



NIOSH HEALTH HAZARD EVALUATION REPORT:

HETA #2003-0064-2913

Degesch America, Inc.

Weyers Cave, Virginia

October 2003

DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health



PREFACE

The Hazard Evaluations and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health (OSHA) Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

HETAB also provides, upon request, technical and consultative assistance to federal, state, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Jeffrey Nemhauser and Chad Dowell of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Dino Mattorano. Analytical support was provided by Data Chem Laboratories and NIOSH Laboratories. Desktop publishing was performed by Ellen Blythe. Review and preparation for printing were performed by Penny Arthur.

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For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Highlights of the NIOSH Health Hazard Evaluation

Evaluation of Phostoxin Exposure at Degesch America

On February 20, 2003, NIOSH investigators conducted a health hazard evaluation survey at Degesch America. The survey looked at potential exposures and health effects from Phostoxin and Magtoxin fumigants manufactured at Degesch America.

What NIOSH Did

- We collected air samples in the warehouse, blending, and tableting areas for phosphine, ammonia, volatile organic compounds, and total dust
- We talked to 10 employees about their health concerns and work environment
- We met with Degesch America's occupational physician
- We reviewed OSHA 200 and 300A logs from 1998 to 2002

What NIOSH Found

- Results from ammonia, volatile organic compounds, and total dust air samples were not in excess of any published occupational exposure limits
- Phosphine exposures during the cleaning of the tablet hood were equal to the short term exposure limit
- Four of 10 employees reported isolated instances of health effects related to past phosphine exposures

What Degesch America Managers Can Do

- Continue to require respiratory protection when cleaning the hood
- Routinely monitor for phosphine during the transferring of cured pellets into the finished product hopper
- Ensure employees are properly trained on the correct use and storage of respirators
- Relocate fixed point phosphine sensors between the worker and source of phosphine

What the Degesch America Employees Can Do

- Make sure nothing breaks the seal of respirators, for example facial hair
- Relay health and safety concerns to appropriate management officials



What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513-841-4252 and ask for HETA Report #2003-0064-2913



Health Hazard Evaluation Report 2003-0064-2913
Degesch America, Inc.
Weyers Cave, Virginia
October 2003

Jeffrey B. Nemhauser, MD
Chad H. Dowell, MS

SUMMARY

On November 13, 2002, the National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at Degesch America, Inc., Weyers Cave, Virginia. The request identified several health concerns believed to be due to exposure to Phostoxin[®] and Magtoxin[®] fumigants manufactured at Degesch America. The HHE request listed the following health problems occurring in workers following occupational exposure: cyanosis, chest pain, nausea, weakness, dizziness, difficult breathing, low blood pressure, seizures, disorientation, muscle twitch, tremors, cough, indigestion, gastric problems, numbness, and cardiac problems.

On February 20, 2003, NIOSH investigators conducted a site visit at Degesch America. The purpose of the site visit was to review the manufacturing process, collect air samples, review pertinent safety and health records, and conduct worker medical interviews to determine if the reported symptoms are related to workplace exposure. An opening conference was held with employee and management representatives. Following this meeting, a walk-through survey of the plant's blending, tableting, packaging, and warehouse areas was conducted. Following the walk-through, NIOSH investigators collected general area (GA) and personal breathing zone (PBZ) air samples for phosphine, ammonia, elements, total dust, and volatile organic compounds (VOCs). The NIOSH medical officer interviewed employees.

None of the air samples collected by NIOSH for ammonia, VOCs, elements, or particulates yielded concentrations in excess of any published occupational exposure limits. However, phosphine exposures during cleaning of the tablet hood were equal to the NIOSH STEL. Four of ten interviewed employees reported isolated instances of health effects that they believed to be consistent with past occupational exposures to Phostoxin, Magtoxin, or aluminum phosphide. Overall, the occurrence of symptoms attributable to occupational exposures at Degesch America has been rare. Nonetheless, occasions for exposure to phosphine levels in excess of exposure limits may occur. Even though engineering controls have been adequately implemented, additional focus can be placed on the respiratory protection program, air monitoring of the transferring of cured pellets, phosphine monitor sensor location in the blend and tablet areas, and inspection of hoppers for leaks. Recommendations in the report address these issues.

Keywords: SIC 2879 (Pesticides and Agricultural Chemicals, Not Elsewhere Classified), Rodenticide, phostoxin, phosphine, and fumigant.

