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AMERICAN AZIDE CORPORATION
CEDAR CITY, UTAH

Eric Esswein, M.S.P.H.
Douglas Trout, M.D., M.H.S.
Thomas Hales, M.D.

PREFACE

The Hazard Evaluations and Technical Assistance Branch of 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 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 and 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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) 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.

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NIOSH INVESTIGATORS:
ERIC ESSWEIN, M.S.P.H.
DOUGLAS TROUT, M.D., M.H.S.
THOMAS HALES, M.D.

SUMMARY

In October 1994, NIOSH received a confidential request for a health hazard evaluation (HHE) at the American Azide Corporation, a sodium azide production facility in Cedar City, Utah. Sodium azide (NaN_3) affects the cardiovascular system by causing peripheral vasodilation potentially leading to hypotension, headache, and other symptoms. Upon contact with water, sodium azide is converted to hydrazoic acid (HN_3), a vapor with health effects similar to NaN_3. On December 14, 1994, NIOSH conducted an initial site visit to the plant, followed by an extensive environmental and medical evaluation on March 13-17, 1995.
The environmental evaluation included observation of work practices in the plant and use of personal protective equipment, and area and personal breathing zone (PBZ) sampling for NaN_3 and HN_3. The medical evaluation included a symptoms questionnaire, ambulatory blood pressure monitoring, and blood analysis for azide.

Twenty-nine PBZ samples were collected during the environmental evaluation. For NaN_3 (expressed as the sum of the particulate and vapor azide concentrations), PBZ concentrations ranged from not detected to 1.7 mg/m^3. The range of minimum detectable concentrations (MDCs) was 0.02 mg/m^3 for sample volumes with a mean of 54 liters (range 21-88 liters) and 0.06 mg/m^3 for a mean sample volume of 203 liters (range 106-288). The analytical limit of detection was reported as 3.0 micrograms (µg) and 2.0 µg, respectively, for NaN_3 and HN_3. Hydrazoic acid PBZ air concentrations ranged from not detected to 1.1 parts per million (ppm). The MDCs for HN_3 were 0.02 ppm and 0.005 ppm, respectively for mean sample volumes of 54 and 203 liters (same sample volume ranges previously mentioned). Eight (28%) of the NaN_3 air concentrations (total particulate and vapor azide concentrations) exceeded the NIOSH recommended exposure level (REL) of 0.3 mg/m^3 (ceiling limit). Four (14%) air concentrations of hydrazoic acid exceeded, or were at, the NIOSH REL of 0.1 ppm (ceiling limit). One air sample collected inside a supplied-air helmet used for respiratory protection revealed a level of hydrazoic acid (0.13 ppm) greater than concentrations measured on the workers lapel (0.05 ppm). The majority (75%) of the PBZ exposures exceeding the NIOSH criteria occurred during packaging and reblending operations in a recently completed portion (the new blender and packaging building) of the facility.
Eleven production workers (including 100% of the chemical operators on duty) participated in the medical evaluation. Headache occurring in the production areas within the six months prior to the evaluation was reported by 10 of 11 (91%)

participants. Nine of 11 (82%) participants reported episodes of 'low' blood pressure during that same time period. During our survey, 4 of 11 (36%) employees reported mild headaches while working in the production areas. One of ten employees whose blood pressure was monitored met our criteria for an episode of hypotension during the workshift (drops in systolic blood pressure

of at least 20 mm Hg, and in diastolic blood pressure of at least 10 mm Hg). This episode was recorded while the employee performed azide packaging in the new blender and packaging building. A 106 minute PBZ sample revealed an air concentration of total sodium azide of 1.7 mg/m^3 (hydrazoic acid concentration was measured at 0.06 ppm). The employee reported no symptoms during this time. None of the blood samples had detectable azide, but the LOD for the analytical method to detect azide in blood was found to be 2800 parts per billion (ppb), which was an order of magnitude greater than expected blood levels.

The NIOSH HHE determined that occupational exposures to sodium azide and hydrazoic acid exceeded the NIOSH REL of 0.3 mg/m^3 (ceiling) for sodium azide and 0.1 ppm (ceiling) for hydrazoic acid. Reported health effects and, in one case, measured blood pressure changes, were consistent with sodium azide/hydrazoic acid exposure. Recommendations are included in this report to further characterize areas of potential exposure, establish protocols for appropriate use of personal protective equipment, and use of engineering controls to prevent potential health effects from exposure to sodium azide and hydrazoic acid.

KEYWORDS: SIC 5169 (Chemicals and Allied Products, Not Elsewhere Classified), sodium azide, hydrazoic acid, blood pressure, hypotension, headache, ambulatory blood pressure monitoring, biological monitoring.

INTRODUCTION

In October 1994, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) from employees of the American Azide Corporation in Cedar City, Utah. In that request, NIOSH was asked to evaluate potential exposure to, and health effects from, sodium azide and hydrazoic acid. Specific health effects noted by the requestors were low blood pressure, headache, lightheadedness, eye irritation, and diarrhea. NIOSH investigators made site visits at the plant in December 1994, and in March 1995.

BACKGROUND

The American Azide Corporation produces sodium azide. Elemental sodium and anhydrous ammonia are batch reacted to produce sodium amide. An amide slurry is reacted with nitrous oxide (N_2O) under pressure and increased temperature in a reactor vessel to produce a raw azide liquor which is processed through settling tanks, dissolution tanks, and a vacuum crystallizer to form a primary slurry. The primary slurry is centrifuged and dried before being transferred to a blender, where an amorphous silica flowing agent is added. The product is gravity screened to customer specifications and bulk packaged into 100 and 200 pound drums and 1200 pound bags for shipment. Reblending and repackaging are done as needed to control grain size and product consistency. The final product resembles a white crystalline powder.

