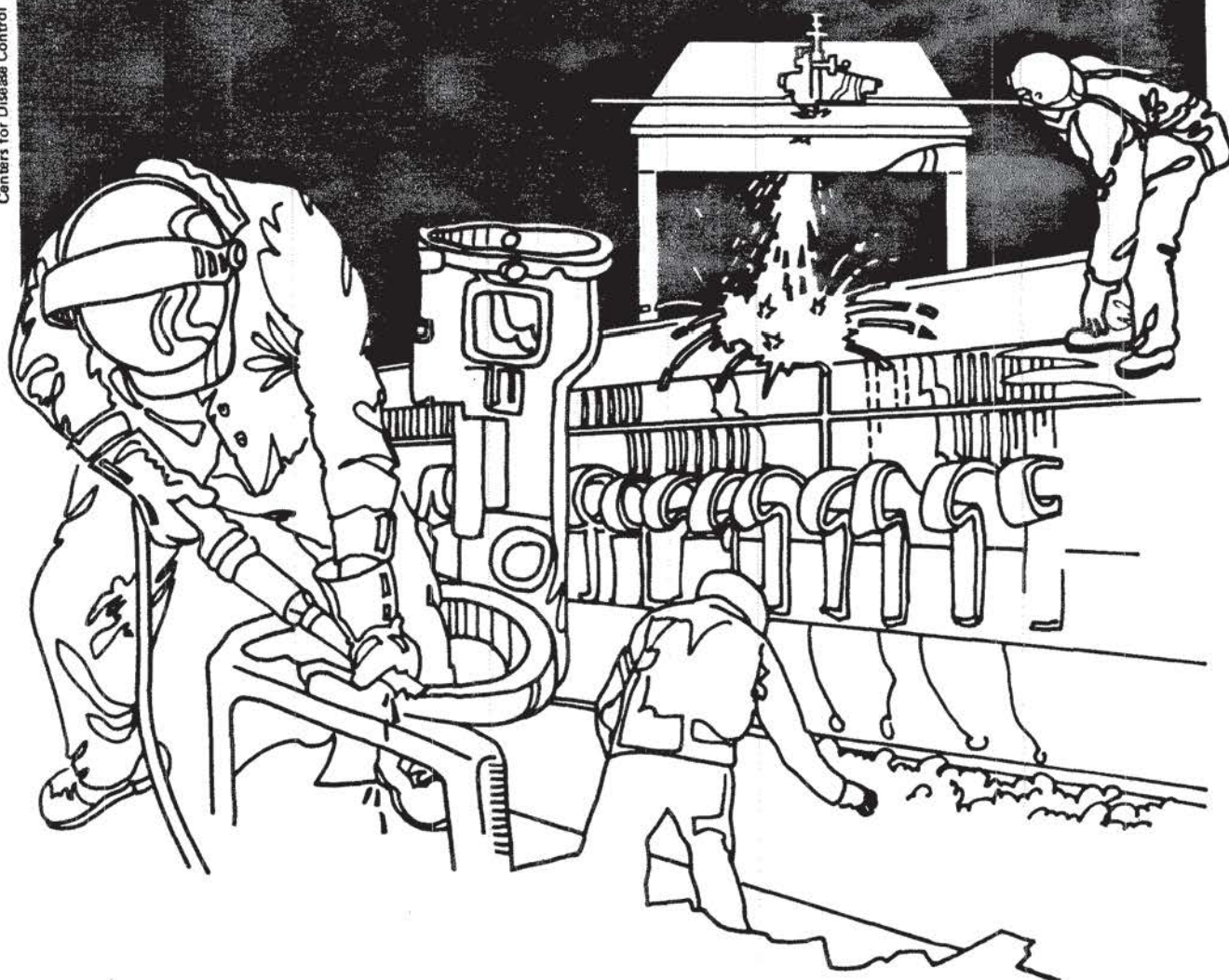


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NIOSH



Health Hazard Evaluation Report

HETA 81-003-980
BABCOCK AND WILCOX COMPANY
MILWAUKEE, WISCONSIN

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 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.