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INTRODUCTION

On November 13, 2002, the National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at Degesch America, Inc., Weyers Cave, Virginia. The request identified several health concerns believed to be due to exposure to Phostoxin[®] and Magtoxin[®] fumigants manufactured at Degesch America. The HHE request listed the following health problems occurring in workers following occupational exposure: cyanosis, chest pain, nausea, weakness, dizziness, difficult breathing, low blood pressure, seizures, disorientation, muscle twitch, tremors, cough, indigestion, gastric problems, numbness, and cardiac problems. This report presents the results of our evaluation, including conclusions and recommendations.

On February 20, 2003, NIOSH investigators conducted a site visit at Degesch America. The purpose of the site visit was to review the manufacturing process, collect air samples, review pertinent safety and health records, and conduct worker medical interviews to determine if the reported symptoms are related to workplace exposure. An opening conference was held with employee and management representatives. Following this meeting, a walk-through survey of the plant's blending, tableting, packaging, and warehouse areas was conducted. Following the walk-through, NIOSH investigators collected general area (GA) and personal breathing zone (PBZ) air samples for phosphine, ammonia, elements, total dust, and volatile organic compounds (VOCs). The NIOSH medical officer interviewed employees.

BACKGROUND

Degesch America is a metal phosphide-based fumigant manufacturer. The company (the only one of its kind in the United States) produces both Phostoxin and Magtoxin fumigants that are packaged on-site. Degesch America currently employs a total of eight workers who produce

("blend") and package fumigants 10 hours per day, 4 days per week. The usual production at times of peak demand is approximately 8 blends per day, although 10 or more blends per day have been produced. During the NIOSH site visit the facility was operating at half normal production of Phostoxin (4 blends per day) due to a decrease in demand. Magtoxin was not produced during our site visit; it is produced in only limited amounts throughout the year.

In the blending area of the plant, raw fumigant ingredients (aluminum phosphide, talc, zinc stearate, and ammonium carbamate) are weighed on a scale and then mixed in a Patterson-Kelly (PK) blender and a Fitz hammer mill to ensure consistency in blend formulation. Following completion of the mixing process, employees transfer the blend into a finished formulation hopper where it remains overnight.

The next day, the blend is gravity fed into tablet presses located inside tablet hoods. This process occurs in the "tableting area" of the plant, a separate room from where blending takes place. Fumigant tablets are then placed into pots for curing, and are ultimately packaged in a variety of ways depending on customer needs.

Throughout the manufacturing process, potential exposures to employees are controlled by the use of engineering controls and personal protective equipment (PPE). Engineering controls include local and general exhaust ventilation and vacuum systems used to clean up spilled material. Dräger[™] respirators equipped with tear gas/phosphine/P100 cartridges are worn by workers while weighing raw ingredients and during transfer of blends within the blending area, and also during the cleaning of the tablet hood in the tableting area. Uniforms are provided for employees to wear and are cleaned by the company.

Ventilation hoods are at locations where workers may be exposed to raw ingredients or metal phosphides via an airborne route. These include the weighing scale within the blending area where drums of raw ingredients are initially opened, the Fitz

hammer mill, the #1 dumper, the tablet press hood, and at various locations where the final product is packaged. Routine maintenance on the ventilation system by the maintenance crew includes lubrication as required and twice weekly checks of belts, filters, and motors.

METHODS

Industrial Hygiene

To evaluate potential worker exposures, GA and PBZ air samples were collected for phosphine, ammonia, VOCs, elements, and particulates.

Phosphine and Ammonia

Phosphine and ammonia gas were measured in the warehouse, blending, and tableting areas using Dräger™ pumps with colorimetric detector tubes. Air was drawn through the tubes with a bellows-type pump and the resulting length of stain within each detector tube (produced by chemical reaction with each sorbent) indicated the proportional concentration of phosphine and ammonia in each environment. The minimal detectable concentration of the Dräger™ tube for phosphine was 0.1 parts per million (ppm) (with an accuracy of plus or minus 15 to 20 percent) and for ammonia was 0.25 ppm (with an accuracy of plus or minus 10 to 15 percent).

Volatile Organic Compounds

One GA air sample was collected in the blending area and four PBZ samples were collected from personnel in the blending and tableting areas to identify VOCs to which the workers may be exposed. These samples, collected on thermal desorption tubes, were attached by Tygon® tubing to sampling pumps calibrated at a flow rate of 50 cubic centimeters per minute (cc/min). Each thermal desorption tube contained three beds of sorbent material: a front layer of Carboxen Y™, a middle layer of Carboxen B™, and a back section of Carboxen 1003™. The thermal desorption tubes for low level VOCs were analyzed by the NIOSH

laboratory using stainless steel tubes configured for thermal desorption in a Perkin–Elmer ATD 400 automatic thermal desorption system and analyzed using a gas chromatograph with a mass selective detector. Since the sampling and analytical techniques for this method have not been validated for these compounds, all results should be considered semi-quantitative. Semi-quantitative results only approximate the true concentration of the measured compounds.

