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Epidemiological–Environmental Study of Lead Acid Battery Workers

I. Environmental Study of Five Lead Acid Battery Plants

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Industrial hygiene measurements were taken at five lead acid battery plants. The average of all personal samples for H_2SO_4 was 0.18 mg/m^3 with a range of "nondetectable" to 1.7 mg/m^3. Highest levels of acid were found in the charging and forming areas of the plants. Stibine and arsine were also detected in the charging and forming areas ($\bar{x}$ = 0.44 and 0.042 mg/m^3, respectively). Arsenic in particulate form was also detected, but levels were low ($\bar{x}$ = 0.00083 mg/m^3). The average mass median aerodynamic diameter of the acid mist as measured by cascade impactors was approximately 5 μm. Air lead results were variable with an overall average of 0.072 mg/m^3 and a standard deviation of 0.11 mg/m^3.

INTRODUCTION

There are approximately 200 plants in the United States engaged in the manufacture of storage batteries with a total workforce estimated to be about 23,000, (U.S. Bureau of The Census, 1976). The most cited hazard in the manufacture of lead acid batteries has been lead exposure. In fact, much of the toxicological information gathered through the years on lead has come from studies of workers in battery plants. Sulfuric acid mist, which is generated during the forming of battery plates, is a recognized irritant although much less information is available on actual worker exposure. Particle size distribution of the acid mist also has not been adequately studied. Stibine and arsine are potential contaminants in the forming areas; however, little information on plant levels is available.

The study reported here is part of a comprehensive epidemiological/environmental investigation conducted at five lead acid battery manufacturing plants. During the time that the environmental sampling was conducted, workers at these facilities were given before and after shift pulmonary function tests and chest x-rays. Respiratory questionnaires were also administered, and examinations for etching of teeth were performed. The investigation of association between environmental and medical measurements is reported separately. The following is a report only of the results of environmental measurements taken at these facilities.

PROCESS DESCRIPTION

All five plants studied (designated A–E), were involved in the manufacturing of lead acid storage batteries. To help acquaint the reader a brief description of the process is offered.

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The initial step is the casting of the grids. The grids are then made into plates by filling them with a lead oxide paste. The plates are then "formed" by charging them in a weak sulfuric acid solution. In this process the paste reacts to form sponge lead in the negative plate and lead dioxide in the positive plate. The plates are kept from making direct contact in the battery by an insulator referred to as a separator. In some batteries the electrolyte is removed after charging. These batteries (referred to as dry charged) are then sealed to prevent deterioration until they are ready for use. Battery life, which actually begins when the acid is added, is therefore extended.

The battery plates can be "formed" before or after they are assembled into the battery cases. When the plates are formed in the cases, less sulfuric acid mist is generated since the case lids tend to keep it confined. This process of forming the plates inside the case is usually referred to as "charging." When the plates are formed outside of the battery cases they are usually placed in large tanks which results in more acid mist generation since the tanks are open.

Typically, local exhaust ventilation was not used in the charging and forming areas. There were however ceiling fans which provided general ventilation.

All plants produced batteries principally for automobile use. Plants B and D also produced larger batteries for industrial purposes.

METHODS

Area sampling. Stibine and arsine samples were collected on charcoal tubes using Dupont P-30 low flow pumps delivering a flow rate of approximately 15 cc/min. Samples were analyzed by atomic absorption spectrophotometry. Particulate arsenic samples were collected on Millipore AA filters using Bendix[1] Model 44 pumps operated at 1.7 liters/min. Analysis involved generation of arsine by the borohydride method followed by atomic absorption analysis. Sampling time for stibine, arsine, and arsenic ranged from approximately 4 to 5 hr.

