-mask elastomeric respirator with organic vapor cartridges and P100 particulate filters while bagging the product, they did not wear a respirator while troubleshooting a clogged OTOS supply line in the expansion building, which took the majority of the shift on the second day of our site visit. The air sampling results showed that between 56%–79% of the total dust sample was OTOS dust (Table 2). Both expansion building employees were overexposed to OTOS on the 2 days of our evaluation (Table 2). Detailed results are in Appendix B, Table B2.

Table 2. Summary of breathing zone air sampling results for OTOS dust in the expansion building, July 2013*

Job title/activity	Sample time (minutes)	Total dust concentration (mg/m^3)	OTOS concentration (mg/m^3)
Expansion operator day 1	673	(0.14)†	0.11
Expansion operator day 2	642	(0.18)†	0.10
Product bagger day 1	674	1.4	0.81
Product bagger day 2	650	0.91	0.56

*There are no NIOSH, OSHA, or ACGIH OELs for OTOS. The manufacturer's exposure limit is 0.1 mg/m^3, 8-hour time weighted average.

†Parenthesis ( ) indicate the result is between the minimum detectable concentration and the minimum quantifiable concentration making this an estimated result.

Wipe Sampling

Aniline was not found on the wipe samples. The limit of detection was 10 micrograms of aniline per sample.

Workplace Observations

We saw leaking pipes throughout the crude building and one substantial steam leak next to an operator's desk. One pipe that contained molten sulfur had buildup of molten sulfur on the floor below the pipe. The employer repaired these leaks prior to our second site visit.

We looked at the expansion building local exhaust ventilation system used to control dust exposure of employees bagging polymer additives. We noticed several deficiencies in the ductwork. The flexible ductwork that attached the bagging unit to the main exhaust duct was pinched (Figure 1) and the excess length of ductwork resulted in dust deposition within the duct (Figure 2). In addition, there was excess ductwork attaching the super sack filling station to the main duct and many bends in the ductwork. These conditions reduced the efficiency of the exhaust ventilation system (Figure 3).

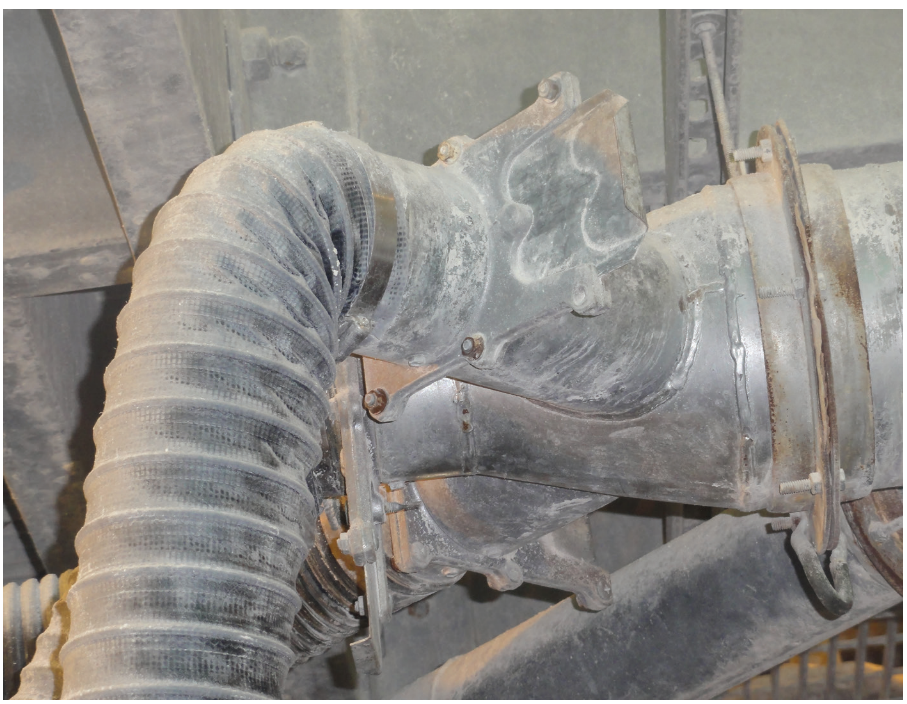

Figure 1. Pinched exhaust ductwork for the OTOS bag filling station. Photo by NIOSH.