Elements and Particulates

One GA air sample was collected in the blending area and four PBZ samples were collected from personnel in the blending and packaging areas to determine the concentrations of airborne particulates and elements.* The element analysis was performed using a Perkin Elmer Optima 3000 DV inductively coupled plasma spectrometer according to NIOSH Method 7300.¹ The samples were also analyzed for total weight gain using the NIOSH Manual of Analytical Methods (NMAM) Method 500.¹ Air samples were collected on 37-millimeter (mm) diameter (0.5–micrometer [µm] pore size) polyvinyl chloride (PVC) filters, using sampling pumps calibrated to draw air at a rate of 2 liters per minute (Lpm).

Medical

The medical evaluation consisted of confidential interviews with employees, workplace observations, and a review of the OSHA Summary of Work-Related Injuries and Illnesses, Forms 200 and 300A (OSHA Logs) from 1998 to 2002. Confidential interviews were held with all eight workers who produce (“blend”) and package fumigants as well as two members of the maintenance staff responsible

* aluminum, arsenic, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, molybdenum, nickel, lead, phosphorus, platinum, selenium, silver, sodium, tellurium, thallium, titanium, vanadium, vanadium, yttrium, zinc, zirconium

for the upkeep of the equipment used to produce and package Phostoxin. All employees interviewed were potentially exposed to phosphine gas as part of their job. Interview questions concerned length of employment at Degesch America, job description, known episodes of exposure to phosphine, and any episodes of work-related illness. Those employees with past episodes of work-related illness were asked to describe their symptoms.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes; this potentially increases the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),² (2) the American Conference of Governmental Industrial Hygienists' (ACGIH[®]) Threshold Limit Values (TLVs[®]),³ and (3) the U.S. Department of Labor,

Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).⁴ Employers are encouraged to follow the NIOSH RELs, the ACGIH TLVs, the OSHA PELs, or whichever is the more protective criterion.

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing 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)]. Employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short-term exposure limits (STELs). However, an employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Phosphine

Severe Health Effects Attributed to Phosphine Exposure

Phosphine (PH₃) is a colorless gas with a “rotting fish”-like odor. Exposure to phosphine gas causes irritation of the mucous membranes, especially those of the upper airways and deep lungs, and may result in pulmonary edema (a build-up of fluid within the lungs). Phosphoric acid, formed when inhaled phosphine gas comes into contact with deep lung tissues, can cause fatal lung damage.⁵ In addition to pulmonary edema, severe poisoning from PH₃ may result in heart muscle damage, critically low blood pressure (cardiovascular collapse), heart rhythm abnormalities, and jaundice with elevated liver enzymes.⁶ Mortality from severe poisoning is high and fatalities due to phosphine toxicity generally occur within the first 24 hours after exposure.⁷

Less Severe Health Effects Attributed to Phosphine Exposure

Intermittent, low concentrations of phosphine gas (probably 0.08 - 0.3 ppm) have been associated with mild headaches.⁵ In 1964, Jones reported the results of a survey of 67 workers exposed to PH₃ from dispensing aluminum phosphide tablets to wheat at two shipping terminals in New South Wales, Australia.⁸ Industrial hygiene sampling identified breathing zone concentrations of phosphine gas up to 11 ppm and intermittently as high as 35 ppm. Reported symptoms included diarrhea (82%), nausea (73%), chest tightness (52%), breathlessness (34%), headaches (83%), and dizziness (35%). Symptoms did not persist following exposure but did reoccur with subsequent exposures. A survey of Indian grain fumigators revealed a similar spectrum of gastrointestinal, respiratory, and central nervous system complaints.⁹ Phosphine concentrations in this survey ranged from 0.17 to 2.11 ppm.

