HETA 94–0402–2573
Xerox Corporation
Webster, New York

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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.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Calvin K. Cook of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Deborah Friedman, Hazard Evaluations and Technical Assistance Branch, DSHEFS. Desktop publishing by Ellen E. Blythe.

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Health Hazard Evaluation Report 94–0402–2573
Xerox Corporation
Webster, New York
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SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) received a request from the International Union of Operating Engineers, Local #71 to conduct a health hazard evaluation (HHE) at the Xerox Corporation located in Webster, New York. The request stated that Xerox power plant workers were concerned about their potential exposures to a biocide containing 1.5% isothiazolinones while performing maintenance duties on water cooling towers. Workers reported cases of dermatitis and skin rash believed to be associated to occupational biocide exposure.

On September 12-15, 1995, environmental monitoring was performed by NIOSH industrial hygienists that included air sampling for isothiazolinones to assess exposures among power plant workers. Thirteen full–shift personal breathing–zone (PBZ) samples, 21 area air samples, and three 15-minute short-term exposure measurements were collected for total isothiazolinones. A symptoms questionnaire was distributed to power plant workers to obtain background and baseline information about their health complaints.

Chlorinated and unchlorinated isothiazolinones were not detected in the full-shift PBZ samples. The limits of detection (LOD) were 0.01 micrograms per milliliter (µg/ml) for chlorinated isothiazolinones and 0.003 µg/ml for unchlorinated isothiazolinones. An area air sample collected above a biocide storage tank for 15 minutes measured an isothiazolinone concentration of 0.92 milligrams per cubic meter (mg/m^3), exceeding a chemical manufacturer's recommended 15-minute short-term exposure limit (STEL) of 0.30 mg/m^3. Currently, there are no occupational exposure criteria established by NIOSH, the Occupational Safety and Health Administration (OSHA), or the American Conference of Governmental Industrial Hygienists (ACGIH) for isothiazolinones. Evaluation of the questionnaires revealed 74% of the respondents reported they had experienced at least one of the acute symptoms of skin, eyes, and respiratory irritation when working with biocides.

NIOSH investigators concluded that there is potential for short-term exposure above a manufacturer's exposure criteria of 0.30 mg/m^3. Dermal exposure to biocides may also pose a health hazard if appropriate protective clothing is not used. However, if handled properly and appropriate precautions are taken, workers should experience little or no problems when working with biocides. Questionnaire results suggest symptoms reported by workers are possibly associated with not using personal protective equipment when working with biocides. Recommendations are made in this report to help prevent worker exposure to biocides during water cooling tower maintenance.

Keywords: SIC 3861 (Photocopy machines) isothiazolinones, biocide, water cooling tower, skin irritation, respiratory irritation, eye irritation, power plant.

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INTRODUCTION

On September 6, 1994, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Union of Operating Engineers, Local #71 to conduct a health hazard evaluation (HHE) at the Xerox Corporation located in Webster, New York. The request stated that Xerox power plant workers were concerned about their potential exposures to a biocide containing isothiazolinones while performing maintenance duties on water cooling towers. Workers reported cases of dermatitis and skin rash believed to be associated to occupational biocide exposure.

In response to the HHE request, on September 12, 1995, an initial site visit was made by NIOSH industrial hygienists that began with an opening conference with Xerox management and union representatives to discuss the nature of the request. On September 13–14, NIOSH investigators conducted industrial hygiene monitoring for biocide exposures among power plant workers. On September 15, a closing conference was held with management, union, and employee representatives to summarize the survey findings and to provide preliminary recommendations.

BACKGROUND AND PROCESS DESCRIPTION

The Webster plant, located on 1000 acres, is the Xerox Corporation's largest manufacturing, engineering, and research center. The Xerox power plant employs about 62 workers (first shift: 46 workers, second shift: eight workers, third shift: eight workers). Power plant workers are responsible for providing general maintenance duties on the plant's water cooling towers and hundreds of heating, ventilating, and air–conditioning (HVAC) systems. A total of 22 cooling towers were on–site; 18 of these towers were biocide treated.