Figure 2. Excess duct work caused dust to accumulate in the duct. Photo by NIOSH.

Figure 3. Excess ductwork to the super sack filling station. Photo by NIOSH.

The production of OTOS was done infrequently, and employees were required to wear respiratory protection while bagging the product. However, exposure monitoring results indicated that the expansion operator, who was not required to wear respiratory protection, was overexposed to OTOS when compared to the manufacturers' recommended limit. Additionally, the employees did not wear respiratory protection while fixing the clog in the OTOS bagging operation and were overexposed to OTOS on the day that task was performed. These results indicate that the local exhaust ventilation system designed to remove dusts from the bagging operation was not working sufficiently. The observed deficiencies in the system included kinked junctions between the main hard duct and the flexible duct work as well as excess ductwork that accumulated OTOS and could be the cause of the decreased efficiency of the system.

Generally, employees wore uniforms, steel-toed boots, hearing protection, safety glasses, and hard hats. We observed an employee get liquid on his skin when removing his protective gloves after collecting a quality control sample of waste water that contained tert-butylamine and crude. We observed two employees using respiratory protection, once in October 2012 and then in July 2013. The first occurred when an expansion employee cleaned out the pipeline used to transfer polymer additives between floors in the expansion building. This process involved two employees, one on the first floor and one on the third. The first floor employee used a lift to reach and open the pipe access. He then used a long stick to dislodge the dried product inside the pipeline. During the task he wore an N95 filtering facepiece respirator. We observed dust on the employee's hair and face after he completed the task. The second instance occurred while an employee was bagging OTOS. The employee reported that employees doing this task were required to wear a respirator while they bagged OTOS. The employee also wore ear plugs, cut-protective gloves, and a uniform shirt with long sleeves.

Limitations

The exposure concentrations we measured in July 2013 may not reflect the same exposure concentrations on other days and in previous years. Our air sampling did not account for possible skin absorption of chemicals.

Conclusions

Employees were concerned about long-term health risks for respiratory ailments, kidney disease, and cancer from workplace exposures. All airborne exposure levels we measured were well below OELs, except for OTOS overexposures in employees bagging OTOS product and troubleshooting a clog in the OTOS bagging operation. These OTOS overexposures and our observations indicate deficiencies in the local exhaust ventilation system. Although the employees used respiratory protection while bagging OTOS, they did not wear respirators while troubleshooting the clog. We found the kidney diseases in former employees to be unrelated to workplace exposure. Employee reports of eye, nose, throat, and skin irritation symptoms during their work shifts were consistent with skin and airborne exposures to irritant workplace chemicals. These symptoms, however, can have many causes and are common in the general public. Additionally, employee concerns about required overtime and the perception of the company's lack of interest in their well-being suggested a lack of effective communication between management personnel and employees.

Recommendations

On the basis of our findings, we recommend the actions listed below. We encourage the polymer additive manufacturing facility 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 at this facility.

Our recommendations are based on an approach known as the hierarchy of controls (Appendix A). 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 personal protective equipment may be needed.

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. Reduce the unnecessary ductwork in the OTOS and BBTS local exhaust ventilation system to prevent dust from accumulating in the low points in the duct.
2. Remove unnecessary bends in the ductwork in the OTOS and BBTS local exhaust ventilation system to improve dust capture at the bagging operation. Ask a ventilation engineer to evaluate the local exhaust ventilation system to determine if the exhaust airflow at the bagging operation is operating as designed.

