WALK-THROUGH SURVEY
OF

Chemetron Corporation
Inorganic Chemicals Division

SURVEY DATE

June 18-19, 1975

SURVEY CONDUCTED AND REPORT WRITTEN BY

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INTRODUCTION

The Division of Surveillance, Hazard Evaluations, and Field Studies of the National Institute for Occupational Safety and Health began studying antimony facilities as a result of a study done by Cunningham and McCallum of Associated Lead Manufacturers, Ltd., which disclosed 17 cases of respiratory cancer among antimony trioxide production workers in England during the last ten years. No such survey had been made of antimony production workers in the USA; therfore, a preliminary investigation was initiated which includes all currently operational primary antimony oxide producing facilities.

DESCRIPTION OF ANTIMONY SMELTING PROCESS

Sulfide ores from South Africa and Bolivia are charged continuously into direct fired rotating kilns. These kilns operate at temperatures of 2000°F. At htis temperature antimony oxide sublimes, and is drawn from the kilns, is cooled and collected in bag type dust collectors. The reaction is $Sb_2S_3 + 4\text{-}1/2\ O_2 \quad Sb_2O_3 + 3\ SO_2$. The product ($Sb_2O_3$) is conveyed pneumatically through a system which sifts the material prior to blending. In the blender the product (Sb_2O_3) may have added to it small quantities (generally less than 5%) of additives as specified by customers. The material is then packaged as required. The ore utilized in this facility contained approximately 25-30% sulfur and approximately 0.5% arsenic. In the past, some antimony cathode metal was used in the processing as well as antimony metal purchases from GSA. The material from GSA contained approximately 0.25% arsenic.

DESCRIPTION OF PLANT

The McGean/Chemetron Plant has been in operation since 1937 with ownership transferring back and forth between Chemetron and McGean. The plant site occupies approximately sixteen acres and contains approximately sixteen main buildings. At this location there have been produced a number of products which include: nickel sulfate; nickel carbonate; antimony oxide; antimony chloride; cuprous chloride, tin, zinc chemicals; sodium antimonate; brighteners, catalyst from depleted uranium hexafluoride; chromium products; cadmium products; cyanide and lead products. Uranium hexafluoride is no longer being processed.

The workforce consists of 82 hourly employees and 48 salaried employees. The hourly employees have been represented for six years by the International Chemical Workers Union and they have a "closed shop".

The plant operates three shifts per day, seven days per week, with a plant-wide seniority system, which means that men rotate throughout the plant. At least 75% of the workforce has worked in the antimony oxide facility during their employment.

MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAM

Chemetron has inplant medical facilities with a full time nurse on the day shift. All of the front line supervisors and hourly employees will or have taken the Red Cross Multimedia first aid course. A physician in Cleveland is retained to perform the pre-employment physical examinations and other emergency care.

The pre-employment physical examination consists of medical history and chest x-ray. Uranium oxide workers (1969-1973) physical examination consisted of a blood smear, urinalysis, chest x-rays and film badges.

The safety program involves a very good accident prevention program with a great deal of emphasis on housekeeping. Failure of employees to comply with the written safety rules is subject to disciplinary action. Chemetron has one full time safety director who is assisted by an operating superintendent. A safety and housekeeping inspection is conducted monthly by a team consisting of salaried and hourly employees. Each person on the inspection team takes notes of violations and at the termination of the inspection each department is rated by each member of the inspection team. The department receiving the highest point value has the department name engraved on a plaque. The department which has had the best record for the year gets to keep the plaque.

Chemetron has established a safety committee consisting of three salaried and three hourly employees. This committee meets monthly to discuss safety violations observed during inspections and to discuss a time table for abatement. In addition, the committee is also responsible for the investigation of accidents.

The company provides the employees with safety glasses, hard hats, safety shoes (up to $15.00 reimbursement) and other safety equipment as determined to be required for a specific job. The employees and the supervision are encouraged to preplan work so that each employee has proper safety equipment before commencing his assignment. Personal protective equipment includes boots, chemical type safety glasses, cover goggles, face shields, gloves, respirators, Scott air pacs and Welch disposable Respirators for chlorine. Each man is provided with two lockers, one for street clothes and one for work clothes. Shower facilities are also available.