Although a recent review article describes two cases of chronic disability due to occupational exposure to PH₃ (one neurological, one respiratory), long-term or cumulative health effects following phosphine exposure are distinctly unusual. Rather, in the majority of cases there are no reported long-term disabilities 30 days after an exposure to this chemical.⁷

Phosphine Odor Threshold

Reports in the scientific literature provide contradictory evidence about the concentration at which the odor of phosphine may be detected by smell (odor threshold).¹⁰ Some sources report that the odor threshold of phosphine is 0.02 ppm, well below the OSHA PEL of 0.3 ppm (see below). This would indicate that phosphine would possess adequate warning properties for workers exposed to potentially toxic levels. Other sources, however, identify a phosphine gas odor threshold of 1.5 to 3 ppm, well in excess of the OSHA PEL. A third source identifies an odor threshold of phosphine at 0.5 ppm but states that it possesses an unreliable odor

response. Finally, studies have shown that workers noticed no odor when working in phosphine concentrations as high as 50 ppm for several minutes with no respiratory protection. This finding suggests that olfactory fatigue** may cause unreliable detection of phosphine by odor. Thus, NIOSH recommends not relying upon an odor to warn workers about the presence of toxic levels of phosphine.⁵

OSHA has established a PEL for phosphine of 0.3 ppm as an 8-hour TWA.⁴ The NIOSH REL for phosphine is 0.3 ppm as a TWA for up to 10 hours per day during a 40-hour work week, and 1 ppm as a 15-minute STEL that should not be exceeded at any time during a workday.² In addition, NIOSH has established 50 ppm as the immediately dangerous to life and health (IDLH) concentration for phosphine gas. An IDLH value is the concentration at which (1) death or irreversible health effects may occur, or (2) escape within 30 minutes from a contaminated environment is prevented due to incapacitation.

Ammonia

Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause burning and tearing of the eyes; acute exposure to high concentrations of gaseous ammonia may produce temporary blindness or more severe eye damage. Exposure to gaseous ammonia may cause chest pain and coughing. Symptoms may be delayed in onset. Exposures to high concentrations of gaseous ammonia may cause burning and blistering of the skin, and have been reported to cause a person to stop breathing and die. Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.^{11,12}

OSHA has established a PEL for ammonia of 50 ppm as an 8-hour TWA.⁴ The NIOSH REL for ammonia is 25 ppm as a TWA for up to 10 hours per day during a 40-hour work week, and 35 ppm as a STEL that should not be exceeded at any time during a

** Loss of the ability to smell an odor following prolonged or high level exposure.

workday. In addition, NIOSH has established 300 ppm as the IDLH concentration for ammonia.²

Volatile Organic Compounds

VOCs comprise a large class of carbon-containing chemicals that share common physical properties. VOCs have a sufficiently high vapor pressure to allow some of the compound to exist in the gaseous state at room temperature. These compounds are emitted in varying concentrations from numerous sources including, but not limited to, combustion sources, adhesives, solvents, paints, cleaners, waxes, and cigarettes. Studies have measured wide variations in VOC concentrations in the workplace, as well as differences in the mixtures of chemicals present. Research suggests that the irritant potency of VOC mixtures can vary. Currently, neither NIOSH nor OSHA have specific exposure guidelines for VOC mixtures. The highly variable nature of the complex VOC mixtures can greatly affect their potential health effect outcome.

Elements

Metals comprise the majority of the known elements and have widespread natural occurrence in the environment. Metals have a wide range of properties, uses, and toxicity. Some metals are essential for life while others have no known biologic function. Other metals are capable of producing disease. Some metals that are essential nutrients can be toxic at higher concentrations. Allowable daily intake (food), maximum contaminant level (drinking water), and industrial exposure guidelines and regulations (e.g., NIOSH REL, OSHA PEL) have been established for many metals.

The toxicity of metals generally depends both on the chemical form of the metal and the immune status, age, and lifestyle factors of the exposed worker. Although many toxic metals can affect more than one organ system, at the lowest doses of exposure, it is often a single organ or tissue that will be predominantly affected.¹³ Several metals (arsenic, beryllium, cadmium, chromium, and nickel) are known to cause cancer. The following table lists the

metals detected at Degesch America, and the corresponding OSHA PEL, NIOSH REL, and ACGIH TLV values.

Particulates, Not Otherwise Classified

Since there may be an infinite number of chemical combinations of airborne particulates it has been the convention to apply generic exposure criteria to this class of occupational contaminants. ACGIH and OSHA have both developed generic criteria for airborne dusts that do not produce significant organic diseases or toxic effects when exposures are kept under reasonable control.³ Formerly referred to as "nuisance dust," the preferred terminology for the ACGIH TLV non-specific particulate criterion is now "Particulates Not Otherwise Classified (PNOC)," or "Particulates Not Otherwise Regulated" (PNOR) for the OSHA PEL.^{3,4}

The ACGIH recommended TLV for exposure to PNOC is 10.0 milligram per cubic meter (mg/m³) (inhalable dust, 8-hour TWA).³ The OSHA PEL for total PNOR is 15.0 mg/m³, determined as 8-hour averages.⁴ NIOSH has not assigned a REL for PNOR.¹⁴