Administrative Controls

The term "administrative controls" refers 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. Monitor for airborne exposures to OTOS and methylene chloride after the local exhaust ventilation system has been modified. Use the results to determine if exposures have been reduced below recommended levels.
2. Provide training on the proper selection and use of gloves and other personal protective clothing for preventing skin contact with chemicals. This training should include information on chemical breakthrough time for specific chemicals and glove types. This information should be available from the glove manufacturer.
3. Avoid skin contact with liquid precursor materials and dried products.
4. Provide training on proper hygiene practices, such as washing hands with soap and water before eating, drinking, smoking, using the toilet facilities, and leaving work. If skin contact occurs, flush the area with large amounts of water, and clean the area with mild soap and water.
5. Train employees on procedures for visually inspecting gloves to determine when they should be replaced.
6. Revise the respiratory protection program to meet the requirements in the OSHA respiratory protection standard, 29 CFR 1910.134. See "Small Entity Compliance Guide for the Respiratory Protection Standard" by OSHA available at https://www.osha.gov/Publications/3384small-entity-for-respiratory-protection-standard-rev.pdf [OSHA 2011]. Ensure that the written program specifies which chemical exposures require respiratory protection, the type of respirator, and the type of cartridges that should be used. In addition, if voluntary use of respirators is permitted, provide employees with a copy of Appendix D, "Information for Employees Using Respirators When Not Required Under the Standard," of the OSHA respiratory protection standard [29 CFR 1910.134].
7. Encourage all employees to report possible work-related health conditions to their supervisor or health and safety manager. Employees with persistent symptoms should be evaluated by an occupational medicine physician or a medical provider who specializes in workplace diseases and illnesses.
8. Follow the OSHA Hazard Communication Standard available at https://www.osha.gov/dsg/hazcom/.
9. Encourage employees to learn about cancer risk factors, measures to reduce risk for preventable cancers, and the availability of cancer screening programs for certain types of cancer.
10. Monitor reported health problems or injuries for trends related to particular job duties, work materials, machines, or areas of the facility for further evaluation and intervention.

11. Improve communication between the employer and employees regarding responses to employee safety and health concerns. A management or employee representative of the safety management team should communicate directly with employees who report health and safety concerns to let the employees know that their input has been received and what will be done to address the concern. If nothing will be done to address the concern, this should also be communicated and the rationale given.

Personal Protective Equipment

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

1. Provide butyl rubber gloves to employees for collecting quality control samples of liquid wastes, and train employees on proper use. Use thin nitrile gloves for short-term tasks instead of bare hands when more hand dexterity is needed, such as when sending the quality control sample to the lab.
2. Provide protective coveralls (e.g., Tyvek® suits) and booties for employees who bag OTOS product. If cloth coveralls are provided, the company is responsible for proper laundering. Employees should not take soiled coveralls home.

Appendix A: 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 STEL or ceiling values. Unless otherwise noted, the STEL 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.

For unusual work schedules, the ACGIH refers to the Brief and Scala model to reduce the TLV proportionately for both exposure time and reduced recovery time [Brief and Scala 1975, 1986]. The reduction factor applies to employees working 12-hour work shifts for 5 or fewer days in a week. The formula is as follows:

TLV reduction factor = (8/hours worked per day) × (hours off work/16)

The calculation for this facility is as follows:

TLV reduction factor = (8/12) × (12/16) = 0.5
Therefore, the adjusted TLV for this facility is obtained by multiplying the 8-hour value by 0.5.

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 RELs 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 RELs are published in the NIOSH Pocket Guide to Chemical Hazards [NIOSH 2010]. NIOSH also recommends risk management practices (e.g., engineering controls,

safe work practices, employee education/training, personal protective equipment, 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) personal protective equipment (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.

Below is a summary of the OELs for the chemicals of interest at the worksite, as well as a discussion of the potential health effects from exposure to these substances.

Aniline

Direct contact with aniline can produce skin and eye irritation [ATSDR 2002]. IARC has classified aniline as group 3, not classifiable as to its carcinogenicity to human [IARC 1982]. The OSHA PEL is 5 ppm as an 8-hour TWA with a skin notation, indicating this chemical can be absorbed through the skin [OSHA 2006a]. NIOSH has not established a quantitative OEL, but considers it an occupational carcinogen [NIOSH 2010]. ACGIH has established a TLV of 2 ppm as an 8-hour TWA with a skin notation [ACGIH 2014].

