HETA 92-0415-2502 APRIL 1995 EVEREADY BATTERY COMPANY MARIETTA, OHIO NIOSH INVESTIGATORS: MELODY M. KAWAMOTO, MD, MS KEVIN HANLEY, MSPH, CIH GREGORY BURR, CIH

SUMMARY

In August 1992, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Oil, Chemical, and Atomic Workers Union (OCAW) Local 3-639 for a health hazard evaluation at the Eveready Battery Company electrolytic manganese dioxide (EMD) plant in Marietta, Ohio. The request was prompted by employee concerns about exposures to sulfuric acid mists in the electrolytic cell room and leach area and a possible association with cancer of the esophagus. NIOSH investigators conducted air monitoring for acid mists, reviewed exposure data collected by the company, and searched for cancer outcomes among current and former plant employees.

Personal breathing zone (PBZ) and area air samples were collected for sulfuric acid and hydrochloric acid in the cell room and leach area. Sulfuric acid was detected in 12 of 18 air samples, in concentrations ranging from less than 0.06 milligram per cubic meter (mg/m³) (the minimum detectable concentration) to 0.5 mg/m³. The highest sulfuric acid concentration was from an area sample located in the cell room near cell G9. All of the sulfuric acid concentrations measured during this evaluation were below the NIOSH, Occupational Safety and Health Administration (OSHA), and American Conference of Governmental Industrial Hygienists (ACGIH) exposure limits of 1 mg/m³, time-weighted average (TWA), which were established to prevent dental erosion and the irritant effects of exposure. Hydrochloric acid was detected in one of eighteen air samples, and only in a trace amount (concentration below the limit of quantitation and estimated to be between 0.14 to 0.44 mg/m³, TWA). Analysis of company exposure records revealed that cell room workers' PBZ exposures to sulfuric acid were higher before the 1987 cell room fire than after post-fire renovations were made (geometric means of 0.43 and 0.06 mg/m³, respectively).

The requester provided death certificates for three former Eveready employees who had died from cancer of the esophagus. A local cancer registry identified 4 cancer patients from the list of 119 current and former employees provided by the company. One of these cancer patients was one of the three previously identified former Eveready employees who had died from cancer of the esophagus. No new cases of esophageal cancer were found. Two of the former employees whose death certificates were provided as the basis for this evaluation were not on the employee list provided by the company. Both had left employment at Union Carbide before Ralston Purina Company, the current parent company, acquired Eveready in 1986. The requester of this evaluation could not estimate how many former Eveready employees were omitted on this basis. However, he believed that employees who were not on the list provided by the company probably had worked at Eveready for short periods of time (such as six months or less). He also believed that the number of the longer term employees missing from the list was probably small.

No current health hazard was identified during this evaluation. The personal breathing zone air concentrations of sulfuric acid measured by NIOSH investigators were below NIOSH, OSHA, and ACGIH occupational exposure criteria. Although the findings suggest a possible excess of cancers of the esophagus among employees at the Eveready Battery Company electrolytic manganese dioxide plant in Marietta, Ohio, an association with work exposures, such as sulfuric acid mist, could not be determined.

Keywords: SIC 3313 (electrometallurgical products, except steel), electrolytic manganese dioxide (nonferrous metal) refining, manganese dioxide ore processing, sulfuric acid (CAS No. 7664-93-9), malignant neoplasm of the esophagus (ICD-9-CM 150), adenocarcinoma of the esophagus (ICD-9-CM 151.0).

INTRODUCTION

In August 1992, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Oil, Chemical, and Atomic Workers Union (OCAW) Local 3-639 for a health hazard evaluation at the Eveready Battery Company electrolytic manganese dioxide (EMD) plant in Marietta, Ohio. The request was prompted by employee concerns about exposures to sulfuric acid (H₂SO₄) mists in the electrolytic cell room and leach area and a possible association with cancer of the esophagus. This evaluation focused on acid mist exposures to workers in the cell room and leach area of the facility.