The American Azide plant was constructed in 1992, is highly automated, and is operated continuously by four rotating shifts of five chemical operators and two maintenance workers. During a normal 12-hour shift, four operators each spend one-half shift in a control room and one-half shift in the plant. The fifth operator generally spends an entire shift in the plant. In the plant, operator tasks include inspection of the azide reactors, sampling product from settling and dissolution tanks, inspection of azide dryers and dislodging "heels" of caked product which often clog the bottom of the azide dryers and interfere with flow of the dried azide to the blender. Product transfer, blending, and packaging are also normal work practices in the plant. Packaging consists of an operator securing a polyethylene liner to the fill spout or locating plastic drums or cardboard containers on the fill platform. The operator controls the filling operation from a control panel in the packaging area. In January 1995, a new packaging and blending facility was built. The new blender and packaging building was configured with a suction extraction (Volkmann® vacuum system) and a screw auger to transfer azide from large transport bags (1200 pound capacity) or hundred pound drums to the blender. Dusts were expected to be reduced in the new blender building with the use of the vacuum and screw auger system and local capture ventilation (high efficiency, portable vacuums) however, the potential for azide dust (and hydrazoic acid vapor) exposure was found to exist, particularly while packing drums and during vacuum transport of the sodium azide.

Personal protective equipment (PPE) is used by the operators while performing many of their routine duties. Safety glasses and protective rubber boots are required to be worn throughout the plant. Supplied air respirators (3M™ 8300 Whitecap™ helmets and hoods), protective gloves and coveralls (in some cases TYVEK® suits), are worn by operators when packaging azide in Area 16. After work in the production and packaging areas, PPE is doffed outdoors before entry into other parts of the plant (such as the control and lunch rooms). Shower facilities are available on-site for workers when they leave the production areas.

EVALUATION CRITERIA

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria suggest exposure levels to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of wide variation in individual susceptibility, some workers may experience occupational illness even if exposures are maintained below these limits. The evaluation criteria do not take into account individual hypersensitivity, pre-existing medical conditions, or possible interactions with other workplace agents, medications being taken by the worker, or other physiologic or environmental conditions.

Evaluation criteria for chemical substances are usually based on the average personal breathing zone (PBZ) exposure to the airborne substance over an entire
8- to 10-hour workday, expressed as a time-weighted average (TWA). Personal exposures are usually expressed in parts per million (ppm), milligrams per cubic meter (mg/m^3), or micrograms per cubic meter ($\mu g/m^3$). To supplement the
8-hr TWA where there are recognized adverse effects from short-term exposures, some substances have a short-term exposure limit (STEL) for 15-minute peak periods; or a ceiling limit, a concentration which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be absorbed through direct contact of the material with the skin and mucous membranes.

The primary sources of evaluation criteria for the workplace are: NIOSH Criteria Documents and Recommended Exposure Limits (RELs),[1] the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs),[2] and the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).[3] These criteria typically change over time as new information on the toxic effects of an agent are known and become available.
The OSHA PELs reflect the economic feasibility of controlling exposures in various industries, public notice and comment, and judicial review; whereas the NIOSH RELs are based primarily on concerns related to the prevention of occupational disease. An additional complication is due to the fact that a Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO v OSHA*, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous 1971 standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A).[4] However, some states which have OSHA-approved State Plans will continue to enforce the more protective 1989 limits. In the interest of occupational health, NIOSH encourages employers to use the 1989 limits or the RELs, whichever criteria are lower.

Sodium Azide

Sodium azide (NaN_3) is a white crystalline solid which is used on a small scale in many commercial applications. Sodium azide produced in this plant is primarily sold as the nitrogen gas-generating substance for inflating automobile supplemental restraint systems (air bags). Sodium azide is soluble in water and liquid ammonia, forming hydrazoic acid (HN_3), the vapor of which may be present where sodium azide is present. It is difficult to assess the toxicity of sodium azide independently; hydrazoic acid may be the ultimate toxic agent in persons exposed to sodium azide.[5]

Sodium azide is a metabolic inhibitor with a mechanism of action similar to that of cyanide. It is mutagenic to plant and animal cells in the laboratory setting.[6,7] The cardiovascular system is the primary organ system affected by sodium azide (effects include peripheral vasodilation potentially leading to hypotension, headache, and weakness).[6,7] Exposure to NaN_3 and hydrazoic acid, at levels causing hypotension, has not been reported to be associated with any permanent adverse effects.[8,9] Ingestion of larger amounts of NaN_3 results in a variety of adverse effects and can be fatal.[10,11] Skin absorption of NaN_3 has been reported in animal studies[12,13] but is not well understood in humans.

No reliable biological monitoring technique is currently available for human exposures to NaN_3.[14,15,16] A high pressure ion chromatographic method, recently developed to measure azide ion in the blood of mice, showed the half-life of azide in mouse blood following intraperitoneal injection to be approximately
60 minutes.[17]

Most case reports of occupational exposure to NaN_3 and HN_3 involve inhalation and ingestion among laboratory workers. Symptoms included lightheadedness, weakness, blurred vision, mucous membrane, eye, and respiratory tract irritation, diarrhea, abdominal complaints, headache, low blood pressure, and palpitations.[6,7,9,10] Hypotension observed among lead azide workers exposed to hydrazoic acid was manifest within one hour of the start of shift and recovered to normal within one hour of the end of shift.[9] Headache has been reported to be the most common symptom after exposure to sodium azide and may last longer than other symptoms.[5] There have been no reports of rebound hypertension when persons are removed from exposure.[16]

NIOSH recommends ceiling limits of 0.1 (ppm) for hydrazoic acid vapor and 0.3 milligrams per cubic meter (mg/m^3) for sodium azide.[1] These limits are identical to the OSHA PELs[3] and the ACGIH TLVs[2] (also ceiling levels), and are designed to provide protection from headache and significant lowering of blood pressure.[18]