Benzothiazole

Benzothiazole can cause central nervous system and respiratory system depression, respiratory irritation, dermal sensitization, and liver and kidney toxicity [Bogert and Husted 1931; Zapór 2005; Ginsberg et al. 2011]. There is some evidence that benzothiazole causes cancer in animals and humans [NTP 1988; Sorahan 2009; Ginsberg et al. 2011]. IARC does not have an evaluation of its carcinogenicity. OSHA, NIOSH, and ACGIH have established OELs. Benzothiazole is a "generally recognized as safe" substance approved by the Flavor and Extract Manufacturers Association as a flavor ingredient [FEMA 1997].

Carbon Disulfide

Carbon disulfide exposure can cause irritant dermatitis, nerve damage, and increased risk of heart and blood vessel diseases in humans. Chronic inhalation exposure may cause atherosclerosis, coronary heart disease, and neurobehavioral effects including psychomotor slowing, positional tremors, peripheral polyneuropathy, hearing loss, and Parkinsonism [ATSDR 2012]. IARC does not have an evaluation of its carcinogenicity. OSHA has established a PEL of 20 ppm as an 8-hour TWA, 30 ppm as a ceiling limit, and 100 ppm as a 30-minute maximum peak [OSHA 2006b]. NIOSH has established an REL of 1 ppm as an 8-hour TWA, and a STEL of 10 ppm. It is also designated with a skin notation indicating this chemical can be absorbed through the skin [NIOSH 2010]. ACGIH has established a TLV of 1 ppm as an 8-hour TWA and has also assigned it a skin designation [ACGIH 2014].

Hydrogen Sulfide

Acute airborne exposures to hydrogen sulfide above 10 ppm have been associated with eye disorders, including conjunctivitis and keratitis [NIOSH 1977]. Conclusive evidence of adverse health effects from chronic exposure at concentrations below 20 ppm is lacking [29 CFR 1910.1000; Beauchamp et al. 1984; Schechter et al. 1989; Glass 1990; NIOSH 1992; HSDB 2014a]. IARC does not have a designation of its carcinogenicity. OSHA has established a ceiling limit of 20 ppm, and a 10-minute maximum peak of 10 ppm [OSHA 2006b]. NIOSH has established a 10-minute ceiling of 10 ppm [NIOSH 2010]. ACGIH has established a TLV of 1 ppm as an 8-hour TWA and a STEL of 5 ppm [ACGIH 2014].

Methylene Chloride

Methylene chloride is metabolized by the body to carbon monoxide and, with high exposures, can cause carbon monoxide poisoning [Fagin et al. 1980]. Prolonged skin contact can result in skin irritation or chemical burns [Wells and Waldron 1984]. Exposure to methylene chloride via inhalation and skin exposure may cause eye and skin irritation; weakness, exhaustion, drowsiness, or dizziness; numbness and tingling of limbs; and nausea [NIOSH 1996, 2010]. It is classified by IARC as group 2, possibly carcinogenic to humans [IARC 1999]. OSHA has established a PEL of 25 ppm as an 8-hour TWA and a STEL of 125 ppm [OSHA 2006a]. NIOSH does not have a quantitative OEL but considers it an occupational carcinogen [NIOSH 2010]. The ACGIH has established a TLV of 50 ppm as an 8-hour TWA and a STEL of 100 ppm [ACGIH 2014].

Morpholine

Morpholine exposure can cause irritation to the skin, eyes, nose, throat, and lungs. It is absorbed through the skin [European Commission 1999]. Animals exposed to morpholine had damage to the liver and kidneys [HSDB 2014b]. It is classified by IARC as group 3, not classifiable as to its carcinogenicity to humans [IARC 1989]. OSHA has established a PEL of 20 ppm as an 8-hour TWA with a skin designation, indicating this chemical can be absorbed through the skin [OSHA 2006a]. NIOSH has established an REL of 20 ppm as an 8-hour TWA, and a STEL of 30 ppm. NIOSH has also assigned a skin notation [NIOSH 2010]. ACGIH has established a TLV of 20 ppm as an 8-hour TWA and has assigned a skin notation [ACGIH 2014].