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.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-003-980
October 1981
Babcock and Wilcox Company
Milwaukee, Wisconsin

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I. SUMMARY

On October 1, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Brotherhood of Boilermakers Union, Local 1849, for a Health Hazard Evaluation of the Babcock and Wilcox Company - Tubular Products Division, Milwaukee, Wisconsin. The request involved the potential for employee exposure to biocides, dispersant and anti-scaling agents as they are added to four separate circulating water systems which cool four annealing furnaces, two reheat furnaces and one air compressor.

NIOSH conducted a combined environmental and medical survey at the Milwaukee facility on November 19-20, 1980. While conducting a walk-through survey on November 19, 1980, NIOSH observed that furnace operators working near cooling systems were potentially exposed to cooling system chemicals. The furnace operators were included in employee monitoring on November 20, 1980. Environmentally the survey involved collecting general and personal airborne samples for dimethylformamide and detector tube monitoring for oxides of nitrogen [nitrogen dioxide (NO₂) + nitric oxide (NO)] and carbon monoxide (CO). Medically the survey involved administering questionnaires to potentially exposed employees.

Results of this evaluation indicate that on the day this survey was conducted, the lubricator and furnace operators were not exposed to hazardous levels of dimethylformamide, carbon monoxide, or oxides of nitrogen (NO + NO₂). Concentrations of seven airborne samples for dimethylformamide ranged from below the limit of detection to 1.01 parts per million (ppm). Airborne concentrations obtained with certified direct reading indicator tubes were 10-15 ppm for carbon monoxide and only trace amounts (less than 2.0 ppm) for oxides of nitrogen (NO + NO₂). All concentrations obtained were below current environmental criteria.

Medical interview data suggested that workers may have been exposed to potentially hazardous levels of DMF in the past.

Based on the results of this survey, NIOSH concludes that on the day the field survey was conducted a health hazard did not exist for the lubricator while adding chemicals to cooling systems or to furnace operators working in the vicinity of the cooling systems. Recommendations are included concerning storage of chemicals and use and storage of personal protective equipment.

Keywords: SIC 3317 (steel pipe and tubes), biocide, dispersant, anti-scaling, circulating water system, dimethylformamide, carbon monoxide, nitrogen dioxide, nitric oxide, hyperglycemia, alcohol intolerance.

II. INTRODUCTION

In October, 1980, NIOSH received a request from the International Brotherhood of Boilermakers Union, Local 1849, to conduct a health hazard evaluation at the Babcock and Wilcox Company - Tubular Products Division, Milwaukee, Wisconsin to evaluate potential employee exposure to biocides, dispersants and anti-scaling agents. These agents were added to four separate circulating water systems which cool four annealing furnaces, two reheat furnaces and one air compressor. Addition of chemicals to the cooling systems required approximately one hour, and was done three times each week. Responsibility for this task was assigned to one employee from the lubricating department on a six-month rotating basis. Symptoms reported in the request included nausea, blurred vision, dizziness, diarrhea, skin rash, and facial flushing.

III. BACKGROUND

The Milwaukee facility was established in 1910 as the Globe Steel Tube Company. Babcock and Wilcox purchased the facility in 1955. This plant manufactured seamless steel tubing ranging in size from 1/2 to 8-5/8" outer diameter. Tubing produced at this facility was processed through one of two mills. Larger tubing (4 - 8-5/8") was processed through Mill No. 1 and smaller tubing (1/2 - 5") through Mill No. 2. The first step in the manufacturing process involved cutting 30-38' solid steel cylinders (billets) into smaller units. These shorter cylinders were sent through a series of processing operations, that included heating, piercing, annealing, drawing, reducing, straightening, and inspection. Tubing produced at this facility was used in power plants, oil wells, and the automotive industry.