Blood Pressure

Blood pressure is affected by multiple factors, including stress, level of activity, diet, and underlying disease, which make measured changes in blood pressure difficult to categorically assign to any one cause. Although a number of studies have attempted to define "normal" ranges of blood pressure, there is no uniform definition for "normal" blood pressure or hypotension. Studies have defined normal blood pressure readings for individuals as those being within one or two standard deviations around the mean of a group to which that individual belongs.[19-22] Others have suggested absolute upper limits for "low" blood pressure of 80/50 (women) or 90/60 (men), recognizing that for some persons these values would not be far from normal.[23] An absolute drop of 10 millimeters of mercury (mm Hg) or more in the systolic or diastolic blood pressure was considered "unusual" in a study of nitrate workers.[24] Clinical trials with antihypertensive agents have used a drop of 10 mm Hg diastolic blood pressure as an indicator of clinical efficacy.[25] A standard definition of orthostatic hypotension is a drop of 20 mmHg in systolic and 10 mmHg drop in diastolic pressures.[23] Others have used the mean blood pressure (MBP) as a measure of comparison. Criteria for determining a "significant" drop in MBP have included using a decrease of 25% in an individual,[26] or a statistically significant decrease of a group.[21,27]

Many of the studies evaluating blood pressure changes among workers have been done using manual blood pressure measurements. Recently, ambulatory blood pressure monitoring (ABPM) has been used to accurately and reliably diagnose and manage hypertension in the clinical setting.[28] ABPM has been reported to reduce the error associated with blood pressure measurements by taking a larger number of measurements and eliminating the "white coat" effect (the transient increase in blood pressure associated with its measurement by a health care worker).[29] ABPM of workers has also been done at industrial sites, hospital emergency departments, and offices, as a tool to evaluate the effects of various workplace factors on blood pressure.[30-34]

METHODS

Initial Site Visit

On December 14, 1994, the initial site visit began with an opening conference and a walk-through tour of the facility. Subsequently, confidential interviews were conducted with five operators. Blood pressure measurements were taken with a standard sphygmomanometer before and after the work shifts of two operators. In an effort to gain baseline date and characterize one operation, area air sampling was performed in the main plant packaging area (Area 16) while operators filled 1200-pound bags with sodium azide. Sampling was conducted using Gilian® battery-operated constant flow personal sampling pumps calibrated on-site to

1 LPM. Sampling media consisted of 37-millimeter (mm), 5-micrometer (µm) pore size polyvinyl chloride (PVC) membrane filters connected in-line with 150/75-milligram (mg) impregnated silica gel (ISG) solid sorbent tubes (SKC® 226-55). Minimum sampling time was five minutes. The sampling and analytical method for NaN_3 and HN_3 used was the OSHA method ID-211.[35]

Follow-Up Site Visit

Industrial Hygiene

Based on observations and the results of area air sampling made during the initial site visit, on March 13-17, 1995, NIOSH investigators made a return visit to the plant to perform PBZ sampling as part of a more extensive industrial hygiene survey. During that week, PBZ and area samples were collected to characterize sodium azide and hydrazoic acid exposures during normal, routine duties of operators, using the sampling methods previously described. To evaluate personal protective equipment, samples were collected in the azide packaging area (Area 16) where supplied-air respirators were being worn by the operators. Samples were collected with the sampling media placed on the employees' lapel and inside the helmet of the air line respirators which were used at the time.

Medical

The follow-up medical evaluation was performed from March 13-14, 1995, and consisted of 1) a questionnaire survey, 2) ambulatory blood pressure monitoring, and 3) blood samples for analysis of azide level. All 10 operators working on March 13 (night shift) and 14 (day shift), and 1 maintenance worker working on March 13, were asked to participate in the evaluation. In addition, five production workers from the neighboring American Pacific Corporation ammonium perchlorate (AP) plant were asked to participate as an unexposed comparison group in the blood pressure monitoring portion of the evaluation. Both groups of employees were informed of the evaluation by both management and NIOSH personnel and provided informed consent prior to participating.

Questionnaire

A symptoms and work history questionnaire was administered at the start of the workshift to all participants in the azide plant. A brief symptom questionnaire was administered during the workshift at the time of the second venipuncture. In addition, periodically during the workshift those employees wearing the blood pressure monitors were asked about activities or work duties they had recently been performing and about current symptoms.

Blood Pressure Monitoring

Ambulatory blood pressure monitors (Advanced Medical Products, Model 5600, Columbia, South Carolina) were used to obtain multiple blood pressure measurements during the workshift. These monitors were worn under the employees' clothing and include electrocardiogram (ECG) leads and blood pressure cuffs. The monitors were used in the "patient-activated" mode (taking a measurement required that the employee activate the monitor by pressing a button). Because of the multiple factors which can affect blood pressure, our primary goal was to perform a descriptive study by evaluating the blood pressure of an individual employee over the course of the workshift, looking for significant drops below the baseline.

Each participant was asked to wear the monitor for one of their usual 12-hour shifts. As each cuff was placed on an employee, calibration was performed by comparing the blood pressure obtained by the monitor with a manual blood pressure obtained using a standard sphygmomanometer attached to the cuff and monitor via a three-way valve. If the systolic and diastolic readings from the monitor and the manual reading were not within 5 mm Hg, the cuff was readjusted until the readings were within 5 mm Hg. The first three manual blood pressure measurements which met the above criteria, taken with the standard sphygmomanometer while the participant had been seated for at least five minutes, were averaged and used as the participants' baseline blood pressure. Participants were asked to activate the monitor at least every 30 minutes, or
any time they felt symptomatic, and were instructed to discontinue movement and straighten the elbow while the blood pressure was being taken.

Prior to analysis, each record was examined for artifact. Heart rate data obtained during periods when the ECG tracings were obscured by artifact were excluded from analysis. Representative ambient temperature measurements were recorded throughout the workplace during the medical evaluation. Because the relationship between ambient temperature and blood pressure as reported in the literature is inconsistent,[24,36-38] no corrections were made to blood pressure measurements for ambient temperature. The criteria used for determining a hypotensive episode during the work shift was a decrease from baseline of at least 20 mm Hg in systolic blood pressure and of at least 10 mm Hg in diastolic blood pressure. In addition, for men, a blood pressure of less than 90 (systolic) and 60 (diastolic) was considered hypotensive; a blood pressure of less than 80 (systolic) and
50 (diastolic) was considered hypotensive for women. The Student's t-test ($p<.05$) was used as a test of significance for comparing the grouped means.