BACKGROUND

At the Eveready EMD plant, manganese ore is electrolytically purified to produce high grade manganese dioxide (MnO₂) powder. Manganese ore is naturally occurring and contains low purity manganese dioxide contaminated primarily by common clay. At the beginning of the purification process, the finely pulverized ore is transferred to a natural gas calciner (reduction furnace), where it is roast-heated at a high temperature to produce manganese oxide (MnO), an acid soluble intermediate. The "roasted" ore is transferred to the leach area into tanks that contain sulfuric acid to produce a manganese sulfate (MnSO₄) solution. The solution is chemically treated to remove soluble impurities, then filtered to remove insoluble impurities. These processes remove iron, molybdenum, and other impurities in the ore.

The purified manganese sulfate solution is pumped into electrolytic cell tanks located in a large cell room. Each cell contains cathodes and anodes (metal plates). Manganese dioxide is deposited onto the anodes when electric current passes through the solution. After sufficient deposits form on the anodes, an overhead crane and hoist lift the plates from the cell and move them to the end of the cell room where the solidified manganese dioxide is stripped from the plates. Sulfuric acid mist, hydrogen gas, and water vapor are generated during the electroplating process. A layer of floating polypropylene balls covers the surface of each cell tank to control acid mist emissions as well as to contain water vapor and maintain cell temperatures. The ventilation system in the cell room, which includes four supply-air fans and eleven roof exhaust fans, can provide a complete air change every two minutes. Sulfuric acid is not generated or used in the finishing area, where the manganese dioxide is neutralized, dried, and milled, and the final product is bagged for shipment.

Operations at the Eveready EMD plant in Marietta, Ohio, began in 1967, as a department of Union Carbide Corporation Metals Division. Other Metals Division departments of the Marietta operations included three ferromanganese-alloy furnace departments. In 1981, Union Carbide sold most of its Marietta metals plants, but continued to operate the EMD plant. In 1986, Ralston Purina Company acquired Eveready, including the Marietta EMD plant. In April 1987,

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a fire in the cell room closed the plant. During the plant closing, some process changes were made and equipment and environmental controls upgraded. Production resumed in July 1988.

Under Union Carbide, some employees transferred between the EMD department and the ferromanganese-alloy furnace departments, which were not acquired by Ralston Purina Company. Maintenance workers in Union Carbide's Department 327 had regularly scheduled six-month rotations between the EMD department and the ferromanganese-alloy furnace departments. When Union Carbide sold its furnace departments, some employees, especially those close to retirement, chose to remain with Union Carbide and transferred to the EMD department. Under Ralston Purina, hourly production workers were temporarily laid off during the plant closure after the 1987 fire. Not all recalled employees returned to work when the plant reopened in 1988.

Most of the production and maintenance employees work during the day shift on weekdays, but continuous leaching and plating operations require some employees to work other shifts. During regular working hours, two employees (chemical operator and relief operator) work in the leach area and four employees (cell operators, sometimes relief operators, and a maintenance worker) work in the cell room.

EVALUATION METHODS

Medical

The union requester provided death certificates for three former Eveready employees who had died of cancer of the esophagus. Eveready provided a list of current and former employees, which included 35 current hourly employees (including production and maintenance workers), 23 current salaried employees (including production foremen), 28 retired hourly and salaried employees, and 33 other former employees. The names and social security numbers for these 119 employees were matched with cancer registries at the Strecker Cancer Center at Marietta Memorial Hospital and the Community Comprehensive Cancer Center at Camden Clark Memorial Hospital (Parkersburg, West Virginia). These cancer registries cover Marietta's county (Washington) and the county across the Ohio River from Marietta (Wood County, West Virginia). The cancer registries were asked to provide the primary cancer site and cell type, date of diagnosis, and date of death (if applicable) for each Eveready employee with a diagnosis of cancer. Names and social security numbers were also matched with the Social Security Death Match Program database for Social Security Administration information on death status.