On November 19-20, 1980, NIOSH conducted a combined environmental and medical survey at the Milwaukee facility. An opening conference and initial walk-through survey were conducted with representatives from union and management. Interviews were held with employees, union representatives, and management personnel.

Interim report no. 1 was distributed in March, 1981. It discussed findings to date, future actions, and recommendations resulting from the initial plant visit. Interim report no. 2 was distributed in October 1981. It discussed environmental results of airborne sampling for dimethylformamide.

IV. METHODS AND MATERIALS

Environmental

The work practices of a lubricator were observed while he was adding chemicals to the cooling systems. During the walk-through survey it was noted that furnace operators who work in the vicinity of the furnace cooling systems were also potentially exposed to cooling system chemicals.

The lubricator's and furnace operators' exposures were evaluated using personal and area silica gel sampling trains. The silica gel tubes were analyzed for dimethylformamide (DMF) using a gas chromatograph equipped with a flame ionization detector following a modification of NIOSH Method S-225.¹ A 12' X 1/8" stainless steel column packed with 5% FFAP on 40/60 Chromosorb T was used at an oven temperature of 120°C. The limit of detection was 0.01 nanogram per milliliter (ng/ml) DMF. DMF was selected for analysis because it is used in greater proportions than other components of the cooling system chemicals and because health concerns stated in the request are consistent with exposure to it. Certified direct reading detector tubes were used to evaluate airborne concentrations of carbon monoxide (CO) and oxides of nitrogen (NO_x) that might potentially arise from the annealing furnaces. Measurement for NO_x by the detector tubes used is nonspecific in that the separate levels of nitrogen dioxide and nitric oxide cannot be determined.

Medical

Three workers were interviewed by the NIOSH physician.

V. EVALUATION CRITERIA

DMF is a colorless liquid with a variety of industrial uses. It has been used as a solvent for liquids and gases and is especially useful when a solvent with a slow rate of evaporation is needed.²

Exposure of humans to DMF has resulted in several reported symptoms, not all of which necessarily appear in a single individual. Eleven synthetic fiber workers were described by Tolot et al. (3) as having prominent symptoms of nausea, vomiting, epigastric or esophageal burning, abdominal pain, diarrhea, loss of appetite, nervousness, and troubles with sleeping. Burning eyes, skin irritation, and alcohol intolerance also were reported within this group. Reinl and Urban (4), in describing 13 workers from the polyacrylonitrile industry with exposure to DMF, reported gastro-intestinal symptoms similar to those described above plus specific evidence of liver abnormality (enlarged liver, right upper quadrant abdominal pain, jaundice, light stool with dark urine, and elevated serum liver enzymes). Other reported symptoms and signs included headache, dizziness, weakness, back pain, loss of weight, scratchy throat, nose bleed, palpitations, skin eruption, and elevated urine porphyrins. Symptoms and lab abnormalities resolved after exposure was stopped. Tolot et al. (5) reported psychological effects (anxiety, agitation, effects on dreaming) with severe acute abdominal pain, epigastric pain, nausea, diarrhea, and loss of weight in a worker with a single episode of high inhalation exposure. Liver biopsies three and four months after the event showed diffuse vacuolation; liver enzyme and liver function tests were normal at that time.

Potter (6) reported a case in which a worker experienced a single episode of combined skin and respiratory exposure to DMF. The immediate symptoms were skin redness and irritation. However, 62 hours later the worker experienced severe epigastric and abdominal pain that spread to the chest and thighs. He was found to have elevated blood pressure, enlarged nontender liver, elevated white blood cell count, and positive tests for urine porphobilinogen but had no objective neurological signs and no abdominal tenderness, rebound tenderness, or rigidity despite his

agonizing abdominal pain. On the third day following onset of symptoms, the pain and blood pressure elevation resolved and the urine test for porphobilinogen became negative.