Biological Monitoring

Two blood samples were collected from each participant into evacuated EDTA-K^+-treated tubes. The first was a pre-shift sample; the second was drawn at some point during the workshift after potential exposure to sodium azide. After venipuncture the blood was frozen immediately with

dry ice. Twenty-seven quality control samples (9 known concentrations in triplicate) were prepared in the laboratory with EDTA-K^+-treated human blood, immediately frozen, and sent to the laboratory with the field samples.

Calculations to estimate a range of azide which would be expected in the blood of occupationally-exposed persons yielded estimates of 250 parts per billion (ppb); therefore, the quality control samples were prepared over the range of 0 to 6000 ppb. The samples were analyzed for azide content by a contract laboratory (Dartmouth Medical School, Department of Pharmacology and Toxicology) using a high pressure ion chromatography method.[17] Because the method for azide analysis had previously been performed only on laboratory animals, the NIOSH study at American Azide needed and received approval from the NIOSH Human Subjects Review Board. In June 1995, study participants were notified in writing of the results of their blood pressure monitoring and blood tests.

RESULTS

Initial Site Visit

In Area 16, area air concentrations of sodium azide and hydrazoic acid sampled at the bag filling station ranged from 1.0 to 7.5 mg/m^3 and 0.45 to 2.81 ppm, respectively. Samples were collected at a flow rate of 1 liter per minute and sample volumes ranged from 30 to 89 liters. All of the operators interviewed reported a history of having headaches associated with work in the production areas, specifically in Area 16, the azide packaging area. Three of the operators reported experiencing intermittent lightheadedness and weakness associated with working in production areas. Two operators reported symptoms of headache, weakness, and lightheadedness associated with blood pressures lower than their baseline (one reported a baseline blood pressure of 120/76 with decreases to 80/40; the other reported a baseline blood pressure of 126/65 with decreases to 100/50). On the day of the NIOSH site visit two operators noted mild to moderate-intensity headaches after performing a routine packaging operation (Area 16). Their blood pressure taken at that time revealed no changes from the blood pressure taken prior to the start of the shift.

Follow-Up Site Visit

Industrial Hygiene

Our walk-through survey revealed that certain operations in the production process, specifically the packaging and blending operations, as well as unscheduled maintenance operations, appeared

to have the potential for employee exposure to sodium azide and/or hydrazoic acid. PPE (including the respiratory protection discussed earlier) was worn by employees during selected operations (inspecting and "dumping" dryers, adding flowing agent to the product, and while packaging azide in Area 16). Although gloves were used by the workers, the potential for dermal exposure to sodium azide was observed in certain situations, such as when handling supplied air lines which were visibly contaminated with azide residue and when preparing to use and packing away PPE which may have had azide residue on the outside surfaces. Azide contamination also appeared to be present (and was confirmed by wipe samples) on the push bars of exit doors in certain areas of the plant. Wipe samples were collected using PVC filters to confirm azide contamination on surfaces, such as doors, that have a high likelihood for unprotected skin contact.

During the follow-up site visit 29 personal and 10 area samples were collected (Tables 1 and 2). PBZ air concentrations for NaN_3 reported as combined total particulate and vapor ranged from not detected to 1.7 mg/m^3. The minimum detectable concentration (MDC) was 0.06 mg/m^3 for sample volumes in a range of 21-88 liters (mean=54 L) and 0.02 mg/m^3 for sample volumes in a range of
106-288 liters (mean=203 L). Hydrazoic acid PBZ air concentrations ranged from not detected to 1.1 parts per million (ppm). The MDCs for HN_3 were
0.02 ppm and 0.005 ppm, respectively for mean sample volumes of 54 and
203 liters with the sample ranges mentioned previously. The analytical limit of detection for the samples was reported as 3.0 micrograms (µg) and 2.0 µg, respectively for NaN_3 and HN_3. Eight PBZ air concentrations exceeded the NIOSH REL of 0.3 mg/m^3 for sodium azide when expressed as total particulate and vapor combined as stated in the OSHA method. Four PBZ samples exceeded or equaled the NIOSH REL of 0.1 ppm for hydrazoic acid vapor. These data are presented in the Tables 1 and 2 along with the ppm amount of hydrazoic acid vapor independent of the particulate azide. Area air concentrations of sodium azide ranged from not detected (samples collected at the outdoor air intakes for instrument air and supplied air) to 0.69 mg/m^3 (sample taken in the new blender building on top of the Volkmann®). Hydrazoic acid area air concentrations ranged from not detected to 0.07 ppm (a 29 minute sample taken above dryer A as the dryer hatch cover was opened and product inspection was conducted). The area of the facility determined to have the predominant overexposures was the new blender building. No respiratory protection was used in this area as work was performed, however engineering controls were used. Portable, high efficiency vacuum collection systems were available and were used by workers to capture fugitive azide particulate escaping from drums or bags as the product was packaged into drums or as it was transferred into the Volkmann® and up the screw auger. Some work practices in this area appeared to put operators at an increased risk of exposure to azide. When operators remove empty drum liners and crumple the bag in front of themselves or against their body, air is forced from the bag toward the operator’s breathing zone. This was seen on several occasions during the NIOSH investigation and the industrial hygiene data support these observations. Samples #13, 14, 16, and 17 were made as operators transferred azide from 200 lb. drums into the Volkmann® and removed the bag liners from the empty drums. These

PBZ samples exceeded the NIOSH REL despite using an appropriate engineering control (portable high efficiency vacuums).

Azide was observed leaking at the threaded coupling of the QA/QC sample collection point of the drum filling station in the new blender building. Samples #25 and 26 which significantly exceeded the NIOSH criteria were collected during drum filling operations. These overexposures to particulate azide and in one case hydrazoic acid suggest a need for improved engineering controls in this area of production. Airborne azide may also be leaking from the Sweko or from other leaks in the filling equipment.
Two PBZ samples which approached or exceeded the REL for HN_3 and did not occur in the new blender building were measured on an operator (Sample #21) in the control room (no respiratory PPE) and on an operator (Sample #44) opening a hatch on an azide dryer. The operator working at the dryer was wearing a 3M™ Whitecap™ supplied air respirator.