Impactor sampling to determine particle size distribution was also conducted using both Andersen and Sierra Impactors. Both units operate on the same principle of impaction; however, the Andersen consists of a series of stages with multiple drilled orifices while the Sierra uses radial slots of varying sizes. In both instruments particles are collected on glass fiber filter paper. The Andersen was operated at 28.3 liters/min and the Sierra at 7 liters/min. The exposed filters from both samplers were analyzed for H_2SO_4 by ion chromotography. Data from this analysis were plotted on log probability paper. Mass median aerodynamic diameter and geometric standard deviation were then estimated directly from the graphs.

Temperature and relative humidity readings were also taken during the work shift.

Personal sampling. Personal samples were collected for sulfuric acid (H_2SO_4) and lead (Pb) by using Bendix Model 44 pumps to draw workroom air at a flow rate of 1.7 liters/min through 37-mm Millipore type AA filters. The filters were

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[1] Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

sealed in two-piece cassettes and attached to the workers' clothing as close to the breathing zone as possible. Tygon tubing was used to connect the cassette assembly to the belt-mounted pump. The samplers were attached and started immediately after the workers finished their before-shift medical tests. The samplers were stopped just before the after-shift pulmonary function tests were conducted. This approach resulted in sampling times ranging from approximately 6 to 7 hr. After sampling, the filters were transferred to glass vials and shipped to the laboratory for analysis.

Using a Millipore filtration apparatus, deionized water was passed through each filter and part of the collected filtrate was anlayzed for H_2SO_4 (detected as total sulfate), using an ion chromotograph equipped with a conductivity detector cell. The remaining filter extract was analyzed for lead via atomic absorption spectrophotometry. The filter was then ashed with nitric acid and analyzed for lead using the same method. Total lead (both soluble and insoluble) was calculated by adding the results from both lead determinations.

RESULTS AND DISCUSSION

Area Sampling

Results of samples taken for stibine, arsine, and arsenic are given in Table 1. Stibine levels ranged from nondetectable to 2.5 mg/m^3 with an average value of 0.44 mg/m^3. Arsine ranged from nondetectable to 0.18 mg/m^3 ($\bar{x} = 0.043$). The highest value for both stibine and arsine occurred in the element formation area of Plant B. Stibine and arsine can be formed whenever inorganic antimony and arsenic are exposed to nascent hydrogen, (NIOSH, 1979). During the forming process, electric current through the battery plates reduces the lead oxide paste to sponge lead in the negative plate and oxidizes the paste to lead oxide in the positive plate. This reaction results in the release of hydrogen gas. The battery plate grids are cast from an alloy of lead and antimony. The antimony is used to

TABLE 1

RESULTS OF AREA SAMPLING FOR STIBINE, ARSINE, AND ARSENIC[a]

Plant	Location	Stibine	Arsine	Arsenic
A	Case formation	0.030	0.013	0.0028
A	Element formation	0.31	0.031	0.00014
A	Case formation	0.031	ND[b]	0.00041
A	Plate formation	ND	0.013	0.0013
B	Formation (ind. batteries)	0.21	0.050	0.0016
B	Element formation	2.5	0.18	0.00053
C	Case formation	0.73	ND	ND
D	Case formation	0.44	0.085	0.00060
E	Case formation	0.066	ND	ND
E	Case formation	0.10	0.037	—

Note. The approximate limit of detection for the three contaminants is as follows: Stibine—0.01 mg/m^3, Arsine—0.01 mg/m^3, Arsenic—0.00006 mg/m^3.

[a] All values reported in milligrams per cubic meter.

[b] ND = Nondetectable.

stiffen the soft lead (Battery Council International, 1972). Tin, copper, and arsenic may also be found in the grids in small amounts. These conditions are therefore favorable for formation of hydrides of antimony and arsenic. Levels of particulate arsenic were low, ranging from nondetectable to 0.0028 mg/m^3 ($\bar{x}$ = 0.00083 mg/m^3).