Excessive concentrations of PNOCs in the workroom air may seriously reduce visibility and may cause unpleasant deposits in the eyes, ears, and nasal passages. Furthermore, PNOCs can contribute to injury of the skin or mucus membranes by direct chemical or mechanical action or by the rigorous skin cleansing procedures necessary for their removal.¹⁵

RESULTS

Industrial Hygiene

Phosphine

Eight GA air samples for phosphine were collected. Results ranged from none detected (ND) to 1 ppm (Table 2). The highest phosphine concentrations

(1 ppm) were collected as GA air samples during the cleaning of the tablet hood, both from immediately outside the hood and inside the hood. These results indicate a potential for phosphine to exceed the NIOSH STEL of 1 ppm.

Ammonia

Eight GA air samples for ammonia were collected. Results ranged from 0.5 ppm to 3 ppm (Table 2). The highest ammonia concentration (3 ppm) was collected as a GA sample during the cleaning of the tablet hood. None of the measured concentrations exceeded the OSHA PEL or the NIOSH REL.

Volatile Organic Compounds

Two workers in the blending area and two workers in the tableting area wore PBZ thermal desorption tubes to monitor for exposure to VOCs. In addition, NIOSH investigators placed one GA thermal desorption tube next to the PK mixer in the blending area. Major compounds detected included acetone, propylene glycol, ethanol, various C₉-C₁₂ aliphatic hydrocarbons, toluene, and pinenes. Many of these compounds are found in ambient air while others may come from waxes and cleaning solvents used at Degesch America.

Elements

One GA air sample and four PBZ air samples were collected for elements from the same locations where the VOC samples were collected. NIOSH analysis detected the following: aluminum, beryllium, calcium, copper, iron, lithium, magnesium, manganese, nickel, sodium, titanium, vanadium, and zinc. The individual sample results for the detected elements are presented in Table 3. None of the 8-hour TWA concentrations exceeded the NIOSH RELs, the ACGIH TLVs, or the OSHA PELs.

PNO

One GA sample and four PBZ air samples were collected for particulates. PNO samples were collected from the same locations where the VOC

and element samples were collected. Individual sample results for particulates (total dust) are presented in Table 3. The total particulate concentrations ranged from none detected (ND) to 0.18 mg/m³. The highest total particulate concentration (0.18 mg/m³) was collected as a PBZ sample from an employee working in the blending area. None of the 8-hour TWA concentrations exceeded the ACGIH TLV or the OSHA PEL.

Medical

Confidential Interviews

Ten workers consented to participate in confidential medical interviews. At the time of the confidential medical interviews, the NIOSH medical officer observed several of the male employees either to have facial hair or not to be clean shaven. As previously stated, all employees interviewed worked in areas in which they were potentially exposed to phosphine gas.

Four of the ten interviewed workers noted having histories of isolated health effects that they felt were consistent with past occupational exposures to Phostoxin, Magtoxin, or aluminum phosphide at Degesch America. Reported health effects included the following: headache, nausea, "feeling tired," a "jittery sensation" after exposure, chest pain, numbness on the left side of the body, excessive sweating, and dizziness. These reported symptoms were not recurrent and all had largely spontaneously resolved within a short period of time. The remaining six employees denied any history of symptoms consistent with occupational illness.

Two employees described multiple episodes of chemical spills over the past 15-20 years. In addition, employees reported that approximately two years prior to the NIOSH site visit, a fully-loaded finished formulation hopper located on the platform above the tablet press exploded. No worker injuries were recorded from this event. Aside from these unplanned events, two employees reported that they were most concerned with exposures occurring while operating the hammer mill.

OSHA Logs

A review of the OSHA Logs from 1998–2002 revealed no recordable occupational illnesses or injuries referable to toxic exposures. The company's occupational physician confirmed that over the past 25 years there have been no episodes of acute workplace toxicity necessitating acute medical intervention.

DISCUSSION

None of the air samples collected by NIOSH for ammonia, VOCs, elements, or particulates yielded concentrations in excess of any published occupational exposure limits. However, phosphine exposures during cleaning of the tablet hood were equal to the NIOSH STEL. As was previously mentioned, NIOSH investigators observed Degesch America employees wearing Dräger respirators equipped with tear gas/phosphine/P100 cartridges while cleaning the tablet hood. Even though engineering controls have been adequately implemented, additional focus can be placed on the respiratory protection program, air monitoring of the transferring of cured pellets, phosphine monitor sensor location in the blend and tablet areas, and inspection of hoppers for leaks.