This plant does not currently employ an industrial hygienist; however routine industrial hygiene sampling is performed by the front line supervisors, the operation's superintendent or by the Safety Director.

The ventilation system in the antimony plant is essentially associated with processing equipment. Due to the negative pressure on the system it is effective in controlling SO_2 and particulates in the work place. A local exhaust ventilation system has been installed where the antimony products are packaged. This system reduces the exposure of the operator during the packaging operation.

Chemetron has recently installed a local exhaust system and baghouse at the zinc pouring area of the foundry. During the walk-through they were not pouring so no assessment of the effectiveness of the system could be made. In discussions with production workers and supervisors concerning the effectiveness of the system design it seems that it does quite well in controlling the fumes generated during the pouring of molten zinc.

The SO_2 generated during the pyro process is presently being discharged to the atmosphere. Plans are being formulated to import crude antimony oxide ore which has been processed in the country of origin, thus eliminating the majority of the SO_2 emissions.

POTENTIAL HEALTH HAZARDS

The following is a list of the potential health hazards observed during the walk-through survey and from the lists of raw materials and products provided by the company.

1. Respiratory and skin exposure to antimony fume and dust*.
2. Respiratory and skin exposure to nitric acid.
3. Respiratory and skin exposure to chlorine.
4. Respiratory and skin exposure to allyl chloride.
5. Respiratory and skin exposure to radioactive material* in the past.
6. Respiratory and skin exposures to Boron trifluoride.
7. Skin exposure to sulfuric acid.
8. Skin exposure to acetic acid.
9. Skin exposure to hydrofluoric acid.
10. Respiratory exposure to sulfur dioxide.
11. Respiratory exposure to arsenic trioxide.*
12. Respiratory exposure to hydrogen sulfide.
13. Respiratory exposure to zinc fumes.
14. Respiratory exposure to filter acid.
15. Skin and mucous membrane exposure to hydrogen peroxide.
16. Skin and mucous membrane exposure to sodium hydroxide.
17. Inhalation, ingestion and skin exposure to epichlorohydrin.*
18. Inhalation, ingestion and skin exposure to muriatic acid (hydrochloric acid).

19. Inhalation and skin exposure to formaldehyde.
20. Inhalation and skin exposure to nickel.*
21. Ingestion exposure to copper chromate. *
22. Ingestion exposure to copper carbonate.
23. Inhalation and ingestion exposure to formic acid.
24. Inhalation and ingestion exposure to sodium arsenate. *
25. Inhalation and ingestion exposure to sodium antimonate.
26. Inhalation exposure to cadmium. *
27. Inhalation exposure to chromium.*
28. Inhalation exposure to manganese.

*KNOWN OR SUSPECTED CARCINOGEN

SAMPLING AND ANALYTICAL PROCEDURES

Nine air samples were collected at a rate of 2.0 liters per minute (lpm) by a MSA Model "G" dampened, sampling pump using 37 mm AA millipore filter, 0.8 micron pore size, as a collection media. The sampling duration was between 6 and 7 hours. The five antimony oxide production workers on the shift all wore samplers. These samples were analyzed for arsenic and antimony. Three general area samples were collected and analyzed for antimony and arsenic and one general area sample was collected and analyzed for arsenic, antimony and nickel.

Air samples for SO_2 were collected with a Drager pump using detector tubes.

RESULTS AND DISCUSSION

The results are included in Table 1. The following is a summary of those results:

Antimony Production Area

Antimony

1. Personal Exposure: The levels ranged from 0.21 to 3.25 mg/m^3, 4 of 5 (80%) of the samples for antimony exceeded the current legal standard of 0.5 mg/m^3 and all of the samples exceeded the Threshold Limit Value (TLV) intended change of 0.05 mg/m^3 of air (Table 1).

2. General Area Samples (Bagging Operation): 1 of 2 (50%) of the samples for antimony exceeded the current legal standard and all of the samples exceeded the TLV level. The levels ranged from 0.43 to 0.83 mg/m^3 of air.

Arsenic

1. Personal Exposure: None of the samples for arsenic exceeded the current legal standard of 0.5 mg/m^3 of air. The sensitivity of the analytical procedure was not adequate to compare the levels with the proposed OSHA standard of 0.004 mg/m^3.

2. General Area Samples (Bagging Operation): None of the samples for arsenic exceeded the current legal standard of 0.5 mg/m^3.

