INDUSTRIAL HYGIENE SURVEY REPORTS

The Harshaw Chemical Company
Gloucester City, New Jersey

ANTIMONY OXIDE PRODUCTION

I. Walk-Thru Industrial Hygiene Survey
May 14 & 15, 1975

II. Air Sampling Industrial Hygiene Survey
June 17, 1975

REPORTS PREPARED BY:

Harry Donaldson
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JULY, 1975

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Center for Disease Control
Division of Field Studies and Clinical Investigations
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I. WALK-THRU INDUSTRIAL HYGIENE SURVEY

The Harshaw Chemical Company
Gloucester City, New Jersey 08030
Telephone: (609) 456-3930

May 14 & 15, 1975

NIOSH PERSONNEL PRESENT:

Hector Blejer
Harry Donaldson
Bruce Gehring (U.C.)
Ronald Young
Stephen Gentry

PERSONS CONTACTED:

Joseph Sigmund - Corporate Industrial Hygienist
Harry Litten - Plant Manager
Robert Whittick - Member of the Plant Health and Safety Committee

PURPOSE OF VISIT:

To make a walk-thru industrial hygiene survey of the antimony oxide production facilities and to take samples, both GA and personal. These samples are to be analyzed for Arsenic and Antimony.

UNION:

O.C.A.W.

SURVEY OF THE HARSHAW CHEMICAL COMPANY'S ANTIMONY PRODUCTION FACILITIES
Gloucester City, N.J. - May 14 & 15, 1975

INTRODUCTION AND GENERAL COMMENTS:

The plant is located in New Jersey on the Delaware River across from Philadelphia. It is in the vicinity of several other chemical plants. The plant consists of one large building on about ten acres. It houses not only antimony oxide production facilities, but also sodium methylate and isopropyl gallate production facilities.

Antimony oxide production was begun here in 1951. The building was originally used in the shipbuilding industry and was built around 1918.

The plant population involved with antimony oxide production consists of approximately 17 operators and 4 maintenance men. The maintenance people work on other processes also. The plant operates 24 hours a day, 7 days a week. The total plant population is about 60 people.

Prior to production of antimony oxide, the plant site, purchased by Harshaw about 1946, was used for the manufacture of chemicals such as nitration grade glycerine, metallic soaps, and miscellaneous chemicals.

The plant has no full-time medical or safety personnel, but it does have a medical program which involves preemployment physicals, periodic x-rays, and biological monitoring for antimony. Safety shoes and respirators are supplied along with air supplied hoods worn when ore is fed to the hoppers.

Maintenance people only are supplied with hard hats. There appears to be no general program covering safety glasses. Showers are provided and are mandatory. Work clothes are supplied.

PROCESS:

Antimony oxide production starts with the feeding of Sb_2S_3 ore to a rotary kiln type furnace operating at approximately 1800°F; 10% excess air is drawn through the furnace. The Sb_2S_3 reacts thus:

$$Sb_2S_3 + 4\text{-}1/2O_2 = Sb_2O_3 + 3SO_2$$

The SO_2 which results from this reaction is pulled through the process and at the present time is being discharged to the environment via a stack approximately 200' high. Under construction is an SO_2 scrubber which will essentially eliminate the SO_2 discharge. Also a material called "saw tooth" (Sb_2O_4) is formed and dropped out of the stream.

After the elimination of SO_2 and "saw tooth," the resulting antimony oxide which has sublimed, passes through coolers to a collector from where it is pneumatically conveyed to a secondary furnace. In this furnace it is re-sublimed, goes through more coolers to a holding tank, and then is bagged.

The "saw tooth" (Sb_2O_4) along with floor sweepings and slag chipped from the furnace is fed to a separate recovery furnace which converts the Sb_2O_4 to Sb_2O_3. The resulting Sb_2O_3 after sublimation and collection is fed into the secondary furnace where it is resublimed along with the Sb_2O_3 preduced in the primary furnace. These combined streams make up the final product.

GENERAL IMPRESSION AND OBSERVATIONS:

During the visit the plant was not in operation due to a main bearing failure on the primary furnace. Though it was expected that the plant would be in operation for the second day of the visit, it was discovered upon repair of the bearing that a cooling water line on the primary furnace had also failed. This resulted in the process being out of operation for another twenty-four hours. Hence, no air samples were collected, though a bulk product and a bulk ore sample were obtained which will be analyzed for arsenic and trace metals.