Prior to the spring months of 1987, when Xerox first began using an isothiazolinone–based biocide, a bromine–based biocide was used for water treatment in the cooling towers. Workers reportedly experienced little or no health problems when working with the bromine–based biocide. However, once the isothiazolinone–based biocide was introduced, power plant workers became concerned about exposures due to reported health complaints among power plant workers, isothiazolinone's known mutagenic properties, as well as the absence of exposure assessment data. Workers were also concerned about potential biocide exposures at outdoor break areas where water mists were believed to drift from cooling towers.

Cooling tower maintenance included general mechanical repairs and water treatment procedures with the use of the biocide Kathon® 886F (1.5% isothiazolinones [1.15% chlorinated, 0.35% unchlorinated]). According to the manufacturer, the Kathon® 886F product was routinely diluted in water cooling towers by a factor of about 93,000. Biocide brand Betz Entec 367 (60% 1–bromo–3–chloro–5,5–dimethylhydantoin) was also used by Xerox for water treatment but to a lesser degree. Cooling towers were generally equipped with a closed loop porta–feed system with an electronic timer that controlled the amount of biocide dispensed into cooling tower reservoirs. The systems intermittently fed about one gallon of the Kathon® 886F biocide every two to three days, depending on the volume and needs of each cooling tower. Porta–feed systems also had a control mechanism that acted as a break to prevent biocide overfeeding that could result in spills. Each system included a 5–gallon Day tank used to store the biocide. These tanks were manually refilled every one to three days by workers.

Potential worker exposure to biocides occurred during the water treatment process when workers refilled Day tanks, changed dispensing pumps, or when performing other maintenance duties on the interiors and exteriors of cooling towers. Worker exposure to biocides could also occur during maintenance at transfers points where worn tubing had deteriorated. According to Xerox Safe Job Procedures, when job tasks required employees to work in water mist dispersed by an adjacent cooling tower, they were instructed to wear NIOSH approved half–face respirators with high efficiency

particulate air (HEPA) cartridges. Protective gloves worn by workers were made of butyl rubber material. Some Day tanks were refilled by using pressurized nitrogen as a carrier gas.

EVALUATION METHODS

Industrial Hygiene Evaluation

Isothiazolinones

In accordance with Rohm & Haas® sampling and analytical method IH8607[1] (the only method available to measure isothiazolinone exposures), 13 full–shift personal breathing–zone (PBZ) samples and 21 area air samples for total isothiazolinones were collected, using impingers attached to battery–operated air sampling pumps calibrated at a flowrate of 1 liter per minute (lpm). Area air samples were collected (downwind) at cooling towers that used the isothiazolinone–based biocide, and at outdoor picnic tables where workers often took breaks during their workshift. Three 15–minute short–term exposure measurements were also made: one collected on a worker while replacing a pump, one collected directly above a Day tank, and another collected at the bottom of a Day tank in operation. To address the concern of biocide mists potentially entering a building occupied by employees, an air sample was collected at the building's air intake grille. Sampling duration ranged from 197 to 527 minutes (mean = 454 minutes) for PBZ samples, and 365 minutes to 662 minutes (mean = 473 minutes) for area samples. Air samples were analyzed by high pressure liquid chromatography (HPLC). The limits of detection (LOD) for the sample set were 0.01 micrograms per milliliter (µg/ml) for chlorinated isothiazolinones and 0.003 µg/ml for unchlorinated isothiazolinones; the limits of quantitation (LOQ) were 0.04 µg/ml for chlorinated and 0.009 µg/ml for unchlorinated. Three field blanks were submitted along with air samples for analyses.

Symptoms Questionnaires

Questionnaires were distributed to all employees working during the NIOSH site visit to obtain background and baseline information about worker health complaints. For employees who were not present during the site visit, arrangements were made to grant them an opportunity to participate in the survey. The questionnaire asked if the employee had experienced acute symptoms of skin, eye, or respiratory irritation believed to be related to their work environment during the past month. The questionnaire also asked about the frequency of occurrence of symptoms reported, and the types of personal protective equipment (PPE) used when working with biocides (e.g., eye protection, gloves, and respirators). The final section of the questionnaire allowed employees to present or discuss other concerns about their health and work environment. Questionnaires were later analyzed to determine the prevalence of reported symptoms.

EVALUATION CRITERIA

General

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 preexisting medical condition, and/or 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, and thus potentially increase 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 the following: (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, OSHA Permissible Exposure Limits (PELs).[4] In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever is the most protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

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 short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term period.