The current OSHA standard for exposure to arsine is 0.2 mg/m^3. The standards for stibine and inorganic arsenic are 0.5 and 0.010 mg/m^3, respectively. These standards are based on 8-hr time-weighted average personal samples. The samples collected for arsine and inorganic arsenic were all below the OSHA standard. Two of the ten samples collected for stibine were higher than the OSHA standard of 0.5 mg/m^3. Note however that the results reported here were from "area" and not "personal" samples. They were also worst case samples in that they were set up to sample air directly above the forming battery plates. They cannot therefore be compared directly to standards.

Particle size distribution data is listed in Table 2 along with temperature and relative humidity. Side-by-side comparison results for the Andersen and Sierra samplers (plotted on log probability paper), are given in Figs. 1–4 for plants A–D respectively.

The average mass median aerodynamic diameter (MMD) of H_2SO_4 mist based on Andersen impactor samples collected at all the plants was about 5 μm. The average geometric standard deviation was about 4. The Sierra sampler estimated somewhat higher values for these parameters with the average MMD being about 6 μm and average GSD about 5. In general though the agreement between samplers is good as the graphs indicate. The data points from both impactors are reasonably linear when plotted on log probability paper indicating a probable log normal distribution of acid mist particulate. The relatively high geometric standard deviation suggests a wide range of particle sizes in the battery plant environment. The MMD ranging from about 3 to 10 μm indicates that a large percentage of these particles are in the respirable range. The potential site of deposition in the respiratory tract is difficult to predict, however, due to the hygroscopic nature of H_2SO_4. It is quite probable because of the low relative

TABLE 2
SULFURIC ACID MIST PARTICLE SIZE DISTRIBUTION USING ANDERSEN AND SIERRA IMPACTORS

		Andersen		Sierra			
Plant	Location	MMD[a]	GSD[b]	MMD	GSD	Temp. (°F)	RH (%)
A	Charging area	4.7	5.0	4.7	7.6	68	28–34
B	Element formation (auto batteries)	7.0	3.7	10	4.6	54–58	49–53
C	Case formation	4.3	3.9	6.3	5.2	72	24
D	Case formation	3.2	2.3	3.7	2.5	75	20–21
E	Case formation	2.6	5.9	—	—	64–66	21–26
E	Case formation	6.6	3.1	—	—	68–70	23–28

[a] MMD = Mass Median Aerodynamic Diameter (μm).
[b] GSD = Geometric Standard Deviation.

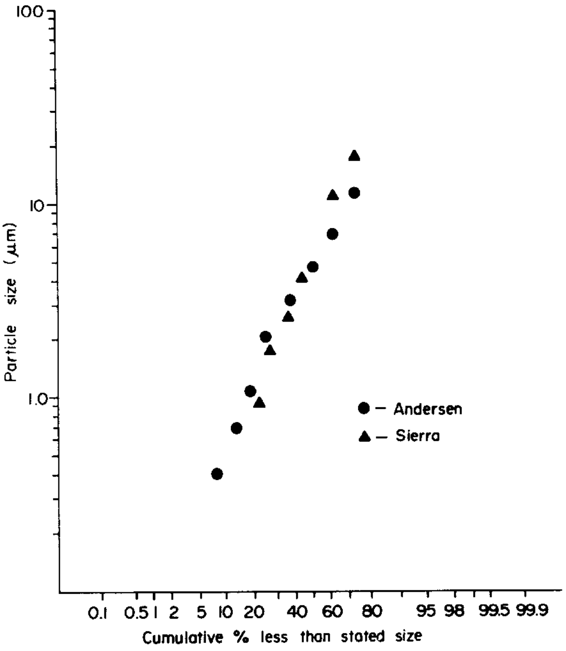

FIG. 1. H_2SO_4 particle size distribution Plant A charging area.