According to the company people the air levels are in excess of the TLV for Sb. The air levels for arsenic also exceed the TLV. At the present time the company is working on a process to reduce the arsenic content of the ore.

The plant has white powder, Sb_2O_3, all over the equipment and walls and to some extent the floors. One of the plant's biggest dust problems is associated with the bagging station where the wrong size bags are currently being used. This results in a cloud of Sb_2O_3 dust every time a bag is filled. The operator of the bagging machine wears an air supplied hood which gives him protection, but this hood does not prevent dust from spreading throughout the plant. When the proper sized bags are obtained for the bagging machine this condition will be improved. To further reduce the dustiness around the bagging station a stall type hood with slot type ventilation should be provided. With this problem under control, the plant will then need to be resurveyed to determine the exposure of personnel to antimony and arsenic. Since there are only a few people on a shift in this plant, it is planned to pin personal sampling pumps on each person in order to obtain this information.

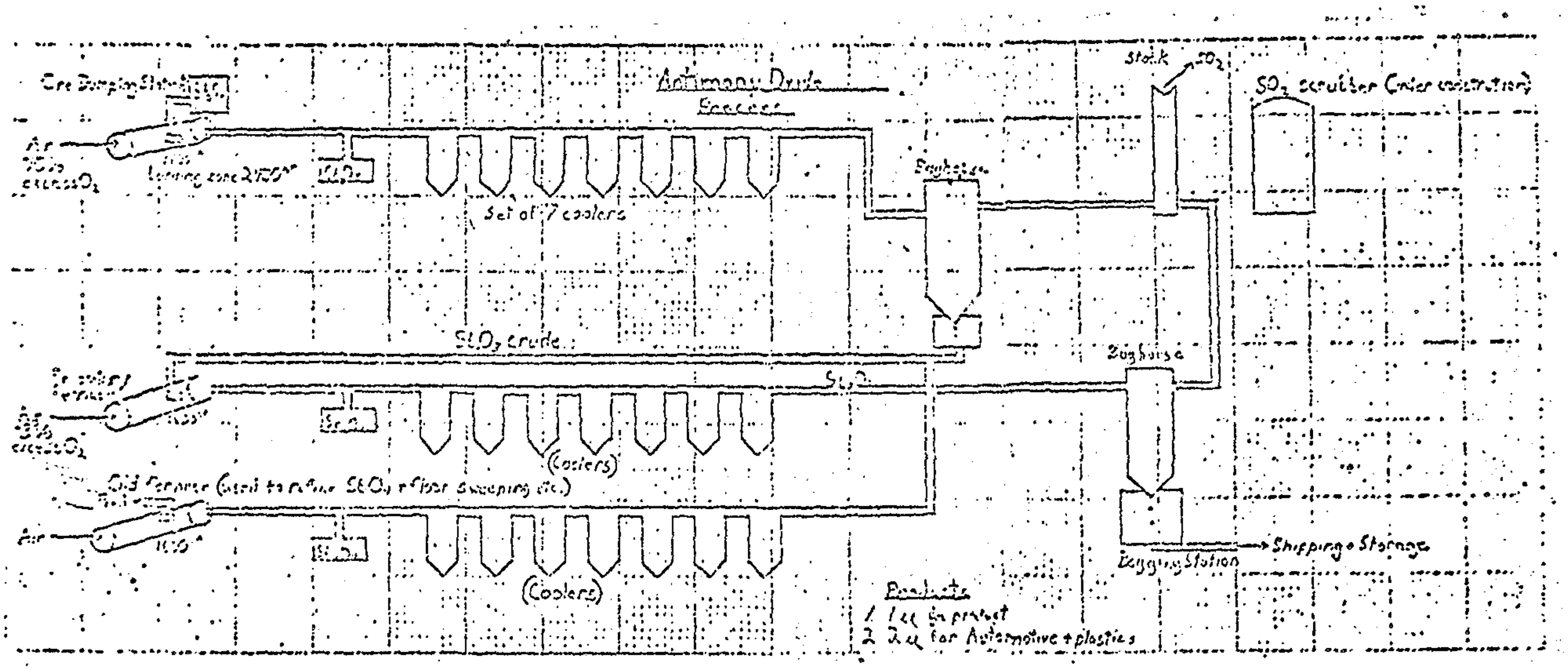
Though the plant was not in operation during our visit, from information gathered from the company and from inspection of the non-operating equipment it appears that besides the problem with the bagging machine that there are other hygiene problems which can best be evaluated after air sampling is done at the plant.