Isothiazolinones

Isothiazolinones are heterocyclic organic compounds present in several chlorinated and unchlorinated forms. For the purpose of this evaluation, methylisothiazolinone and methylchloroisothiazolinone (MI/MCI–886) are the compounds of concern. These isothiazolinones are nonoxidizing anti–microbial agents that are effective against gram–positive and gram–negative bacteria, as well as fungi, yeast, algae, and legionella pneumophila.[5,6] These compounds are commonly used in a variety of consumer and industrial products. In consumer products, they are used as a preservative for water–based cosmetic and toiletry products in concentrations that range from 3 to 15 parts per million (ppm).[5,7] Consumer products include toiletries such as shampoos, hair conditioners, liquid soaps, body creams, eye cosmetics, and topical medications. Isothiazolinones are used industrially as antibiofoulants and slimicides in metal working fluids, paper mills, swimming pools, leather and fabrics, and water cooling towers. For industrial use, concentrations typically ranged from 15,000 to 143,000 ppm before dilution.[7]

In acute isothiazolinones toxicity studies, moderate to high toxicity to rats and high toxicity to rabbits occurred when administered orally.[50] The major signs of acute toxicity in these animal studies were severe gastric irritation, lethargy, and lack of muscle coordination. When applied dermally to rabbits, these compounds were moderately toxic, causing symptoms of lethargy, severe cutaneous irritation, and scab formation.

Aqueous concentrations of isothiazolinones ranging from 1.1% (11,000 ppm) to 14% (140,000 ppm) were corrosive in eye irritation studies on rabbits.[5] Aqueous dilutions with concentrations of 0.056% (560 ppm) were nonirritating; 0.28% (2,800 ppm) was slightly to moderately irritating; 0.56% (5,600 ppm) and 1.75% (17,500 ppm) were moderately to severely irritating; and 2.8% (28,000 ppm) and 5.6% (56,000) were severely irritating (corrosive). No information was located regarding exposures among humans.

Dermal irritation and sensitization potential of isothiazolinones in humans have been studied extensively. The irritation produced by the biocide is dose dependent: 400 to 800 ppm was strongly irritating; 200 ppm is slightly irritating; and essentially nonirritating at 100 ppm. Patch testing for sensitization has determined positive reactions at 100 ppm.[5,8] However, in one case a positive

reaction was discovered in a human subject as low as 10 ppm.[8] Delayed skin burns have been observed in a water treatment worker followed by contact with an aqueous solution containing 1.15% isothiazolines.[5] However, studies suggest isothiazolinones do not induce photosensitization.

Acute inhalation exposure to 425 ppm air concentrations of isothiazolinones was evaluated in rats. The major signs of toxicity were dyspnea, salivation, and lesions that included pulmonary congestion, edema, and hemorrhages. Rats experienced decreased weight gain, pulmonary hemorrhages, and swollen livers when exposed to aerosolized isothiazolinone concentrations as high as 12 ppm for 6 hours daily, 5 days a week for 2 weeks.[5] The no–observable–effect–level (NOEL) was less than 2.8 ppm. No exposure data was located regarding human inhalation exposure.

An Ames Salmonella–mammalian microsome mutagenicity test demonstrated significant mutagenic activity in water extracts collected from a hospital water cooling tower treated with isothiazolinones.[9] The concentration required to produce detectable mammalian cell mutations was 0.30 ppm. To reach these levels in testicular tissue in a 154 lb. man, exposure to 21 milligrams of isothiazolinones would be required.

Carcinogenicity studies have determined no local or systemic tumorigenic effects in mice.[5] Low concentrations of dimethylnitrosamine (DMN), a carcinogenic impurity, have been detected in mixtures of chlorinated and unchlorinated isothiazolinone compounds. However, subsequent development of a chemical process to remove the impurity has limited the presence of DMN in isothiazolinone mixtures to concentrations ranging from 0.1 to 0.8 ppm, which poses no carcinogenic risks according to the Food and Drug Administration (FDA).[5]

The Rohm and Haas® Chemical company, a leader in manufacturing isothiazolinones, recommends an 8–hour TWA exposure criteria of 0.10 mg/m^3 (0.01 ppm), with a STEL of 0.30 mg/m^3 (0.03 ppm) over a 15–minute period. The German government's Maximum Workplace Concentration (Maximale Arbeitsplatz–Konzentration [mAK]) standard is established at 0.05 mg/m^3 (0.005 ppm) based on an 8–hour TWA.[10] These exposure criteria are all based on total isothiazolinones (chlorinated and unchlorinated). Currently there are no exposure criteria established by NIOSH, OSHA, or ACGIH. Nalco Chemical Company, the biocide supplier of Xerox, recommends an 8–hour TWA concentration of 0.50 mg/m^3 (0.05 ppm).