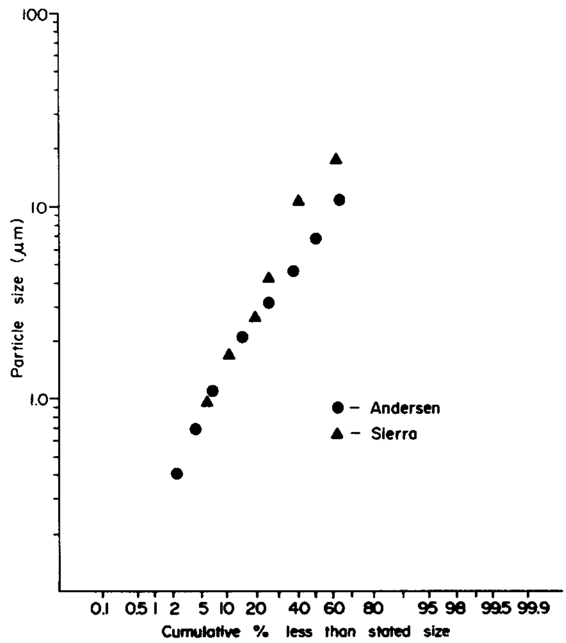

FIG. 2. H_2SO_4 particle size distribution Plant B element formation.

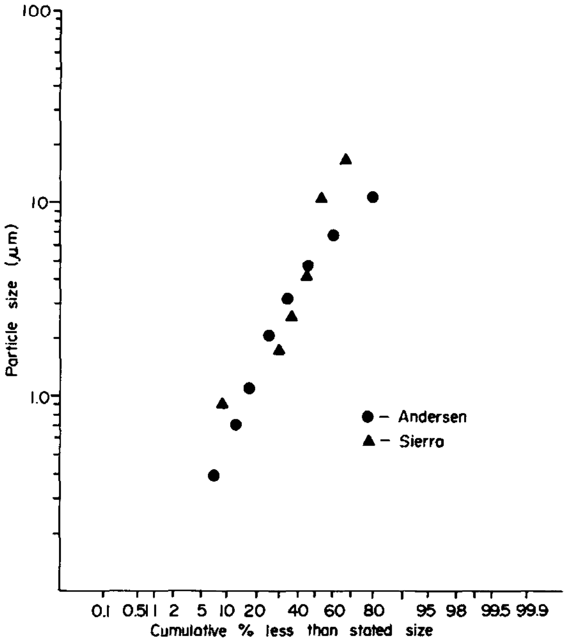

FIG. 3. H_2SO_4 particle size distribution Plant C case formation.

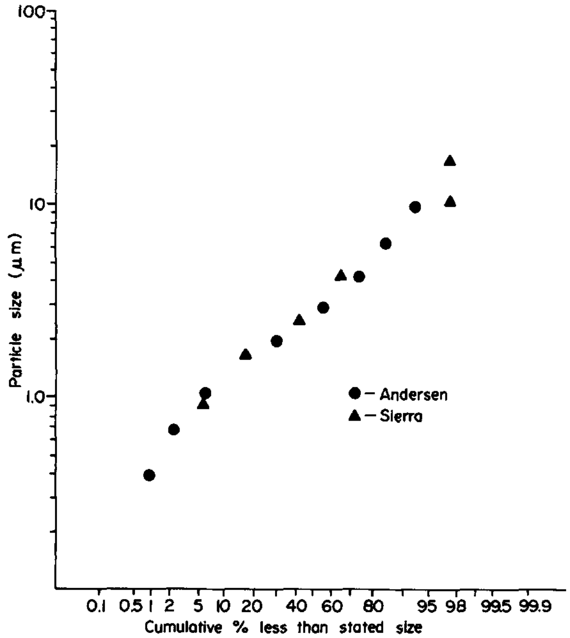

FIG. 4. H_2SO_4 particle size distribution Plant D case formation.

humidity of the plant (relative to the respiratory tract) that upon inhalation, the H_2SO_4 particles grow, thus inhibiting their ability to penetrate deep in the lung.