Experimental data from exposure of cats and rabbits to DMF has shown fatty liver degeneration, with or without necrosis. In addition, some cats showed elevated blood sugar for up to 24 hours, with sugar in the urine, after intraperitoneal injection of DMF.⁷

Skin absorption can be a major contributor to the body burden of DMF.⁸ Lauwerys⁽⁹⁾ found that worker volunteers in acrylic fiber production developed DMF metabolite levels in the urine that were three times higher when they wore self-contained breathing apparatus but no skin protection when compared to wearing long-sleeved impermeable gloves but no breathing protection. Efforts to quantify skin absorption had to be terminated because two of the seven volunteers developed incapacitating abdominal symptoms within two days of working without gloves.

The TLV for DMF was established in reference to inhalation exposure. In general, the current ACGIH and OSHA environmental criteria of 10.0 ppm based on an 8 hr time-weighted average (TWA) are considered to provide a level below which workers would not be expected to experience any adverse health effects from inhalation exposure. Both criteria have notations concerning the fact that skin absorption is an additional consideration.^{10,11}

Alcohol intolerance following DMF exposure is a common finding. Consumption of as little as one half pint of beer within a few hours to four days following DMF exposure can result in onset of marked facial flushing, chest tightness, shortness of breath, dizziness, and nausea that develop within a few hours of the alcohol ingestion.^{12,13} DMF causes this effect by impairing the liver's ability to metabolize alcohol, which results in build-up of acetaldehyde in the body.¹² Compliance with the current environmental criteria for airborne exposure of 10 ppm for DMF does not necessarily prevent such alcohol-induced symptoms.¹⁰

Environmental criteria for CO range from 35 ppm/10 hr TWA for NIOSH to 50 ppm/8 hr TWA for OSHA and ACGIH.^{10,11} Environmental criteria for oxides of nitrogen are 25 ppm for NO₂ (NIOSH, OSHA and ACGIH) and range from 1.0 ppm (for NIOSH as a ceiling value) to 5.0 ppm for NO (OSHA and ACGIH).^{10,14}

VI. RESULTS AND DISCUSSION

Environmental

Results of environmental samples collected for DMF are included in Table I. A total of seven airborne samples were collected. DMF concentrations ranged from below the limit of detection to 1.01 parts per million (ppm). These values are all below the present environmental criteria of 10 ppm for both the OSHA permissible exposure limit (PEL) and the ACGIH threshold limit value (TLV).^{10,11} The highest level obtained was for a sample worn by the lubricator while he was adding chemicals to the cooling systems. Chemical addition required 25 minutes on the day of the NIOSH survey. A second sample worn by the same lubricator for the entire shift had an airborne concentration of 0.15 ppm.

Certified direct reading indicator tubes were used to evaluate the potential for employee exposure to CO and NO_x (NO + NO₂) while working near annealing furnaces. Concentrations for CO ranged from 10 to 15 ppm. The values were less than 50% of the current environmental criteria which range from 35 ppm/10 hr time-weighted average (NIOSH) to 50 ppm/8 hr time-weighted average (OSHA and ACGIH).^{11,14} Concentrations for NO_x were below 2.0 ppm which was the lowest scale reading on the detector tubes. Only trace amounts of NO_x were detected. The detector tubes used to sample for oxides of nitrogen collected NO and NO₂ simultaneously. The trace amounts detected indicate that concentrations for both gases were below current environmental criteria which are 25.0 ppm for NO₂ and range from 1.0 ppm (NIOSH-ceiling value) to 5.0 ppm (OSHA and ACGIH) for NO.^{11,14}

The lubricator was wearing a chemical cartridge respirator, goggles, protective apron, gloves and sleeves while adding chemicals to the cooling systems. These should reduce the potential for chemical exposure. However, the employee seemed unfamiliar with basic respirator qualitative fit tests which the respirator user can utilize at his work site. Maintenance and storage of some of the personal protective equipment (apron, gloves, sleeves) was inadequate. Protective equipment and the buckets used to transport chemicals were stored in the same cabinet.