Typical analyses for antimony concentrates (ore) and the antimony oxide product are appended along with a flow sheet of the process. Results of air samples when collected, analyzed, and evaluated will be appended to this report.

HARSHAW DATA

ANTIMONY CONCENTRATES	TYPICAL VALUES
Antimony	59.5
Sulfur	25.6
SiO_2	4.0
Calcium	0.2
Magnesium	2.0
Iron	1.5
Aluminum	0.2
Lead	0.1
Nickel	0.2
Copper	0.1
Arsenic	0.3
Selenium	<1 part per million
ANTIMONY OXIDE	
Antimony trioxide	99.2
Antimony tetraoxide	0.3
Copper	<0.0001
Nickel	<0.001
Iron	0.0003
Lead	0.06
Arsenic	0.3
Sulfate	0.01
SiO_2	0.02
Selenium	<1 part per million

The values for the antimony concentrates are based on the last ten (10) lots of concentrate. The typical values for antimony oxide are based on analytical work completed since December, 1972.



PROCESS FLOW SHEET

II. AIR SAMPLING INDUSTRIAL HYGIENE SURVEY

The Harshaw Chemical Company,
Gloucester City, New Jersey

June 17, 1975

ANTIMONY OXIDE PRODUCTION FACILITIES

SURVEY CONDUCTED BY:

Harry Donaldson
Stephen Gentry

AIR SAMPLING SURVEY OF THE HARSHAW CHEMICAL COMPANY'S ANTIMONY PRODUCTION FACILITIES Gloucester City, N.J. - June 17, 1975

INTRODUCTION:

Air samples were collected on the day shift on June 17, 1975 at the Antimony Oxide Production Facilities of the Harshaw Chemical Company, Gloucester City, N.J. The plant had been in operation for only a few days following about a two-week shutdown at which time the kilns were relined and general shutdown-type maintenance was performed. The operation of the plant appeared to be normal except that the primary kiln was being run at a temperature lower than the previous visit - about 1600°F vs. 1800°F. The management explained that this lower operating temperature was necessary until sufficient slag was built up on the kiln lining so as to prevent damage to the furnace. It was also pointed out that the volume of production at the lower temperature was about the same as at the higher temperature which was noted on the previous visit. It appears that for all practical purposes, depending on plant conditions, type of ore, and other factors, the operating range of the primary kiln is between 1600-1800°F, with the secondary kiln operating nearer to 1600°F.

MONITORING PROCEDURES:

Twelve air samples were collected using personal pumps at a flow rate of 2.0 liters per minute, on 37 mm AA Millipore membrane filters, 0.8 pore size. The sampling time was approximately seven hours. Four of the samplers were worn by the workmen. This constituted the entire operating crew. The plant has only 17 operators covering an operation which runs continuously three shifts per day. In addition to the four personal samples above, eight general area samples were collected at strategic locations around the plant. These locations included the bagging operation, the ore hopper, and at the vicinity of other operations both inside the building and out of doors between the building housing the kilns and the building housing the coolers.

RESULTS OF THE AIR SAMPLES COLLECTED:

Results appended, show the following ranges:

	Sb, Mg/m³ 1.8 - 8.7	As, Mg/m³ 0.0017 - 0.056
BZ SAMPLES (4)	2.7 - 8.7*	0.0155 - 0.056*
GENERAL AREA SAMPLES (8)	1.8 - 5.6	0.0017 - 0.016

*Sample #3 which gave a high value may have become contaminated.

Examination of the data shows all the antimony values to be above the current TLV of 0.5 Mg/m^3 and with the exception of Sample #8 which showed an arsenic level of 0.0017 Mg/m^3 all other samples are above the arsenic standard proposed in the 1975 criteria document for inorganic arsenic. Sample #3 which gave high results of 8.7 Mg/m^3, Sb and 0.056 Mg/m^3, As was probably contaminated as the result of a spill around the bagging operation which resulted in the operator becoming covered with antimony oxide powder. When the operator cleaned himself off with compressed air after this spill, the cap came off the filter cassette he was wearing. If Sample #3 is thrown out, the range for airborne antimony and arsenic is reduced as follows:

Sb,Mg/m^3	As,Mg/m^3
1.8 - 5.6	0.0017 - 0.0267

This indicates that the antimony levels are above the 0.5 Mg/m^3 OSHA standard. The arsenic levels are below the current OSHA standard of 0.5 Mg/m^3 but are above the proposed OSHA standard of 0.004 Mg/m^3.