When PPE is appropriate, proper maintenance and use is necessary to protect workers from occupational exposures to hazardous and toxic dusts. During the site visit, NIOSH investigators observed the improper storage of respirators. For example, at the end of the shift respirators were left in the work environment above an exhaust hood. Respirator cartridges continue to absorb contaminants as long as they are stored in the work environment; this results in decreased cartridge service life. In addition, interior surfaces of the respirator can become contaminated. The fact that employees have facial hair and were not clean shaven would also indicate that workers at this facility are not receiving sufficient education about proper respirator use; thus, current practice is not in accordance with OSHA's respiratory protection standard (Title 29 CFR 1910.134).

Currently, Degesch America allows for continued use of respirator cartridges after an extended time in storage. Inappropriate reuse of respirator cartridges or improper storage of cartridges can result in breakthrough of contaminants earlier than what may be predicted by the end-of-service-life calculations performed in Degesch America's respiratory protection program. Chemicals collected on the first layers of the absorbent may, during times of non-use, desorb and redistribute to the back layers of the cartridge (i.e., those layers of the cartridge that are closest to the worker). This redistribution of chemicals may result in a worker inhaling the chemical at the time of respirator reuse.¹⁶

The process of transferring cured pellets into a finished product hopper for packaging is performed for approximately 10 minutes a day. During the NIOSH investigation, the phosphine concentration was measured at half the NIOSH STEL. In general, when a concentration is measured at half the exposure limit, additional actions are required to ensure that concentrations do not exceed the exposure limit. Actions can range from more closely monitoring the exposure to making engineering adjustments.

Degesch America management representatives raised a question about the slow response time for the fixed point solid-state phosphine monitors installed in two locations throughout the plant. At the time of our visit, the monitors were installed in the blending room and tableting room; both monitors were behind the workers in relation to the source of the phosphine. Electrochemical and solid-state sensors each have advantages and disadvantages. The advantage of solid-state sensors is the longevity of the sensor life. The advantage of electrochemical sensors is that they are fairly selective. One disadvantage of both is the slight delay, up to one minute, in detecting phosphine gas. This delay is in addition to the amount of time required for the phosphine to reach the monitor. Monitor reaction time, in the current locations, can be decreased by locating the monitors between the source of phosphine and the workers.

Four of ten interviewed employees reported isolated instances of health effects that they believed to be

consistent with past occupational exposures to Phostoxin, Magtoxin, or aluminum phosphide. Overall, the occurrence of symptoms attributable to occupational exposures at Degesch America has been rare. Nonetheless, occasions for exposure to phosphine levels in excess of exposure limits may occur. For example, some employees reported that during the blending process, aluminum phosphide that has been manufactured in Germany creates noticeably more airborne dust than does the use of domestically manufactured aluminum phosphide. Based on these reports, elevated environmental levels of the German-made aluminum phosphide during times of peak production may potentially result in phosphine levels in excess of exposure limits.

Exposure to phosphine at low levels (10 ppm) is associated with a variety of symptoms; the isolated symptoms experienced by Degesch America employees are consistent with these. If PPE has not been worn or has been improperly worn, it would be insufficient to protect employees exposed to phosphine at levels at or above the STEL.

CONCLUSIONS

None of the air samples collected by NIOSH for ammonia, VOCs, elements, or particulates yielded concentrations in excess of any published occupational exposure limits. However, phosphine exposures during cleaning of the tablet hood were equal to the NIOSH STEL. Four of ten interviewed employees reported isolated instances of health effects that they believed to be consistent with past occupational exposures to Phostoxin, Magtoxin, or aluminum phosphide. Overall, the occurrence of symptoms attributable to occupational exposures at Degesch America has been rare. Nonetheless, occasions for exposure to phosphine levels in excess of exposure limits may occur. Even though engineering controls have been adequately implemented, additional focus can be placed on the respiratory protection program, air monitoring of the

transferring of cured pellets, phosphine monitor sensor location in the blend and tablet areas, and inspection of hoppers for leaks.

RECOMMENDATIONS

Despite the overall low concentrations of chemicals identified by air sampling during the NIOSH visit, the NIOSH investigators recommend that further measures to minimize exposures should be taken. Employees work in areas where exposure to phosphine gas is occurring at concentrations equal to the STEL although engineering controls are currently in place. In the past, following chemical spills, exposures may have exceeded the STEL. Of note, however, there have been no recordable occupational illnesses or injuries due to these exposures.