SO_2

No SO_2 was detected within the antimony production facility. (Table II)

Locker Room

Antimony

The general area sample collected in the change room was below the current legal standard for antimony of 0.5 mg/m^3 of air. However, the sample did exceed the proposed TLV of 0.05 mg/m^3. (Table 1)

Arsenic

The general area sample collected in the change room was below the current legal standard of 0.5 mg/m^3 for arsenic.

Nickel Sulfate Operation

Nickel, Antimony, Arsenic

The general area sample collected in this area was below the current legal standard and TLV for these contaminants.

RECOMMENDATIONS

Nickel Sulfate Production Area - Install a self-contained breathing apparatus at the operators station for emergency egress. Hydrogen sulfide is more dense then air therefore it would settle in low places. If because of an accident, the operator would have to come down off of the stand, and go to the corner of the building to get the proper protective equipment it could be fatal. Characteristic of H_2S is that the olfactory system is fatiqued rapidly when exposed to high concentrations of H_2S, therefore, lethal concentrations can not be detected by the characteristic odor. It is recommended that a monitor be purchased with an alarm system set to actuate at or below the TLV for hydrogen sulfide.

Antimony Oxide Production Area - Conduct comparative tests on the local exhaust systems at the antimony oxide packaging stations. Redesign, if necessary, these systems on the basis of the findings from the comparative tests and the concentration data .

Foundry - Sample the area in the vicinity of the zinc molds to determine if the local exhaust system is effective in controlling the worker exposure to zinc fumes.

Material Handling - Continue education of the workers in the hazards of handling corrosive materials such as acids and caustics. Make certain that impervious gloves, aprons or clothing are provided when the job requires their usage and emphasize the usage of eye protection such as face shields, splash goggles or chemical goggles while handling these materials.

General - Due to the fact that the production workers are exposed to a number of different toxic materials it is recommended that the company consider providing the workers with work clothes along with a laundering service so that the worker's family is not exposed to toxic materials picked up in the work place. If it is not feasible for the company to launder on site, then a viable alternative would be to contract with a commercial laundry that has the capabilities of cleaning contaminanted work clothing. This laundering requirement may be written into future standards promulgated for exposure to toxic materials.

The purpose of this study is to ascertain if antimony is a carcinogen though the mechanism of a retrospective mortality study. In the case of Chemetron it would not be possible to define the causative agent, should an increased incidence of cancer be observed, because the plant population is potentially exposed to other known or suspected carcinogens such as nickel, arsenic, chromium, epichlorohydrin and in the past radioactive materials. The problem is compounded by the fact that the production workers work under a plant seniority system rather than a departmental seniority system, therefore, a worker could and usually is exposed to one or combination of carcinogens. It is recommended therefore that the retrospective mortality study be done at another facility.

TABLE 1

Contaminant Concentration, mg/m^3

Job Description & Area	Type of Sample	Sample Volume, ft^3	Concentration		
			Antimony	Arsenic	Nickel
Furnace Operator	BZ	0.71	1.25	0.039	--
Furnace Operator	BZ	0.77	3.25	<0.035	--
Packager	BZ	0.76	0.21	<0.035	--
Process	BZ	0.76	1.20	<0.035	--
Packager	BZ	0.74	0.78	<0.035	--
Locker Room	GA	0.75	0.28	<0.035	--
Nickel Sulfate Facility	GA	0.71	0.01	<0.035	0.018
Bagging Operation	GA	0.60	0.43	<0.035	--
Bagging Operation	GA	0.60	0.83	<0.035	--
OSHA, Current Standard		N/A	0.5	0.5	1.0
OSHA, Proposed Standard		N/A	--	0.004	--
NIOSH Recommended		N/A	--	0.002	--
TLV - ACGIH		N/A	0.05*	0.05*	0.1*