To compare sodium azide and hydrazoic acid concentrations inside and outside of the air line respirators, three sets of samples (#s 42 & 43; 44 & 45; 48, 49, & 50) were taken while operators dumped a dryer and packaged azide in Area 16. In all cases, sodium azide as a particulate was not detected inside the supplied air hoods. However, in two sample sets (taken on the same operator but at different times and during a different work procedure) hydrazoic acid was detected
(7.6 µg/sample and 7.8 µg/sample, or 0.13 and 0.10 ppm, respectively) inside the hood of the respirator. In fact, the concentrations of hydrazoic acid inside the PPE in one case was double the concentration outside the hood. In both cases, the level measured inside the PPE exceeded or equaled the NIOSH REL of 0.1 ppm (as a ceiling concentration) for hydrazoic acid.

In a third sample (#43), a trace amount of hydrazoic acid (between LOD and LOQ) was detected inside the hood, and 0.05 ppm was detected outside the hood, as the operator opened a dryer hatch cover and inspected the product.

Medical

Ten operators (100% participation rate) and one maintenance person from the azide plant, and five operators from the ammonium perchlorate (AP) plant, participated in the follow-up medical evaluation. All participants from the azide plant answered the questionnaires. The azide participants included 10 men and
1 woman; ages ranged from 27 to 42 years, with a mean of 33. None of the azide participants reported a history of high blood pressure. During our evaluation, seven of the operators had duties during their shift divided between the control room and the production areas, and the other three operators and the maintenance person worked only in the production areas. The AP plant participants, whose participation included wearing the blood pressure monitors only, included four men and one woman; ages ranged from 19 to 50 years, with a mean of 32. One of the AP plant participants reported having high blood pressure in the past, but none reported taking

medication for high blood pressure.

Information concerning symptoms occurring in the last six months is presented in Tables 3 and 4. Headache was the most common symptom reported; the headaches most commonly occurred in the packing areas of the plant. Nine of the 11 participants reported at least one instance in the last six months of 'low' blood pressure occurring after working in a production area (an automatic blood pressure cuff is available to all employees in a central area). The 'low' blood pressures reported in the questionnaires ranged from 77/40 to 102/40.

The only symptoms reported during our ambulatory blood pressure monitoring were mild headaches in four employees. Two reported the headaches after using the Volkmann® in the new blender building, one after working near the amide reactors, and one after working in the filter wash area. A PBZ air sample on one of the operators was obtained one hour prior to the report of the headache, while the operator was using the Volkmann® ; air levels of sodium azide and hydrazoic acid were 0.16 mg/m^3 and 0.02 ppm, respectively, during the 153-minute sample, which included a lunch break.

Blood Pressure Monitoring

Ten of the 11 azide employees participated in the blood pressure monitoring portion of the evaluation. Nine of the ten wore the monitors for the majority of a shift (approximately nine hours); one wore the monitor for approximately five hours. All five operators from the AP plant participated in the evaluation by wearing blood pressure monitors for a portion of their shift (approximately four hours). Table 5 presents the blood pressure data. The difference between the number of "BP Attempts" and "BP Obtained" in Table 5 is due to the monitor not recording a blood pressure during a cycle. The inability of the monitor to record a blood pressure when activated may be due to a number of factors, some of which include excessive noise, excessive motion, or improper positioning of the arm. No data were recorded for one of the AP employees (number 11), due to cuff slippage.

Table 6 presents the heart rate data. The difference between the number of "HR Attempts" and "HR Obtained" in Table 6 is due both to the monitor not recording a heart rate during that activation cycle (as above), and to the exclusion from analysis of those measurements affected by artifact (as discussed in Methods). The source of the artifact in all cases appeared to be disrupted connection of the ECG leads, probably due to movement.

One employee (employee #5 in Tables 5 and 6) met our criteria for hypotension during a workshift, with a blood pressure decrease from a baseline of 119/81 to 99/62 and 98/66 in measurements taken one-half hour apart while the employee was performing a packaging operation (Table 7). This employee was monitored for approximately five hours and had three sets of ABPM measurements obtained during that time. Monitoring was discontinued at the employee's request. The employee reported no symptoms throughout the workshift (including

after the ABPM ended). A blood pressure taken manually 60 minutes after packaging was complete, while the employee was on break, revealed a blood pressure of 116/78. This employee was working in the new blender building filling drums with sodium azide. A PBZ air sample (#25 in Table 1) collected on this operator during the packing operation (and one hour after the last blood pressure measurement) revealed the highest particulate sodium azide and combined total azide levels measured in this study (1.7 mg/m^3).

Seven of the azide participants were monitored while working in both the control room and the production areas of the plant (Table 8). For each individual, we found no significant differences between the mean blood pressure in the control room and that in the production area. Three persons had a significantly higher mean heart rate in the production area. When the data from these seven participants were evaluated together (Table 9), there were no significant differences in the mean blood pressures between the control room and the production area. The mean heart rate in the production area (99) was higher than that in the control room (83) ($p<0.01$).

Biological Monitoring

Eight of the participants provided paired blood samples for azide analysis, and two provided a single blood sample. The analysis of the quality control samples revealed a limit of detection (LOD) of the analytic method of 2800 ppb, with
47% recovery above the LOD. None of the participants' blood had detectable azide concentrations.

DISCUSSION

Our data show that exposures exceeding the NIOSH REL for both sodium azide and hydrazoic acid are occurring at this sodium azide production plant. Exposures were documented primarily in the new blender building, during both packaging and azide transfer operations using the Volkmann® vacuum. In this area respiratory PPE was not worn by workers. In the main plant, exposure potential was documented in the packaging area (Area 16) and in the dryer area (when opening dryer hatches and inspecting product). Respiratory PPE is commonly worn in these areas. The industrial hygiene sampling results indicate that the 3M™ Whitecap™ helmet air line respirators appear to be effective in protecting the operators from sodium azide particulate exposure, but not hydrazoic acid vapor exposure. In fact, hydrazoic acid levels measured inside the helmets were similar or greater than levels outside the helmets. In two of the three cases, concentrations of hydrazoic acid exceeded the REL. The reasons for this are not

immediately clear. It is possible that azide residue on an operator's clothing or hair or inadequately decontaminated PPE (helmets and hoods) are responsible for the release of hydrazoic acid. This may be due to particulate azide hydrolyzing upon contact with moisture from perspiration or exhaled breath. This may explain the anecdotal reports NIOSH investigators received from workers that headaches and episodes of hypotension were occurring despite the

use of respiratory PPE. The reasons for hydrazoic acid detected in the control room are also not clear, but it could be due to sodium azide-contaminated clothing releasing hydrazoic acid, or the acid vapor entering the ventilation system of the control room.