Improvements can be made to further reduce exposure to hazardous and toxic dusts and chemicals at Degesch America. Based upon the measurements and observations made during the NIOSH survey, the following recommendations are provided to improve worker safety:

1. Workers should continue to use respiratory protection during hood cleaning. Phosphine samples collected during the cleaning of the tablet press hoods, both from the outside and inside the hood, indicate a potential for the NIOSH STEL value to be exceeded.
2. The process of transferring cured Phostoxin pellets into the finished product hopper should be routinely monitored to ensure that the NIOSH STEL is not exceeded. Concentrations one-half the STEL were measured in this evaluation. Should the STEL be exceeded, respirators should be required until engineering controls can be implemented.
3. More scrupulous adherence to all aspects of the use of personal protective equipment is needed. The company should modify the respirator program and training as follows.

- Workers wearing respiratory protection must either be clean shaven or wear respirators suitable for use with facial hair (e.g., supplied air hooded respirators or loose fitting powered air purifying respirators).

- Respirators should be maintained in a clean condition and stored in a manner that will protect them from damage in accordance with 29 CFR 1910.134. OSHA requires that respirators be stored to protect them from damage, contamination, dust, sunlight, extremes of temperature, excessive moisture, and damaging chemicals.¹⁷ Manufacturer's instructions should be followed with regard to the cleaning and sanitizing of respirators prior to storage. Respirators should not be stored in lockers, tool boxes, or left unprotected on workbenches unless they are in a protective carrying case or carton.¹⁸

- Respirators with cartridges left in place should not be stored for extended periods of time after their initial use. Cartridge manufacturers can provide guidelines as to the appropriate and safe reuse of respirator cartridges following extended periods of storage. The relative humidity and the airborne concentrations of phosphine and ammonia should be taken into consideration.

4. The fixed point phosphine sensor in the tableting area should be relocated to the immediate area of the workers or additional sensors should be added. Sensors should be located between the tablet hood and the worker, to allow the phosphine to be detected at the source of exposure. One or more phosphine monitors should also be added to the warehouse portion of the plant to detect leaks in the raw metal-phosphide drums. Also, one or more phosphine monitors should be added to the blending area, for example next to the temporary hopper storage area and between the scale and #1 dumper.

5. Hoppers containing metal-phosphide product, both powder and tablet, should be routinely inspected for leaks. A sample collected inside one hopper had a phosphine concentration of 8,000 ppm.

This has the potential to increase exposures in the area surrounding the hopper storage. Therefore, leaking hoppers should be repaired quickly or removed from use.

6. Employees experiencing health symptoms consistent with an occupational exposure to phosphine gas, aluminum phosphide, Phostoxin, or Magtoxin should seek immediate medical attention. Early reporting is necessary to determine the work-relatedness of the experienced symptoms.

REFERENCES

1. NIOSH [1998]. Eller PM, ed. NIOSH manual of analytical methods. Vol. 4. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

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

3. ACGIH [2003]. 2003 TLVs® and BEIs®: threshold limit values for chemical substances and physical agents. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

4. CFR [2002]. 29 CFR 1910.1000. Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

5. NIOSH [1999]. NIOSH Alert: Preventing Phosphine Poisoning and Explosions during Fumigation. Washington, DC: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational

Safety and Health, DHHS (NIOSH) Publication No. 99-126.

6. Carter DE, Sullivan JB [2001]. Intermetallic semiconductors: arsine, phosphine, and inorganic hydrides. In: Sullivan JB, Krieger GR, eds. *Clinical Environmental Health and Toxic Exposures*, 2nd rev. ed. Philadelphia: Lippincott Williams & Wilkins, p. 961.

7. Brautbar N, Howard J [2002]. Phosphine toxicity: report of two cases and review of the literature. *Toxicol and Indust Health* 18:71-5.

8. Jones AT, Jones RC, Longley EO [1964]. Environmental and clinical aspects of bulk wheat fumigation with aluminum phosphide. *Am Ind Hyg Assoc J* 25:376-9.

9. Misra UK, Bhargava SK, Nag D, Kidwai MM, Lal MM [1988]. Occupational phosphine exposure in Indian workers. *Toxicol Lett* 42:257-63.

10. Zaebst DD, Blade LM, Burroughs GE, Morrelli-Schroth P, Woodfin W [1988]. Phosphine exposures in grain elevators during fumigation with aluminum phosphide. *Appl Ind. Hyg.* 3(5):146-54.

11. Hathaway GJ, Proctor NH, Hughes JP [1996]. *Proctor and Hughes' chemical hazards of the workplace*. 4th ed. New York, NY: Van Nostrand Reinhold.

12. NIOSH [1988]. Occupational health guidelines for chemical hazards—occupational health guideline for ammonia. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 88-118.