N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide (OTOS)

OTOS can cause eye irritation, acute and chronic skin irritation, and chronic respiratory irritation [Manufacturer's name withheld 2013]. Continuous oral administration of high doses (600 ppm) of OTOS to rats over 2 years resulted in benign and malignant urinary tumors (cancers of the cells lining the urinary tract) [Hinderer et al. 1986]. No reproductive effects were seen. IARC does not have an evaluation of its carcinogenicity. OSHA, NIOSH, and ACGIH have not established OELs. The manufacturer's limit is 0.1 mg/m^3 [Manufacturer's name withheld 2013].

Appendix B: Tables

Table B1. Air sampling for aniline during crude production, July 2013

Location	Sample time (minutes)	Sample volume (liters)	TWA concentration (ppb)
Crude operator breathing zone	672	122*	Not detected
NaSH operator breathing zone	572	113	Not detected
Crude operator breathing zone	670	134	4.0†
NaSH operator breathing zone	677	135	Not detected
NIOSH recommended exposure limit	—	—	**Carcinogen**
OSHA permissible exposure limit	—	—	**5000**
ACGIH TLV adjusted for 12-hour	—	—	**1000**
Area sample – expansion desk	605	120	30
Area sample – crude desk	607	121	3.0
Area sample – expansion desk	672	134	4.0
Area sample – crude desk	672	133	4.0

Note: The minimum detectable concentration of aniline in air was 1.0 ppb for a 127 liter sample.

*The post-calibration flowrate was 11% less than the pre-calibration value and therefore we used the lower flowrate to calculate sample volumes and TWA exposure concentrations.

†We used the minimum detectable concentration for the first 415 minutes to calculate an overall sample concentration because aniline was not found on the first of two sequential air samples.

Table B2. Air sampling in the expansion building during OTOS production and bagging, July 2013

Location	Sampling time (minutes)	Sample volume (liters)	Concentration total dust (mg/m^3)	Concentration OTOS (mg/m^3)
AE operator breathing zone	673	1010	(0.14)*	0.11
OTOS bagger breathing zone	674	1011	1.4	0.81
AE operator breathing zone	642	931	(0.18)	0.10
OTOS bagger breathing zone	650	975	0.91	0.56
Company OEL for OTOS	—	—	—	**0.1**
Area sample – OTOS filling unit	605	877	0.41	0.29
Area sample – near window	613	920	0.69	0.57
Area sample – OTOS filling unit	656	984	0.48	0.42
Area sample – near window	655	983	2.85	1.3

*Results in parentheses are between the minimum detectable concentration (0.07 mg/m^3) and the minimum quantifiable concentration (0.23 mg/m^3) for a 982 liter air sample making this an estimated concentration.

References

ACGIH [2014]. 2014 TLVs® and BEIs®: threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

AIHA [2014]. AIHA 2014 Emergency response planning guidelines (ERPG) & workplace environmental exposure levels (WEEL) handbook. Fairfax, VA: American Industrial Hygiene Association.

American Lung Association [2010]. Occupational lung disease. In: State of lung disease in diverse communities 2010. pp. 63–68. [http://www.lung.org/assets/documents/publications/solddc-chapters/occupational.pdf]. Date accessed: June 2014.

ATSDR [1996]. Toxicological profile for carbon disulfide. Atlanta, GA: U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.

ASTDR [2002]. ToxFAQs™ for aniline. [http://www.atsdr.cdc.gov/toxfaqs/tfacts171.pdf]. Date accessed: June 2014.

ASTDR [2012]. Addendum to the 1996 toxicological profile for carbon disulfide (update). Atlanta, GA: U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.

Balmes JR, Scannell CH [1997]. Occupational lung diseases. In: LaDou J ed. Occupational and environmental medicine. 2nd rev ed. Stamford, Connecticut: Appleton and Lange, pp. 305–327.