RESULTS

Industrial Hygiene Evaluation

The short–term exposure measurement collected above a Day tank revealed a 15-minute TWA biocide concentration of 0.92 mg/m^3. If this had been a PBZ sample, it would have exceeded the Rohm and Haas® recommended 15–minute PBZ STEL of 0.30 mg/m^3 for total isothiazolinones by a factor of three. An area sample collected at an outdoor picnic table revealed only a trace concentration, well below the Rohm and Haas® recommended exposure criteria of 0.10 mg/m^3 as an 8–hour TWA. Total isothiazolinones were not detected in the remaining 32 air samples and 3 field blanks collected during this HHE. Although air sampling results revealed generally low isothiazolinone exposure concentrations among Xerox power plant workers, dermal exposure still exists during handling and application of the biocide.

Symptoms Questionnaire

The questionnaire results are shown in Tables 1 and 2. Thirty–one of the 62 power plant employees returned questionnaires to NIOSH investigators (with a response rate of 50%). Evaluation of the questionnaires revealed 48% of the respondents reported that they had "*sometimes*"[1] experienced eye and respiratory irritation during their workshift

[1] "*Sometimes*" means less than half the time; "*usually*" means more than half the time.

within the past month, while 45% experienced skin irritation. Sixteen percent of respondents reported that they "*usually*" experienced skin and eye irritation, while 13% usually experienced respiratory irritation within the past month. Thirty–nine percent of respondents reported "*never*" experiencing skin and respiratory irritation during their workshift, while 36% never experienced eye irritation. No respondents reported "*always*" experiencing skin, eye, and respiratory irritation.

Further evaluation of questionnaire data determined that 74% of the respondents experienced at least one of the acute symptoms; 39% of the respondents experienced at least one acute symptom *sometimes*; 35% of the respondents *usually* experienced at least one acute symptom; and 26% of the respondents *never* experienced acute symptoms. (These figures are not presented in the Tables.)

Table 1

Symptoms reported by 31 employees	Usually	Sometimes	Never
Skin	16%	45%	39%
Eye	16%	48%	36%
Respiratory	13%	48%	39%

Questionnaire results also revealed the percentage of workers taking precautions to reduce their exposures to biocides with the use of personal protective equipment. Most notable was that 84% of respondents reported wearing protective gloves at least sometimes when working with biocides; however, 87% reported not wearing eye protection. Seven percent of the respondents reported that the use of gloves, eye protection, and respirators were not applicable to their work.

Table 2

PPE usage reported by employees (n=31)	Percentage of employees using PPE when working with biocides		
	Yes	No	N/A‡
Gloves	84%	9%	7%
Eye Protection	6%	87%	7%
Respirator	29%	64%	7%
‡ N/A = not applicable			

The final section of the questionnaire allowed employees to discuss other concerns about their health and work environment. The issues presented were general concerns about the toxic and mutagenic properties of biocides; worker unawareness of safe job procedures when working with or around biocides; and insufficient air changes in equipment rooms.

DISCUSSION AND CONCLUSIONS

Based on the result of a short–term area air sample that exceeded the Rohm and Haas® 15–minute exposure criteria by a factor of three, there is a potential for worker overexposure to occur during short–term maintenance activities. However, the 15–minute area air sample collected was staged to represent a worst case exposure scenario. Therefore, unless an employee worked directly over the head space of a Day tank for up to 15 minutes, the area air sample collected was not likely to be indicative of a worker's typical short–term exposure. In fact, no isothiazolinones were detected in a 15–minute short–term air sample collected on a worker while replacing the pump of a Day tank. All other PBZ samples for isothiazolinones were also none–detected.

Although full–shift PBZ air sampling results revealed low TWA exposure concentrations for isothiazolinones among Xerox power plant workers, a 15–minute short–term area measurement suggests there is the potential for overexposures to occur. Questionnaire results suggest symptoms reported by workers are possibly associated with not using PPE when working with biocides. Dermal exposure to biocides may also pose a health hazard if appropriate protective clothing is not used. However, if handled properly and appropriate precautions are taken, workers should experience

little or no problems when working with biocides.