Most of the workers surveyed reported headache and palpitations in the past six months while working in the production areas. While these symptoms are not specific for azide exposure, given our environmental data, these symptoms could be secondary to exposure to sodium azide or hydrazoic acid, and could be related to episodes of hypotension. Nine of the 11 participants reported at least one episode of self-documented 'low' blood pressure using an automatic BP cuff supplied by the company after they worked in the azide production area.

During our evaluation, four persons reported mild headaches after working in the production areas. Two of these persons reported these symptoms after performing packaging in the new blender building, a procedure where exposures above the REL were documented by our air sampling. One operator, who was asymptomatic, met our criteria for a hypotensive episode while packing drums in the new blender building and was found to have exposure to sodium azide five times the NIOSH REL.

There are very few studies examining occupational inhalation exposure to sodium azide and resultant health effects. Exposure of workers to hydrazoic acid at levels between 0.3 and 3.9 ppm caused "rapid and severe" fall in blood pressure among lead azide workers.[9] Studies of sodium azide as a hypotensive agent revealed that 0.65 - 1.3 mg, administered orally, can cause hypotension among hypertensive humans.[8] The basis for the current limits of exposure involves the known hypotensive action of sodium azide at low levels combined with a "reasonable" margin of safety.[18]

It is not clear why, given the exposures to sodium azide and hydrazoic acid which were documented in our evaluation, relatively few symptoms were reported during our site visit. This may in part be explained by significant differences which exist in the "sensitivity" of different individuals to the effects of sodium azide.[8] Further industrial hygiene and medical evaluations are needed to more accurately assess the exposure-response relationship for sodium azide.

Our definition of a hypotensive episode, as with others used in the literature,[26,28] is somewhat subjective. Because of the large number of variables which can effect blood pressure, we have chosen our criteria to be relatively conservative (specific) for detecting a drop in blood pressure. The use of other criteria for hypotension, (such as that utilizing the standard deviation around the mean of another population), may not be appropriate in our descriptive study with a small number of observations. In addition, we did not use the mean blood pressure of our small group of azide workers as a comparative standard because of potential bias of the data towards finding no effect (employees who have intermittent exposure to sodium azide could potentially have more variation in blood pressure).

There are several limitations to our blood pressure data. First, the baseline blood pressure, taken in a setting which could give rise to a "white coat hypertension" effect, may be artificially high. Second, four participants changed clothing and showered when changing from plant duty to control room duty; the blood pressure monitors were not re-calibrated when the cuff was placed on for the second time. And third, the small number (three) of blood pressure measurements taken on the operator found to have a hypotensive episode does not allow for multiple comparisons of that person's blood pressure during other activities in which there was no exposure to sodium azide. Despite these factors and the substantial variation in blood pressure among all those monitored (which was expected), the only drop in blood pressure which met our criteria for hypotension occurred during a time when the operator was documented to have exposure to sodium azide at more than five times the NIOSH REL (the highest level measured in our study).

The biological monitoring was not successful due to limitations of the analytical method in detecting azide in the part per billion range. The lack of a method to monitor the absorbed dose of sodium azide decreases our ability to correlate the reported non-specific symptoms and observed changes in blood pressure with the measured environmental exposures to sodium azide and hydrazoic acid.

RECOMMENDATIONS

1. American Azide should conduct a complete industrial hygiene evaluation to characterize all areas of the plant having the potential for sodium azide and hydrazoic acid exposures. Because routes of exposure to sodium azide and hydrazoic acid include inhalation and ingestion, and may include skin absorption, all routes of exposure should be considered in the industrial hygiene survey.

    a. Ongoing automation and improvements in the production process should be beneficial in reducing employee exposure to sodium azide and hydrazoic acid. When there are significant engineering or process changes, an industrial hygiene evaluation should be conducted in those areas to document exposures and evaluate the need for engineering controls.

    b. Engineering controls (such as the use of local exhaust ventilation) should be developed to control airborne levels of sodium azide and hydrazoic acid. When engineering controls are found to be inadequate, based on the industrial hygiene survey, personal protective equipment should be used to protect employees.

    c. American Azide should investigate why, despite using air line respirators, operators are exposed to hydrazoic acid. Workers should be instructed in the proper use and application of the PPE, specifically the need for adequate decontamination after use and the importance of preventing clothing from becoming contaminated with azide residue.

2. Employees should be encouraged to report to their supervisor symptoms and work practices which may be associated with sodium azide or hydrazoic acid exposure. This data should be retained as a log and reviewed periodically to aid in the identification of areas in the plant or specific job tasks which may be associated with exposures to sodium azide or hydrazoic acid.

3. Work practices in the new blender building should be modified to reduce operator's risk of exposure to particulate azide when removing and disposing of the plastic liners from the cardboard drums of azide. Closing the empty bag around the vacuum hose and removing the air from the drum liner before it is removed from the drum may be practical. Additionally, capture velocity can be improved with the addition of a small circular flange, or bell mouth attachment to the end of the portable vacuum hose.

4. More effective local exhaust ventilation should be used in the new blender building at the drum filling station. The practice of damp wiping azide residues from packed drums should be discontinued, this practice could result in the release of hydrazoic acid. Vacuum methods would be one option for consideration.

5. An assessment should be made to evaluate PBZ exposures when operators disconnect from supplied air lines and move (unprotected) from floor to floor after dumping a dryer. The work practices which were observed involved inspecting and dumping the dryer then when the operators were finished, disconnecting from the supplied air manifold and walking down the stairs to the next landing and connecting back onto the supplied air system. Exposure to particulate azide or hydrazoic acid vapor is possible during the time when the operators are not using the air-line system. If exposures are determined to exceed the REL, use of a NIOSH-approved air-line respirator with an auxiliary self-contained air supply with sufficient breathing air to insure protection when the operator disconnects from the airline and moves from floor to floor is recommended. NIOSH currently assigns a protection factor of 25 (protection to 25 times the REL) for loose fitting hoods and helmets under the approval TC-19C-69, which would include the 3M™ Whitcap™ helmet system.