13. Goyer RA, Clarkson TW [2001]. Toxic Effects of Metals. In: Klaasen CD, ed. *Casarett and Doull's toxicology. The basic science of poisons*, 6th rev. ed. New York: McGraw-Hill Publishers, p. 813.

14. NIOSH [1997] NIOSH pocket guide to chemical hazards. 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. 97-140.

15. NIOSH [1981]. NIOSH/OSHA occupational health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 81-123.

16. Moyer ES [1983]. Review of influential factors affecting the performance of organic vapor air-purifying respirator cartridges. *Am Ind Hyg Assoc J* 44(1):46-51. 1983.

17. CFR [2002]. 29 CFR 1910.134 Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

18. NIOSH [1987]. Guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

**Table 1. Exposure Limits
Degesch of America, Inc.
Weyers Cave, Virginia
HETA 2003-0064
February 20, 2003**

Metal	OSHA PEL	NIOSH REL	ACGIH TLV
Aluminum	15	5	10 (dust)
Beryllium	0.002; C 0.005	0.0005, Ca	0.002, Ca
Calcium	15 as CaCO ₃	10 as CaCO ₃	10 as CaCO ₃
Copper Dust	1 (dust)	1 (dust)	1 (dust)
Iron	10 (dust)	5 (dust)	--
Lithium	--	--	--
Magnesium	15 (dust) as oxide	--	--
Manganese	C 5	1; STEL 3	5 (dust)
Nickel	1	0.015, Ca	0.05, Ca
Sodium	--	--	--
Titanium	15 as TiO ₂	lowest feasible, Ca	10
Vanadium	C 0.5 (respir.) as V ₂ O ₅	C 0.05	0.05 (respir.) as V ₂ O ₅
Zinc	15 (ZnO dust)	5; C 15 (ZnO dust)	10 (ZnO dust)

All values in milligrams per cubic meter (mg/m³)

Ca = carcinogen

C = ceiling

**Table 2. Direct Reading Air Sampling Results
 Degesch of America, Inc.
 Weyers Cave, Virginia
 HETA 2003-0064
 February 20, 2003**

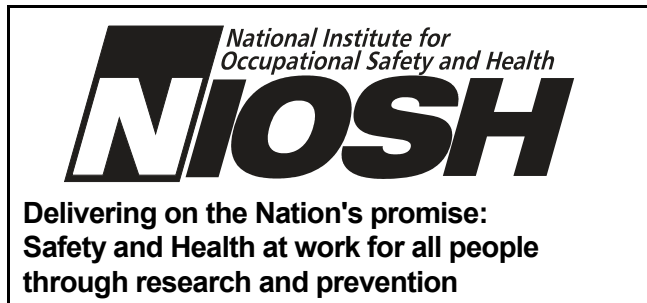
	Ammonia (ppm)	Phosphine (ppm)
Outside hammer mill	1.5	0.1
Outside barrel dumper	0.75	ND
Cleaning pellet maker from outside hood	1	1
Cleaning tablet press hood	3	1
Cleaning tablet press hood	3	0.5
Area outside press hood	0.5	0.1
Transfer of pellets back into hoppers	1	0.5
Warehouse area	0.75	0.1

**Table 3. Air Sampling Results
 Degesch of America, Inc.
 Weyers Cave, Virginia
 HETA 2003-0064
 February 20, 2003**

	Blending Area Worker	Blending Area Worker	Tableting Area Worker	Tableting Area Worker	Blending Area Next to PK Mixer
Total Dust	0.047	0.18	0.13	0.13	ND
Aluminum	0.02	0.01	0.01	0.02	0.006
Beryllium	0.00002	ND	ND	ND	ND
Calcium	0.04	0.009	0.010	0.005	ND
Copper	0.0002	0.0002	0.0003	0.0002	0.0003
Iron	ND	0.02	ND	ND	ND
Lithium	ND	ND	0.001	ND	0.0003
Magnesium	0.002	0.007	ND	0.002	ND
Manganese	ND	0.0005	0.0003	0.0002	ND
Nickel	0.0009	0.001	ND	0.0007	ND
Sodium	0.06	0.05	0.07	0.05	0.06
Titanium	ND	0.0004	0.001	0.0005	ND
Vanadium	ND	ND	0.0003	ND	ND
Zinc	0.001	0.002	0.001	0.0007	0.0009
Results reported as a average concentration over 190 minutes, including the cleaning period. It is assumed the concentraion remains the same throughout the day. Concentrations in mg/m3.					

DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
4676 Columbia Parkway
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