Industrial Hygiene

Personal breathing zone (PBZ) and area air samples were collected in the cell room near operating electrolytic cells and above a chemical solution tank in the leach area. Two successive

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samples were collected on each worker and in each area location over a work shift during normal working conditions. Total sample durations for each worker and each area location were approximately 7 to 7.5 hours (nearly the entire shift). The air samples were collected on ORBO 53 sorbent tubes at a flowrate of 200 cubic centimeters per minute according to NIOSH Sampling and Analytical Method No. 7903. Once collected, the samples were desorbed in a mixture of sodium carbonate and sodium bicarbonate, then analyzed by ion chromatography. The limits of detection (LOD) and quantitation (LOQ) for this sample set for hydrochloric and sulfuric acids are shown in the following chart.

Compound	Limit of Detection	Limit of Quantitation					
Hydrochloric Acid	7 μg/sample	22 µg/sample					
Sulfuric Acid	3 µg/sample	9.1 μg/sample					
μg/sample = micrograms of analyte per sample Collection Method: NIOSH Sampling and Analytical Method No. 7903							

EVALUATION CRITERIA

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria are exposure limits to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of the 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 sensitivity, pre-existing medical conditions, medicines taken by the worker, possible interactions with other workplace agents, or environmental conditions.

The primary sources of evaluation criteria for the workplace are NIOSH Criteria Documents and Recommended Exposure Limits (RELs),² the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs),³ and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs).⁴ These occupational health criteria are based on the available scientific information provided by industrial experience, animal or human experiments, or epidemiologic studies. It should be noted that RELs and TLVs are guidelines, whereas PELs are legally enforceable standards. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and, as such, tend to be conservative. The OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. 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 standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A), which were originally promulgated in 1971.³ However, some states with

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OSHA-approved state plans continue to enforce the more protective ("final rule") limits promulgated in 1989. For exposures with evaluation criteria, NIOSH encourages employers to use the 1989 OSHA PEL or the NIOSH REL, whichever is lower.

Evaluation criteria for chemical substances are usually based on the average 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 TWA where adverse effects from short-term exposures are recognized, some substances have a short-term exposure limit (STEL) for 15-minute periods; or a ceiling limit, which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be appreciably absorbed through direct contact of the material or its vapor with the skin and mucous membranes.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, pre-existing medical conditions, previous exposures, or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical-specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent become available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

Sulfuric Acid

Sulfuric acid (H₂SO₄) is a severe irritant to the eyes, mucous membranes, and skin. Concentrated sulfuric acid is a corrosive, which can cause severe burns on contact and eventually result in tissue scarring. Sulfuric acid mists can cause eye, nose, and throat irritation, respiratory irritation (such as cough and bronchoconstriction), and dental erosion. The extent of respiratory irritation depends on factors such as air concentration, particle size, temperature, and humidity.⁵ NIOSH, ACGIH, and OSHA have established evaluation criteria for sulfuric acid at 1 mg/m³ as a TWA to prevent dental erosion and the irritant effects of exposure.

A number of epidemiologic studies have indicated that exposure to sulfuric acid mist and other acid mists are associated with cancer. After review of these studies, the International Agency for Research on Cancer (IARC) determined that there is sufficient evidence that occupational exposure to strong inorganic acid mists containing sulfuric acid is carcinogenic.⁶ This

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determination was based on the demonstration of epidemiologic associations between occupational exposures to strong acid mists (mostly sulfuric acid mists) and excess risks for laryngeal cancer⁷⁻¹⁰ and lung cancer.¹¹⁻¹³ A study based on the findings of the general population (not just workers) found that any exposure to sulfuric acid was associated with a higher risk for cancer of the esophagus, but no dose-response relationship was seen (that is, an association between higher exposure and higher risk was not established).¹³ In their annual reports issued in March 1995, the ACGIH Committees on Threshold Limit Values and Biological Exposure Indicies proposed that sulfuric acid be listed as a suspected human carcinogen.¹⁴