Beauchamp RO Jr., Bus JS, Popp JA, Boreiko CJ, Andjelkovich DA [1984]. A critical review of the literature on hydrogen sulfide toxicity. Crit Rev Toxicol *13*(1):25–97.

Bogert M, Husted H [1931]. Contribution to the pharmacology of the benzothiazoles. J Pharmacol Exp Ther *45*(2):189–207.

Brief RS, Scala RA [1975]. Occupational exposure limits for novel work schedules. Am Ind Hyg Assoc J *36*(6):467–469.

Brief RS, Scala RA [1986]. Occupational health aspects of unusual work schedules: a review of Exxon's experiences. Am Ind Hyg Assoc J *47*(4):199–202.

Brown SP, Leigh TW [1996]. A new look at psychological climate and its relationship to job involvement, effort, and performance. J Appl Psych *81*(4):358–368.

CFR. Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register. 29 CFR 1910.1000.

CDC (Centers for Disease Control and Prevention) [2012]. Chemicals, cancer, and you. Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention. [http://www.atsdr.cdc.gov/emes/public/docs/Chemicals,%20Cancer,%20and%20You%20FS.pdf]. Date accessed: June 2014.

EPA [2013]. Technology transfer network air toxics web: carbon disulfide. [http://www.epa.gov/ttn/atw/hlthef/carbondi.html]. Date accessed: June 2014.

European Commission [1999]. Recommendation from the scientific committee on occupational exposure limits for morpholine. Scientific committee on occupational exposure limits, Employment, Social Affairs and Inclusion, European Commission, SUM 81.

Fagin J, Bradley J, Williams D [1980]. Carbon monoxide poisoning secondary to inhaling methylene chloride. Br Med J *281*(6253):1461.

FEMA [1997]. Flavor and Extract Manufacturers Association: benzothiazole. Prepared by Technical Resources International, Inc. under contract No. NO2-CB-50511. [http://ntp.niehs.nih.gov/ntp/htdocs/chem_background/exsumpdf/benzothiazole_508.pdf]. Date accessed: June 2014.

Ginsberg G, Toal B, Kurland T [2011]. Benzothiazole toxicity assessment in support of synthetic turf field human health risk assessment. J Toxicol Environ Health *74*(17):1175–1183.

Glass DC [1990]. A review of the health effects of hydrogen sulphide exposure. Ann Occup Hyg *34*(3):323–327.

HSDB [2014a]. Hazardous substances data bank: hydrogen sulfide. The National Library of Medicine's TOXNET system, National Institutes of Health, Department of Health and Human Services. [http://toxnet.nlm.nih.gov]. Date accessed: June 2014.

HSDB [2014b]. Hazardous substances data bank: morpholine. The National Library of Medicine's TOXNET system, National Institutes of Health, Department of Health and Human Services. [http://toxnet.nlm.nih.gov]. Date accessed: June 2014.

Hempel-Jorgensen A, Kjaergaard SK, Mølhave L, Hudnell KH [1999]. Sensory eye irritation in humans exposed to mixtures of volatile organic compounds. Archiv Environ Health *54*(6):416–424.

Hinderer R, Lankas G, Knezevich A, Auletta C [1986]. The effects of long-term dietary administration of the rubber accelerator, N-oxydiethylenethiocarbamyl-N-oxydiethylene sulfonamide, to rats. Toxicol Appl Pharmacol *82*(3):521–531.

Hudnell HK, Otto DA, House DE, Mølhave L [1992]. Exposure of humans to volatile organic mixture. II. Sensory. Archiv Environ Health *47*(1):31–38.

IARC [1982]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: some aromatic amines, anthraquinones, and nitroso compounds, and inorganic fluorides used in drinking water and dental preparations. Volume 27, supplemental 7. Lyon, France: World Health Organization, International Agency for Research on Cancer. [http://monographs.iarc.fr/ENG/Monographs/suppl7/suppl7.pdf]. Date accessed: June 2014.