The lubricator did not wear protective clothing while collecting samples of cooling system material for laboratory analysis. The lubricator splashed liquid on his hand while collecting samples. Gloves would reduce the potential for skin absorption.

Medical

The lubricator who added chemicals to the water-cooling systems at the time of the NIOSH visit and the other employees who had held the position for the two prior six-month intervals were interviewed. Symptoms reported included headaches, lightheadedness, dizziness, nausea, vomiting, muscle aches, fatigue, intervals of blurred vision, nose bleeds, mood fluctuations, occasional intolerance of even small quantities of alcohol, increased thirst, and increased urination.

All but three of these symptoms were consistent with previous case reports of respiratory or skin exposure of humans to DMF. The remaining three symptoms--intervals of blurred vision, increased thirst, and increased urination--were suggestive of possible hyperglycemia and might be consistent with the experimental finding in cats of transient blood sugar elevation after DMF exposure.

VII. RECOMMENDATIONS

1. Chemicals presently stored outside of the existing chemical storage enclosure should be moved into the enclosure. In addition, containers of chemicals should not be permitted to stand open. Chemical containers that might be exposed to water spills should be elevated to prevent corrosion.
2. Personal protective equipment should be stored in a cabinet separated from the chemical storage area. Buckets used to transport chemicals from the storage area to additional sites should not be stored with personal protective equipment. In addition all personal protective equipment should be cleaned periodically and should be cleaned prior to use by another employee.
3. Employees should be trained in the proper handling of chemicals and in the proper use and care of personal protective equipment. This training should be given to employees before they begin working with chemicals, and supervisors should periodically observe employees during the addition of chemicals to see that proper work practices are being followed.
4. The respirator program should be upgraded to include the basic requirements of the Occupational Safety and Health Administration standard - 1910.134.¹¹ This would assure that all employees whose job activities require respirators or who request a respirator are properly trained in the use, maintenance, and storage of respirators.
5. Employees should be informed of the potential for severe medical symptoms if skin exposure to DMF occurs. In particular, in case a major accidental exposure should occur, workers and management personnel should be able to inform medical personnel that severe abdominal symptoms might occur that could mimic appendicitis or other conditions that might require surgery.
6. Employees should be informed that even small amounts of alcohol ingestion after working with DMF may result in facial flushing and other symptoms, even if the air concentrations of DMF are below the health standards.

VIII. REFERENCES

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IX. AUTHORSHIP AND ACKNOWLEDGEMENTS

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available, upon request, from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address.

Copies of this report have been sent to:

1. Authorized Representative of Employees, Local 1849, International Brotherhood of Boilermakers.
2. Babcock and Wilcox Company-Tubular Products Division, Milwaukee, Wisconsin.
3. NIOSH, Region V.
4. OSHA, Region V.

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.

TABLE I
RESULTS OF ENVIRONMENTAL SAMPLING FOR DIMETHYLFORMAMIDE

BABCOCK AND WILCOX COMPANY
MILWAUKEE, WISCONSIN
HETA 81-003

November 20, 1980

<u>Job and/or Location</u>	<u>Type of Sample</u>	<u>Sampling Period</u>	<u>Sample Volume</u>	<u>Concentration ppm</u>
Furnace Operator	Personal	0710-1452	68 Liters	N.D.
Lubricator	Personal	0652-1430	87 Liters	.15
Lubricator	Personal*	1125-1149	4.9 Liters	1.01
Furnace Operator	Personal	0720-1457	49 Liters	N.D.
Bay C	Area	0728-1459	45 Liters	N.D.
Furnace #1 & 19	Area	0729-1459	91 Liters	N.D.
Furnace #2 & 110	Area	0755-1502	86 Liters	N.D.

Environmental Criteria (ppm) as an 8-hour TWA

OSHA - 10 ppm⁽¹⁾
ACGIH - 10 ppm⁽²⁾

* Sample worn by lubricator only during addition of chemicals