*Notice of Intended Changes

TABLE II

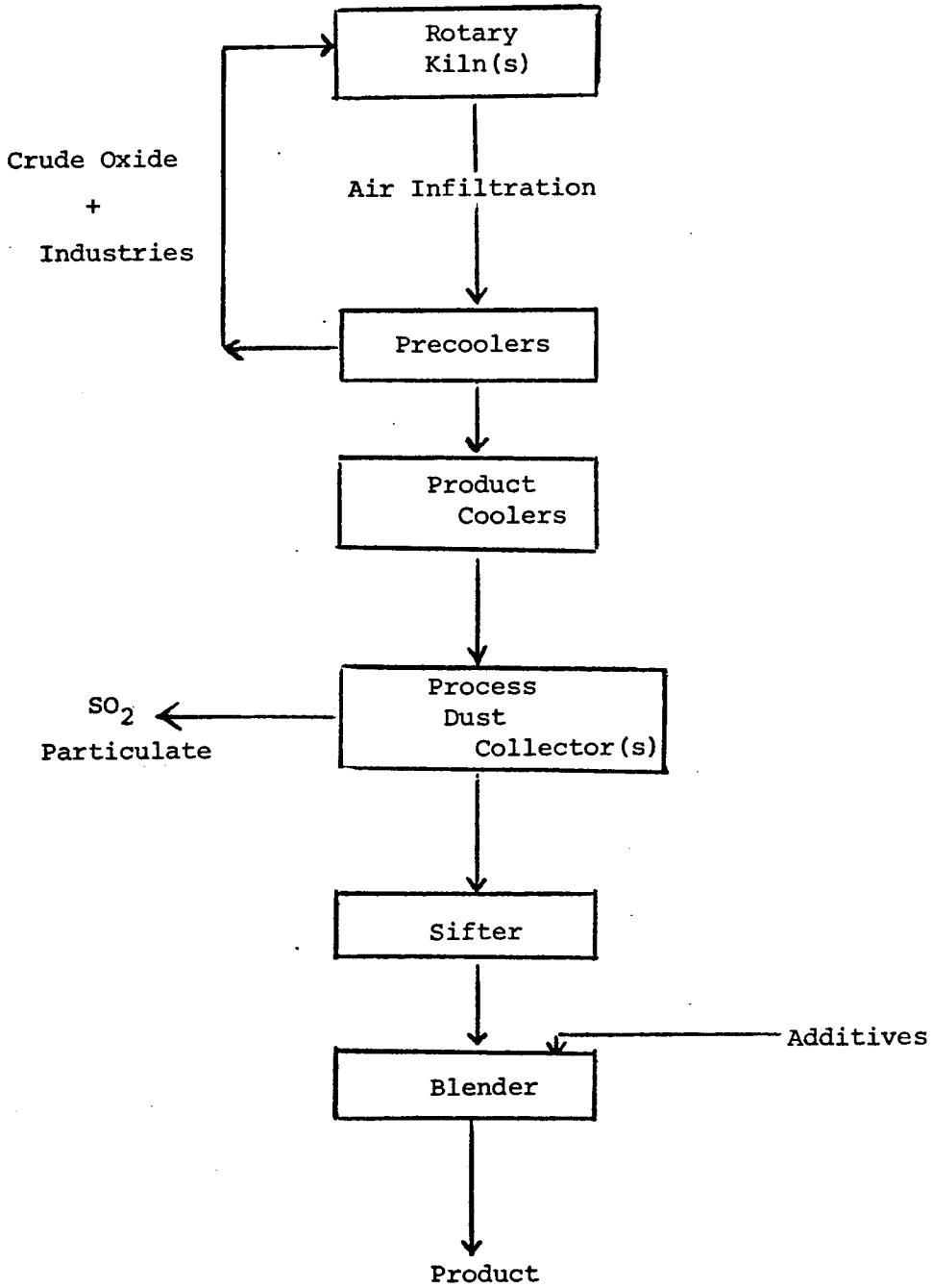
Sulfur Dioxide Concentration

Location	Number of Exposed	SO_2, ppm
Primary Furnace	1	ND*
Primary Furnace Coolers	1	ND*
Primary Furnace Baghouse		ND*
Refuming Furnace	1	ND*
Refuming Furnace Coolers	1	ND*
Refuming Furnace Baghouse		ND*
Bagging	2	ND*
OSHA Legal Standard		5.0
OSHA Proposed Standard		2.0
NIOSH Recommended		2.0
TLV - ACGIH		5.0

*Notice of Intended Changes

FLOW SHEET

Antimony Oxide
Antimony Ore $Sb_2 S_3$
and/or
Crude Oxide $Sb_2 O_3$



MATERIAL FLOW