FINDINGS

Medical

A local cancer registry identified 4 cancer patients from the list of 119 current and former employees provided by the company. One of these cancer patients was one of the three previously identified former Eveready employees who had died from cancer of the esophagus. (This "cluster" of esophageal cancers was the basis for requesting this health hazard evaluation.) The local cancer registry reported that this patient had adenocarcinoma of the esophagus. His usual occupation, as listed on his death certificate, was production foreman. According to his personnel records, he had not worked as a chemical operator or cell room worker. However, the requester of this evaluation reported that this employee had been exposed to sulfuric acid mists during his nearly 17 years of employment. The three other Eveready employees with cancer, as identified by the local cancer registry, had diagnoses of verrucous (wart-like) carcinoma of the cheek, melanoma on the skin of the trunk, and ocular (eye) melanoma. No additional employees with cancer were found through the Social Security Death Match Program.

Two of the former employees whose death certificates were provided as the basis for this evaluation were not on the employee list provided by the company. Both had left employment at Union Carbide before Ralston Purina Company, the current parent company, acquired Eveready in 1986. The requester of this evaluation could not estimate how many former Eveready employees were omitted on this basis. However, he believed that employees who were not on the list provided by the company probably had worked at Eveready for short periods of time (such as six months or less). He also believed that the number of the longer term employees missing from the list was probably small. A local cancer registry reported that the cell type of one of these former employees with cancer of the esophagus was adenocarcinoma. His death certificate listed his usual occupation as engineer and that he had worked for Union Carbide Metals. The other former employee with cancer of the esophagus was not listed in either cancer registry. His cancer cell type and usual occupation were not specified on his death certificate.

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Industrial Hygiene

Table 1 contains the results of the PBZ and area air samples. A total of five workers and four locations were monitored, each with two samples, for a total of eighteen measurements. PBZ evaluations were performed on two cell processors and a cell monitor who worked in the cell room, and two chemical operators who worked in the leach area. Sulfuric acid concentrations ranged from less than 0.06 mg/m³ (the minimum detectable concentration) to 0.5 mg/m³, all below the established NIOSH, OSHA, and ACGIH exposure limits of 1 mg/m³, TWA. In the cell room, the only PBZ sample with sufficient sulfuric acid to accurately quantitate was the morning sample of the cell monitor (concentration of 0.2 mg/m³). Trace amounts (concentrations between 0.06 to 0.18 mg/m³) of sulfuric acid were detected in the remaining five PBZ samples from the cell room. The highest sulfuric acid concentrations from the area samples in the cell room were measured near cell number G9. Sulfuric acid concentrations appeared to increase with increasing distance between the area sample location and the wall with the supply-air fans. Results were approximately 0.3, 0.4 and 0.5 mg/m³, respectively, for measurements in rows B, D and G. In the cell room, hydrochloric acid was detected in one of twelve air samples collected, and only in a trace amount (concentration below the limit of quantitation and estimated to be between 0.14 to 0.44 mg/m³, TWA). It was detected from the area sample near cell number G9 in the cell room, the location with the highest measured sulfuric acid concentration. Sulfuric acid and hydrochloric acid mists were not detected in any of the PBZ and area samples collected in the leach area.