RECOMMENDATIONS

1. Caution should be taken to avoid inhalation exposure during maintenance by keeping the lid on the Day tank whenever possible. In addition, damaged or worn rubber tubing, which connects the porta–feed biocide discharge pump to the Day tanks, should be replaced with more durable tubing material (e.g., Teflon®) to help prevent biocide leaks that lead to worker exposures during maintenance.

2. According to Xerox's Safe Job Procedures, workers are instructed to wear half–face respirators with HEPA cartridges when they are required to work in the mist of an adjacent cooling. Although HEPA cartridges are effective against cooling tower mists, half–face respirators may not adequately protect workers in the event of accidental biocide splashes to the eyes and face. For better protection, the use of a full–face respirator, or a face shield with the half–mask respirator should be considered and included in the Safe Job Procedures.

3. Based on the questionnaire results, 87% of employee respondents reported not wearing eye protection when working with biocides and 64% reported not wearing respiratory protection, yet 65% and 61% of the respondents experienced eye and respiratory irritation, respectively. To ensure workers are properly protected, employee training should be provided by qualified safety and health personnel to instruct workers on how to properly use PPE, why they are to be used, and how important it is for workers to wear PPE in accordance with OSHA regulation 1910.132.[11] Training should also cover Safe Job Procedures to ensure workers are aware of such procedures.

4. For tasks that do not require the use of full–face respirators, employees should be instructed to wear eye protection with half–mask respirators to prevent eye injury in the event of accidental biocide splash to the face. Typical safety glasses are not sufficient in protecting eyes against chemical splashes. Splash protective goggles or face–shields are more appropriate for use. Additionally, if the use respirators are required for specific maintenance jobs to protect workers from potentially elevated biocide air concentrations, a respiratory protection program must be established in accordance with OSHA regulation 1910.134.[12]

5. A job safety analysis should be performed during maintenance activities of cooling towers to help identify specific tasks or work practices that contribute to exposures. Additional benefits of a job safety analysis would be to improve job procedures and assist in instructing new employees.

6. Workers who perform maintenance duties on cooling towers containing biocides are instructed to wear protective gloves. If proper glove material is not selected, these biocides can be absorbed through the skin. The biocide manufacturer reports that neoprene, polyvinyl chloride, and butyl rubber materials offer good permeation resistance to both the isothiazolinone and bromine–based biocides. While these glove materials offer permeation resistance to these chemicals, a glove's resistance to cuts, snags, abrasions, punctures, or tears must also be considered. Another factor is an adequate sleeve (or cuff) length to protect the forearm from biocide exposure.

7. Nearly all porta–feed systems were located near or at eye wash stations in the event workers receive an accidental chemical splash to their eyes and face. There were, however, a few systems that did not appear to have an eye wash station in the immediate area. According to the American National Standard Institute for emergency eye wash and shower equipment, they should be located within a travel distance of no more than 10 seconds or 100 feet from porta–feed systems or other chemical processes that pose potential harm to workers.[13] Training should also be provided about the presence of eye wash stations and the procedures for using them.

8. There were worker concerns of biocide overfeeding to cooling towers due to improper programing of electronically controlled porta–feed systems. Each porta–feed electronic timer should

be carefully evaluated to ensure feeding rates and schedules meet the manufacturer's suggested specifications.

9. In accordance with OSHA regulation 1910.1200, biocide material safety data sheets (MSDSs) were provided at each of the porta–feed systems.[14] However, hazard communication could be further improved by providing more visible signs or placards that give workers an immediate understanding of the toxicity of the biocide. Management should also provide employees with information and training on other hazardous substances in their work area at the time of their initial assignment, and whenever a new hazard is introduced into a work area.

10. The following recommendations would be applicable in any situation where employees are handling materials which may cause skin irritation or sensitization.

a. Workers should be periodically educated about the adverse effects of the chemicals which they work with and the types of work practices that will minimize their exposure to them.

b. Good housekeeping should be emphasized. Workers should be instructed to thoroughly clean and rinse where skin contact has been made with biocides.

c. Any skin problem should be immediately reported to the medical department.

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