It is interesting to note in Table 2 the difference in MMD in two samples collected in the same area of Plant E. The first sample was collected at the beginning of the forming cycle while the second was collected toward the end. It was observed that as the batteries formed, bubbling of the electrolyte increased indicating more evolution of H_2 gas. Since this bubbling generates the acid mist, it seems reasonable that more violent bubbling would result in larger H_2SO_4 particles becoming airborne. During the start of the cycle (when only slight bubbling is detectable), only the smaller particles can become airborne.

Personal Sampling

Results of personal sampling for H_2SO_4 and Pb by department for each plant are presented in Tables 3–7. The average of all of the H_2SO_4 measurements taken was 0.18 mg/m^3 with a range of nondetectable to 1.7 mg/m^3 and standard deviation of 0.24 mg/m^3. H_2SO_4 levels were usually highest from samples collected on workers in the charging and forming areas of the plants. The general method used to control H_2SO_4 in the charging and forming areas was dilution ventilation consisting of large ceiling fans. In most cases the ceilings were high which may also have helped keep the levels down. The exception was Plant D which had a low ceiling in the charging area and this probably accounts for the higher exposures found at this facility. The H_2SO_4 levels found at these plants are generally lower than those reported previously. Malcolm and Paul (1961), in a study of dental erosion in battery plant workers, reported levels ranging from 3.0 to 16.6 mg/m^3 in the forming area. In the charging areas levels varied from less than 0.8 to 2.5 mg/m^3. El-Sadik *et al.* (1972) reported concentrations ranging from 26.12 to 35.02 mg/m^3 in one battery plant and 12.55 to 13.51 mg/m^3 in another. No information concerning processes sampled or locations was given. Anfield and Warner (1968) conducted an environmental study of H_2SO_4 levels in five industrial operations, two of which were lead acid battery plants. Average levels of 1.38 and 0.97 mg/

TABLE 3
RESULTS OF PERSONAL SAMPLING FOR H_2SO_4 AND Pb BY DEPARTMENT IN PLANT A[a]

		H_2SO_4	Pb
Department	*n*	$\bar{X}$ (SD)	$\bar{X}$ (SD)
Plate formation	4	.077 (.051)	.096 (.057)
Element formation	4	.21 (.13)	.19 (.096)
Assembly	6, 7[b]	.053 (.014)	.060 (.059)
Charging	10	.043 (.023)	.061 (.099)
Finishing	3	.050 (.013)	.024 (.013)
Shipping	4	.045 (.034)	.010 (.013)
Receiving	1	.035	.011
Miscellaneous	2	.076 (.013)	.025 (.020)

[a] All values reported in milligrams per cubic meter.

[b] First number is sample size for H_2SO_4, second number is sample size for Pb.

TABLE 4

RESULTS OF PERSONAL SAMPLING FOR H_2SO_4 AND Pb BY DEPARTMENT IN PLANT B[a]

		H_2SO_4	Pb
Department	n	$\bar{X}$ (SD)	$\bar{X}$ (SD)
Forming	13	.28 (.18)	.14 (.14)
Forming (industrial)	5	.18 (.080)	.16 (.071)
Dry charge	9	.19 (.13)	.070 (.068)
Shipping	13	.086 (.058)	.047 (.10)
Wire	2	.029 (.014)	.0055 (.0078)
Cable	4	.050 (.030)	.025 (.018)
Grid cast	2	.026 (.0078)	.028 (.0085)
Office	2	.046 (.030)	.033 (.047)
Boost line	2	.066 (.0064)	.012 (.0)
Construction	3	.048 (.021)	.013 (.011)

[a] All values reported in milligrams per cubic meter.

m^3 were reported for area samples in the forming operations of both plants. The Public Health Service conducted a rather extensive health survey in the storage battery industry (U.S. Public Health Service, 1941). Although this study concentrated on the lead problem, a short discussion of the case formation area was included. The authors stated that H_2SO_4 was scarcely detectable by odor or nasal irritation and two samples showed concentrations of 0.1 and 0.4 mg/m^3.