Eveready records of employee exposures to acid mists were reviewed. Eveready collected a total of 87 samples on employees from May 1977 through March 1994. All of the samples for acid mists were collected in the cell room; none were obtained from the leach area. The vast majority (79, or 91%) of the measurements were conducted on production (manufacturing) employees; the remaining eight PBZ evaluations were obtained on maintenance personnel (mechanics or electricians). Based on these records, employee sulfuric acid mist exposures ranged from nondetectable (<0.002 mg/m³) to 1.84 mg/m³. The records indicate that employee PBZ exposures to sulfuric acid mists after the 1987 fire were substantially lower than exposures before the fire (Table 2). The geometric mean exposure for all jobs after the fire was 0.06 mg/m³ compared with 0.43 mg/m³ before the fire. The highest PBZ concentrations were observed on production employees. The highest concentration was 1.84 mg/m³ before the fire, but decreased to 0.21 mg/m³ after cell room modifications were made. Of the 69 measurements made by Eveready before 1988, 10 (14%) exceeded the occupational exposure criteria of 1 mg/m³ and 33 (48%) exceeded 0.5 mg/m³. None of the PBZ results after 1988 exceeded 0.5 mg/m³.

DISCUSSION

Cancer is common in the United States. About one in three people will eventually develop cancer and about one of every five deaths is from cancer. 15 Because cancers are so common, they often appear to occur in clusters. Cancers, however, are of different cell types, involve different tissues or organs, have different causes, and have different expected outcomes. When these factors are not taken into consideration, the number of cancer cases may seem high, particularly among a small group of people who have something in common, such as working in the same building or department. Sometimes, cancers that occur close together in time and in place (geographically) have a common cause. On the other hand, they might have occurred coincidentally from unrelated causes. Confirming that a cancer "cluster" is work-related depends on confirming the specific cancer cell type (such as squamous cell carcinoma or adenocarcinoma) and site of origin (such as lung), then either identifying a potential causative factor (such as asbestos) or showing a consistent epidemiologic association with a specific job title, occupation, process, or industry. The rate for the specific cancer in "exposed" workers must be higher than the rate for that cancer in comparison populations (such as "unexposed" workers or the population-at-large). To be biologically reasonable, the exposure must have taken place before the diagnosis was made. In addition, sufficient time (latency period) must have passed between the time of exposure and date of diagnosis to allow development and detection of the cancer. Most cancers require a period of 10 to 20 years from time of first exposure to a cancer-causing agent until the time of clinical detection.²³ Because cancer is the second leading cause of death in the United States, determining whether exposures at a workplace could have caused a cancer "cluster" can be difficult, especially when: (1) the cluster includes many types of cancer, (2) the types of cancer are common in the U.S. population, (3) the number of each type of cancer is small, (4) the population defined to be "at risk" (such as exposed workers) is relatively small, (5) the time between the exposure to the suspected causal factor and the diagnosis is relatively short, and (6) the association is not biologically reasonable.

Historically, up to 95% of cancers originating in the esophagus have been squamous cell carcinomas. In the Western world, well known risk factors include alcohol and tobacco. Since the 1970s, however, the incidence rate of adenocarcinoma of the esophagus has been rising, especially among white men. The primary site for this type of cancer is typically in the lower third of the esophagus. In the past, adenocarcinoma of the esophagus has been linked to Barrett's esophagus (a condition often associated with esophageal reflux), showed that tobacco and alcohol may contribute to the risk of developing adenocarcinoma of the esophagus, but this does not explain its rapidly rising rate. He incidence rate of melanoma has been increasing over a longer time period. The lifetime risk for malignant melanoma is expected to reach 1 per 100 individuals by the year 2000. Melanoma usually affects the skin (cutaneous), but also can involve the eye (ocular). Well-known risk factors for cutaneous melanoma include ultraviolet light (such as sun exposure) and genetic factors (such as fair skin). Ocular melanoma is less common, but may also be related to ultraviolet light exposure and genetic

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factors.²¹ Verrucous carcinoma is a slow growing malignant cancer that is potentially destructive. It is common in tobacco chewers.²² Lung and laryngeal cancers, the types of cancers epidemiologically associated with exposure to sulfuric acid mists, were not found among the employees at the Eveready EMD facility in Marietta.