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AUTHORSHIP AND ACKNOWLEDGEMENTS

Report prepared by:

Eric J. Esswein, M.S.P.H.
Industrial Hygienist
Industrial Hygiene Section

Douglas B. Trout, M.D., M.H.S.
Medical Officer
Medical Section

Thomas Hales, M.D.
Chief
Medical Section

Field Assistance: Gina Solomon, M.D.
Michael B. Miller, D.O., M.P.H.

Originating Office: Hazard Evaluations and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations and Field Studies

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Table 1 - Personal Sampling Results
HETA 95-0023, American Azide Co., March 1995

Sample #	Title/Location/Activities	Time Sampled (minutes)	NaN_3[1] (mg/m^3)	HN_3[1] (ppm)	Total- NaN_3 +HN_3(mg/m^3)
9	Operator, New Blender Bldg	55	N.D.	Tr.	Tr.
10	Operator, New Blender Bldg	50	0.22	Tr.	0.22
11	Maintenance, Area 16	284	Tr.	0.03	0.09
12	Rover (through entire plant)	284	Tr.	0.02	0.05
13	Operator, New Blender Bldg	59	**0.32**	0.04	**0.43**
14	Operator, New Blender Bldg	64	**0.83**	0.05	**0.97**
15	Operator, Control Room	288	N.D.	0.02	0.05
16	Operator, New Blender Bldg	68	0.21	0.04	**0.31**
17	Operator, New Blender Bldg	68	**0.54**	0.04	**0.66**
18	Operator, at Centrifuge	196	Tr.	0.03	0.09
19	Operator, Area 16, packing	88	Tr.	Tr.	Tr.
20	Operator, Dumping Dryer	8	#	**1.1**	#
21	Operator, Control Room	79	N.D.	0.07	0.19
22	Operator, Dumping Dryer	47	0.23	Tr.	0.23
23	Operator, Area 16, Driving Fork Lift	78	0.13	Tr.	0.13
24	Operator, at Centrifuge	58	N.D.	0.05	0.15
25	Operator, New Blender Bldg.Packing Drums	106	**1.6**	0.06	**1.7**
26	Assisting Operator, New Blender Bldg-Packing Drums	135	**0.63**	**0.10**	**0.90**
33	Operator, adding H_2O to Sedimentation Tank	20	N.D.	N.D	N.D.
42	Operator, Opening Dryer Sample Inside Hood	21	N.D.	Tr.	Tr.
43	Operator, Opening Dryer Hatch, Sample on Lapel	44	Tr.	0.05	0.14
44	Operator, Opening Dryer Hatch, Sample Inside Hood	32	N.D.	**0.13**	**0.34**
45	Operator, Opening Dryer Hatch, Sample on Lapel	45	N.D.	0.06	0.16

Table 1 Continued - Personal Sampling Results
HETA 95-0023, American Azide Co., March 1995

46	Operator, New Blender Bldg-Using Volkmann®, xfering Azide	153	0.16	0.02	0.21
47	Operator, Driving Fork Lift, Area 16, when packing	62	0.16	N.D.	0.16
48	Operator, Drum Packing Azide, Area 16 Sample on Lapel	33	N.D.	N.D.	N.D.
49	Operator above, New sample	25	Tr.	N.D.	Tr.
50	Operator above , Inside Hood	43	N.D.	**0.1**	0.28

[1] **NIOSH RELs (Ceiling): Sodium azide - 0.3 mg/m^3,**
Hydrazoic acid vapor - 0.1 ppm.

N.D. = not detected, MDC = 0.02 - 0.06 mg/m^3 (NaN_3) and 0.02 - 0.005 ppm (HN_3)
 # = filter cassette fell into dryer, laboratory analyzed with 7800 micrograms/sample
Tr = trace, (concentration between LOD and LOQ)

Table 2 - Area Sampling Results
HETA 95-0023, American Azide Co., March 1995

Sample #	Location	Time Sampled (min)	NaN_3 (mg/m^3)	HN_3 (ppm)	Total-NaN_3+HN_3 (mg/m^3)
34	New Blender Bldg, atop Volkmann®	55	0.69	Tr.	0.69
53	Area 16	110	N.D.	Tr.	Tr.
54	Area 16 - Right of drum packer	108	Tr.	Tr.	Tr.
55	Sweko, PBZ height	114	0.11	0.04	0.18
56	D Cell, 1st Floor Reactor Bay	426	N.D.	N.D.	N.D.
57	Dryer Area	413	0.09	0.04	0.18
58	E Cell, 1st Floor Reactor Bay	424	N.D.	Tr.	Tr.
59	"A" Dryer, 2 ft above dryer as dryer hatch was opened	29	Tr.	0.07	0.13
60	Outside Air Intake	204	N.D.	N.D.	N.D.
61	Outside Air Intake	204	N.D.	N.D.	N.D.

[1] NIOSH RELs (Ceiling): Sodium azide - 0.3 mg/m^3, Hydrazoic acid vapor - 0.1 ppm;
Tr = trace, (concentration between LOD and LOQ)

Table 3 - Frequency of Symptoms Reported by 11
American Azide Employees in Last Six Months
HETA 95-0023, American Azide, March, 1995

SYMPTOM	Number of times in the last six months			
	Never	1-2	3-7	>8
Headache	1	5	5	0
Lightheadedness	6	3	2	0
Increased heart rate or palpitations	2	4	4	1
Eye irritation	9	2	0	0
Decreased blood pressure	2	6	3	0

Table 4 - Frequency of Headache Reported by 11 American
Azide Employees in Last Six Months by Location
HETA 95-0023, American Azide Co., March 1995

LOCATION	Number of times in the last six months			
	Never	1-2	3-7	>8
Re-blending Area	6	3	2	0
Packing Area	2	5	4	0
Control Room	10	1	0	0
Other	9	0	0	0