The higher levels reported in the past are not surprising. First, due to ventilation improvements and differences in processes there probably are lower levels now than in the past. More importantly, however, the samples taken in the above-mentioned studies were area samples while those reported here are personal exposure measurements. Workers in the forming department do not spend much time in this area after the plates are connected and the current is applied. Since

TABLE 5

RESULTS OF PERSONAL SAMPLING FOR H_2SO_4 AND Pb BY JOB IN PLANT C[a]

		H_2SO_4	Pb
Job classification	n	$\bar{X}$ (SD)	$\bar{X}$ (SD)
Battery finishing	4	.037 (.017)	.024 (.0030)
Assembly	7	.052 (.019)	.061 (.029)
Stacking	2	.024 (.0021)	.089 (.043)
Forming	13	.095 (.041)	.28 (.28)
Paste machine operator	1	.035	.10
Mac machine operator	3	.024 (.027)	.094 (.048)
Circuit tender	2	.12 (.028)	.042 (.011)
Grid casting	1	.066	.011
Plate parting	1	.034	.079
Material handler	2	.042 (.022)	.089 (.029)
Battery repair	2	.27 (.30)	.080 (.043)

[a] All values reported in milligrams per cubic meter.

TABLE 6

RESULTS OF PERSONAL SAMPLING FOR H_2SO_4 AND Pb BY DEPARTMENT IN PLANT D[a]

		H_2SO_4	Pb
Department	*n*	$\overline{X}$ (SD)	$\overline{X}$ (SD)
Boosting	14, 15[b]	.56 (.30)	.021 (.012)
Boosting/finishing	16	.42 (.33)	.044 (.076)
Formation	1	1.7	.046
Burning	1	.033	.054
Receiving/shipping	5	.096 (.055)	.021 (.0096)
Assembly	10	.22 (.13)	.070 (.042)
Finishing	1	.098	.014
Industrial	10	.088 (.057)	.054 (.025)
Battery assembler	1	.065	.023

[a] All values reported in milligrams per cubic meter.

[b] First number is sample size for H_2SO_4, second number is sample size for Pb.

the personal sampler integrates time spent in both low and high concentrations, these time-weighted average values will be lower than general area samples taken in areas of high concentration.

With only a few exceptions, levels of H_2SO_4 were below the current OSHA standard of 1 mg/m^3 which is intended to prevent irritation of the respiratory passage and injury to the teeth.

The average of all air lead determinations in the five plants was 0.072 mg/m^3 with a range of nondetectable to 0.98 mg/m^3 and a standard deviation of 0.11. NIOSH, in a revised inorganic lead criteria document, recommended a standard of 0.10 mg/m^3 as determined from a time-weighted average exposure (NIOSH, 1978). The current OSHA standard for lead is 0.050 mg/m^3 (OSHA, 1978). Battery manufacturers have until June of 1986 to achieve the 0.050 mg/m^3 standard through engineering controls. Until then, the actual plant levels can be as high as 0.2 mg/m^3 (the previous standard), as long as personal exposures are lowered

TABLE 7

RESULTS OF PERSONAL SAMPLING FOR H_2SO_4 AND Pb BY DEPARTMENT IN PLANT E[a]

		H_2SO_4	Pb
Department	*n*	$\overline{X}$ (SD)	$\overline{X}$ (SD)
Casting	1	.032	.083
Pasting	3	.064 (.013)	.37 (.075)
Assembly	5	.22 (.13)	.31 (.25)
Charging	20	.31 (.29)	.034 (.026)
Shipping	26	.064 (.030)	.019 (.010)
Maintenance	2	.059 (.0071)	.058 (.026)
Receiving	1	.063	.051
Superintendent	1	.18	.065

[a] All values reported in milligrams per cubic meters.

through personal protective equipment (OSHA, 1981). Since lead levels found in this study were frequently above both the present OSHA standard and NIOSH recommendation, and occasionally higher than the previous OSHA standard of 0.2 mg/m^3, better control methods are encouraged.

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