Although three cases of esophageal cancer among the relatively small Eveready work force probably represents a statistical excess, an association with work exposures, such as sulfuric acid mist, could not be determined. One epidemiologic study showed an association between sulfuric acid exposure and esophageal cancer, ¹³ but did not show a dose-response relationship (that is, higher exposures were not associated with increased rates of esophageal cancer). The esophageal cancers in this epidemiologic study were classified by site of origin and all cell types were included. ¹³ Therefore, most of the cell types were probably squamous cell carcinomas, which are far more common than adenocarcinomas of the esophagus.

Although the production foreman with adenocarcinoma of the esophagus had worked at Eveready for almost 17 years, his exposure to sulfuric acid mists could not be reliably estimated. Occupational exposures for production foremen are difficult to estimate because they typically have highly variable potentials for exposure. Exposures for any one foreman may vary from day to day or even from hour to hour, and would not necessarily represent exposures for other foremen. In addition, historical data on the exposures of production foremen were not available. The duration of employment for the two Union Carbide employees with cancer of the esophagus could not be determined. One of these employees was an engineer and, therefore, probably had much lower exposures than production workers such as cell room workers.

According to the results of environmental sampling conducted by Eveready, PBZ sulfuric acid exposures in the cell room after the 1987 fire are substantially lower than before the fire. Although more electrolytic cells were added to the cell room after the fire, the geometric mean PBZ exposure to sulfuric acid after the fire is 7 times lower than before the fire. On several occasions, exposures before the fire exceeded the occupational exposure criteria of 1 mg/m³ and the maximum concentration observed was 1.84 mg/m³, TWA. Following the 1987 fire, the cell room was rebuilt and significant process and work activity changes were made. These changes included the use of polypropylene balls instead of parrafin wax to control sulfuric acid emissions from the electrolytic cells, a more efficient plate hoisting mechanism, and improved dilution ventilation.

Workers' exposures to sulfuric acid measured during this investigation were well below the NIOSH, ACGIH, and OSHA occupational health criteria to prevent dental erosion and irritant effects of exposure. The concentrations of sulfuric acid from PBZ samples on cell room workers were considerably lower than those of area samples collected near the electrolytic cells. These findings are consisent with NIOSH investigators' observations that cell processors do not remain next to the electrolytic cells during the entire work day.

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CONCLUSIONS

- PBZ air concentrations of sulfuric acid measured during this NIOSH evaluation were below the NIOSH, OSHA, and ACGIH occupational exposure criteria to prevent dental erosion and the irritant effects of exposure. Air concentrations measured by NIOSH investigators were similar to those measured by Eveready during surveys of the cell room and adjoining areas in 1993 and 1994.
- Company records suggest that cell room employee exposures to sulfuric acid before the 1987 fire were sometimes above the NIOSH, OSHA, and ACGIH occupational exposure criteria. The records also show that sulfuric acid concentrations declined following post-fire modifications, which included installation of additional dilution ventilation.
- Area air sampling results collected in the cell room during this NIOSH survey ranged from 0.29 to 0.50 mg/m³. Lower PBZ results for cell room employees are consisent with NIOSH investigators' observations that cell processors do not remain next to the electrolytic cells during the entire work day.
- Although three cases of esophageal cancer among the relatively small Eveready work force probably represents a statistical excess, an association with work exposures, such as sulfuric acid mist, could not be determined.

RECOMMENDATIONS

- Eveready should monitor sulfuric acid exposures whenever changes (such as process, engineering controls, or work activities) are made that could change employees' potential for exposure or whenever potentially exposed employees report persistent symptoms that are consistent with overexposure.
- Ventilation exhaust and supply air rates should be maintained during the winter months (especially when doors are closed to keep the cold out and the heat in) to ensure an adequate level of exposure control.