IARC [1989]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: some organic solvents, resin monomers, and related compounds, pigments, and occupational exposures in pain manufacture and painting. Volume 47. Lyon France: World Health Organization, International Agency for Research on Cancer. [http://monographs.iarc.fr/ENG/Monographs/vol47/mono47-11.pdf]. Date accessed: June 2014.

IARC [1999]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: re-evaluation of some organic chemicals, hydrazine, and hydrogen peroxide. Volume 71. Lyon, France: World Health Organization, International Agency for Research on Cancer. [http://monographs.iarc.fr/ENG/Monographs/vol71/volume71.pdf]. Date accessed: June 2014.

IARC [2012]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: occupational exposure in the rubber manufacturing industry. Volume 100F. Lyon France: World Health Organization, International Agency for Research on Cancer. [http://monographs.iarc.fr/ENG/Monographs/vol100F/mono100F-36.pdf]. Date accessed: June 2014.

Manufacturer's name withheld [2013]. Morpholin-4-yl morpholine-4-carbodithioate, N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide [Material Safety Data Sheet].

National Kidney Foundation [2013]. About chronic kidney disease. New York: National Kidney Foundation. [http://www.kidney.org/kidneydisease/aboutckd.cfm]. Date accessed: June 2014.

NIOSH [1977]. Criteria for a recommended standard: occupational exposure to hydrogen sulfide. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-158.

NIOSH [1992]. Recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

NIOSH [1996]. Methylene chloride: immediately dangerous to life or health concentration documentation. [http://www.cdc.gov/niosh/idlh/75092.HTML]. Date accessed: June 2014.

NIOSH [2010]. NIOSH pocket guide to chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2010-168c. [http://www.cdc.gov/niosh/npg/]. Date accessed: June 2014.

NIOSH [2014]. NIOSH manual of analytical methods (NMAM®). 4th ed. Schlecht PC, O'Connor PF, eds. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication 94–113 (August 1994); 1st Supplement Publication 96–135, 2nd Supplement Publication 98–119; 3rd Supplement 2003–154. [http://www.cdc.gov/niosh/docs/2003-154/]. Date accessed: June 2014.

NTP [1988]. Technical report on toxicology and carcinogenesis studies of 2-mercaptobenzothiazole in F344N rats and B6C3F1 mice. National Toxicology Program, Washington (DC): U.S. Government Printing Office. DHHS Publication No. (NIH) 88–2588.

OSHA [2006a]. Occupational Safety and Health Standards, Subpart Z, Toxic and hazardous substances, 1910.1000 table Z-1, Limits for air contaminants. [https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992&p_text_version=FALSE]. Date accessed: June 2014.

OSHA [2006b]. Occupational Safety and Health Standards, Subpart Z, Toxic and hazardous substances, 1910.1000 table Z-2, [https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9993]. Date accessed: June 2014.

OSHA [2011]. Small entity compliance guide for the respiratory protection standard. [https://www.osha.gov/Publications/3384small-entity-for-respiratory-protection-standard-rev.pdf]. Date accessed: June 2014.

Pincus JD [1986]. Communication satisfaction, job satisfaction, and job performance. Hum Commun Res *12*(3):395–419.

Schechter MT, Spitzer WO, Hutcheon ME, Dales RE, Eastridge LM, Steinmetz N, Tousignant P, Hobbs C [1989]. Cancer downwind from sour gas refineries: the perception and the reality of an epidemic. Environ Health Perspect *79*:283–290.

Sorahan T [2009]. Cancer risks in chemical production workers exposed to 2-mercaptobenzothiazole. Occup Environ Med *66*(4):269–273.

Spector PE [1986]. Perceived control by employees: a meta-analysis of studies concerning autonomy and participation at work. Hum Relations *39*(11):1005–1016.

Wells GG, Waldron HA [1984]. Methylene chloride burns. Br J Ind Med *41*(3):420.

Zapór L [2005]. Benzothiazole: documentation of maximum admissible values for occupational exposure. Podstawy I Metody Oceny Slrodowiska Pracy *45*:37–48.

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