Table 5 - Ambulatory blood pressure monitoring data - blood pressure data
HETA 95-0023, American Azide Co., March 1995

Emp[1].	Baseline BP	Time Measured	# BP Obtained[2]/ Attempts[3]	Mean BP +/- SD[4]	S_{max}[5]	S_{min}[5]	D_{max}[6]	D_{min}[6]
1	115/80	9:50	11/14	119/78 +/- 7/5	128	108	89	72
2	115/90	7:58	12/16	118/82 +/- 7/5	129	105	91	72
3	131/98	9:30	6/11	139/97 +/- 9/6	153	126	102	88
4	135/98	9:21	16/18	130/84 +/- 7/7	144	122	99	70
5	119/81	4:56	3/5	103/68 +/- 7/7	111	98	76	62
6	115/79	9:46	11/28	132/83 +/-11/12	150	115	106	61
7	136/92	10:05	12/15	129/87 +/- 7/6	143	121	96	76
8	101/79	10:17	10/19	105/73 +/- 13/8	135	93	89	64
9	113/82	9:00	15/17	129/83 +/-12/13	154	112	105	58
10	118/84	8:36	14/17	125/84 +/- 10/8	146	109	94	72
11(AP)		4:08	N/A[7]					
12(AP)	120/81	4:05	6/6	122/89 +/- 4/5	82	95	116	125
13(AP)	109/77	4:15	16/16	121/79 +/- 9/7	142	106	89	65
14(AP)	99/72	3:51	7/8	107/78 +/- 6/7	119	98	88	69
15(AP)	106/77	3:25	3/7	125/87 +/- 7/2	131	117	89	85

[1] Employees 1-10: Azide employees; 11-15: AP employees. [2] Number of blood pressure measurements obtained by monitor. [3] Number of times monitor was activated. [4] Mean pressure obtained throughout monitoring period +/- standard deviation. [5] Maximum and minimum systolic blood pressure during monitoring period. [6] Maximum and minimum diastolic blood pressure during monitoring period. [7]No measurements taken.

Table 6 - Ambulatory blood pressure monitoring data - heart rate data
HETA 95-0023, American Azide Co., March 1995.

Emp[1].	Time Measured	# HR Obtained[2]/ Attempts[3]	Mean HR +/- SD[4]	HR_{max}[5]	HR_{min}[5]
1	9:50	11/14	92 +/- 10	113	78
2	7:58	14/16	100 +/- 33	167	74
3	9:30	3/11	103 +/- 11	115	93
4	9:21	9/18	93 +/- 8	107	81
5	4:56	4/5	95 +/- 18	118	77
6	9:46	11/28	100 +/- 13	128	83
7	10:05	12/15	108 +/- 15	130	85
8	10:17	10/19	104 +/- 17	130	78
9	9:00	15/17	73 +/- 4	81	66
10	8:36	14/17	87 +/- 11	109	75
11	4:08	N/A[6]			
12	4:05	5/6	96 +/- 6	101	88
13	4:15	16/16	78 +/- 10	101	64
14	3:51	7/8	104 +/- 12	120	82
15	3:25	5/7	87 +/- 11	104	79

[1] Employees 1-10: Azide employees; 11-15: AP employees.
[2] Number of heart rate measurements obtained by monitor.
[3] Number of times monitor was activated.
[4] Mean heart rate +/- standard deviation.
[5] Maximum and minimum heart rate during monitoring period.
[6] No measurements taken.

Table 7 - Ambulatory blood pressure monitoring of individual
American Azide employee
HETA 95-0023, American Azide Co., March 1995.

TIME	Blood Pressure	Heart Rate
1000 (Set-up)	119/81[1]	Not obtained
1025	111/76	77
1101	99/62	84
1134	98/66	102
1327	Not obtained	118

[1] Baseline blood pressure.

Table 8 - Mean values and standard deviation for systolic and diastolic blood pressures and heart rate: Control room versus production areas by individual HETA 95-0023, American Azide Co., March 1995.

Employee	Measurement	Control Room	Production Area
2	SBP[1] +/- SD	120 +/- 8	114 +/- 5
	DBP[2] +/- SD	82 +/- 4	81 +/- 9
	HR[3] +/- SD	81 +/- 5 [4]	148 +/- 19 [4]
3	SBP	133+/- 6	144 +/- 9
	DBP	97 +/- 5	96 +/- 7
	HR	N/A[5]	N/A
4	SBP	130 +/- 6	130 +/- 7
	DBP	86 +/- 7	82 +/- 7
	HR	N/A	N/A
7	SBP	126 +/- 3	132 +/- 9
	DBP	89 +/- 5	85 +/- 8
	HR	97 +/- 8 [4]	123 +/- 6 [4]
8	SBP	96 +/- 4	108 +/- 14
	DBP	68 +/- 4	74 +/- 8
	HR	91 +/- 12	109 +/- 16
10	SBP	130 +/- 6	128 +/- 16
	DBP	81 +/- 7	85 +/- 17
	HR	74 +/- 4	73 +/- 5
11	SBP	122 +/- 11	128 +/- 8
	DBP	81 +/- 9	87 +/- 6
	HR	80 +/- 5 [4]	95 +/- 11 [4]

[1]Systolic blood pressure. [2]Diastolic blood pressure. [3]Heart rate. [4]Statistically significant difference between control room and production area, $p<.05$. [5] No data available.

Table 9 - Ambulatory blood pressure monitoring data:
Control room versus production areas by group
HETA 95-0023, American Azide Co., March 1995.

	# Participants[1]	# Measurements[2]	Mean Value - Control Room	Mean Value - Production Areas
Systolic BP	7	110	124 +/- 11	125 +/- 14
Diastolic BP	7	110	84 +/- 8	82 +/- 11
Heart Rate	7	103	83 +/- 10[3]	99 +/- 20[3]

[1]During our evaluation seven participants worked in both the control room and the production areas of the plant while being monitored.
[2]Total number of blood pressure or heart rate measurements made among the seven participants.
[3]Statistically significant difference between control room and production area, $p<0.01$.