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Copies of this report have been sent to:

- 1. Eveready Battery, Marietta, OH
- 2. Ralston Purina, St. Louis, MO
- 3. OCAW, Local 3-639
- 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 1 Acid Mist Concentrations Eveready Battery Company Electrolytic Manganese Dioxide Plant, Marietta, Ohio Sampling Date: August 23, 1994 HETA 92-0415

				Sample Volume (liters)	Concentration (mg/m³, TWA)	
Sample Number	Туре	Location	Sample Period		Sulfuric Acid	Hydrochloric Acid
5	PBZ	Cell Processor	07:03 → 11:25	52.4	Trace	ND
14		(Stripping)	11:25 → 14:50	41.0	Trace	ND
6	PBZ	Cell Processor	07:08 → 11:27	51.8	Trace	ND
15		(Stripping)	11:27 → 14:51	40.8	Trace	ND
7	PBZ	Cell Processor	07:14 → 11:29	51.0	0.2	ND
16		(Monitoring)	11:29 → 14:52	40.6	Trace	ND
3	Area	Cell Room	08:24 → 11:36	38.4	0.29	ND
12		at Cell No. B9	11:36 → 15:04	41.6	0.34	ND
2	Area	Cell Room	08:20 → 11:34	38.8	0.36	ND
11		at Cell No. D4	11:34 → 15:02	41.6	0.41	ND
4	Area	Cell Room	08:29 → 11:40	38.2	0.50	Trace
13		at Cell No. G9	11:40 → 15:06	41.2	0.46	ND
8	PBZ	Chemical (Leach)	07:56 → 11:54	47.6	ND	ND
17		Operator	11:54 → 15:11	39.4	ND	ND
9	PBZ	Chemical (Leach)	08:01 → 11:56	47.0	ND	ND
18		Operator	11:56 →15:18	40.4	ND	ND
1	Area	Leach Area	08:13 → 11:29	39.2	ND	ND
10		at Tank No. 1	11:29 → 14:58	41.8	ND	ND
Minimum Detectable Concentration (MDC)			50.0	0.06	0.14	
Minimum Quantifiable Concentration (MQC)			50.0	0.18	0.44	

Comments and abbreviations: Area = area air sample

mg/m³ = milligrams per cubic meter

ND = not detected

PBZ = personal breathing-zone air sample

Trace = Concentration is between the minimum detectable and minimum quantifiable

concentrations $(0.06 - 0.18 \text{ mg/m}^3)$.

TWA = time-weighted average

Table 2
Comparison of Sulfuric Acid Mist Exposure Evaluations Before and After the 1987 Fire
Historical Data Collected by the Company During 1977-1994
Eveready Battery Company Electrolytic Manganese Dioxide Plant, Marietta, Ohio
HETA 92-0415

	Number	Sulfuric Acid Concentrations (mg/m³), Time-Weighted Averages						
	of evaluations	Minimum*	Maximum	Average (s.d.)	Geometric Mean (s.d.)			
All jobs								
All Years (1977-94)	87	0.0014	1.84	0.48 (0.40)	0.28 (3.8)			
Pre-fire (before 1987)	69	0.057	1.84	0.57 (0.40)	0.43 (2.4)			
Post-fire (after 1988)	18	0.0014	0.21	0.11 (0.07)	0.06 (4.9)			
Production jobs								
All Years (1977-94)	79	0.0014	1.84	0.51 (0.40)	0.33 (3.4)			
Pre-fire (before 1987)	67	0.057	1.84	0.58 (0.40)	0.44 (2.4)			
Post-fire (after 1988)	12	0.0014	0.21	0.11 (0.07)	0.06 (4.8)			
Maintenance jobs								
All Years (1977-94)	8	0.0014	0.29	0.11 (0.08)	0.07 (5.1)			
Pre-fire (before 1987)	2	0.09	0.29	0.19 (0.14)	0.16 (2.3)			
Post-fire (after 1988)	6	0.057	0.13	0.09 (0.05)	0.05 (5.9)			

^{*}Non-detectable results were assigned a value equal to the limit of detection divided by the square root of 2.