GENERAL OBSERVATIONS OF THE PROCESS AND PROCESS VENTILATION:

Though the plant process appears to be satisfactory for the manufacture of antimony oxide, it apparently was designed with the idea that hygienic conditions would be controlled by the negative pressure on the system necessary to pull combustion air through the process and exhaust SO_2 out through the 200' stack. Unfortunately, the negative pressure does not take care of all hygienic problems.

In general it appears that the process equipment as a whole should be re-examined by competent process engineers. Possibly some of the process duct work should be resized so that powder does not drop out of the stream and plug the system. More clean-out ports may be needed in the process duct work where periodic plugging occurs. Improved local exhaust ventilation and hooding are needed, especially around the bagging operation. In addition to the need for ventilation improvements, at the time of this visit the bagging machine was in need of repair. The greatest problem, however, with the bagging operation is the use of bags that are too small. This results in a cloud of dust being blown all over the room each time a bag is filled. The management recognizes this problem and larger bags are on order. However, according to Mr. Sigmund, the Corporate Industrial Hygienist, the delivery date on these new bags is about a year away.

The company recognizes that steps must be taken to improve the inplant air levels for both antimony and arsenic. They indicated that they have been working on a process that will reduce the arsenic in the ore which is currently running 0.3 to 0.5% arsenic. The urgency of more effective dust control was emphasized by the fact that companion samples taken by the company showed approximately the same results as those reported in this Study for arsenic and antimony.

As a result of this survey, the company has engaged the environmental consulting firm of Spotts, Stevens and McCoy, Inc. to survey their situation and to make recommendations leading to the control of airborne dust resulting from their processes. In addition, the company has taken steps to procure additional monitoring equipment and they plan to take personal samples on a regular basis.

CONCLUSIONS AND RECOMMENDATIONS:

On the basis of a single sampling survey at the antimony oxide facility of the Harshaw Chemical Company in Gloucester City, New Jersey, it can be concluded that the airborne levels at this plant with respect to antimony exceed Federal standards for this material, and the airborne levels for arsenic are below the current Federal standards but above the proposed OSHA standards.

It is recommended:

(1) That the process as a whole be examined by competent process engineers, and changes made necessary to reduce fuming and eliminate plugging of process streams;

(2) That improvements in hooding and ventilation be made, especially around bagging operation, which at the time of this visit was in need of repairs;

(3) That a stepped-up effort be made to procure proper size bags for the bagging of the antimony oxide product, so as to eliminate the cloud of dust currently generated in the filling of each bag;

(4) That improved work practices, especially in respect to the elimination of the use of compressed air for cleaning clothing, be instituted and strictly enforced.

GA and Personal Samples
Harshaw Chemical Company
Gloucester City, New Jersey
June 17, 1975

LOCATION	TIME ON	TIME OFF	TOTAL MIN	FLOW RATE lpm	VOLUME (Air)	Sb Mg/m^3	As Mg/m^3	TYPE OF SAMPLE
SAMPLE 1 - Operator - New System.	8:30 AM	3:30 PM	420	2	0.840	2.7	0.0169	Personal
SAMPLE 2 - Operator - Miscellaneous.	8:30 AM	3:30 PM	420	2	0.840	5.0	0.0267	Personal
SAMPLE 3 - Bagging & No. 4 man.	8:30 AM	3:30 PM	420	2	0.840	8.7*	0.0560*	Personal
SAMPLE 4 - Ore Dumper (Wore air hood)- Sampler not under hood.	8:30 AM	3:30 PM	420	2	0.840	4.5	0.0155	Personal
SAMPLE 5 - Top of coders.	8:55 AM	3:35 PM	400	2	0.800	5.6	0.0061	General Air
SAMPLE 6 - At bagging station.	8:45 AM	3:30 PM	405	2	0.810	2.3	0.0143	General Air
SAMPLE 7 - At ore hopper operator wears air-supplied hood to dump ore.	8:45 AM	3:30 PM	405	2	0.810	2.8	0.0092	General Air
SAMPLE 8 - Ore feed, second level outside.	8:45 AM	3:35 PM	410	2	0.820	1.8	0.0017	General Air
SAMPLE 9 - On I beam over-bagging operation.	9:00 AM	3:30 PM	390	2	0.780	2.6	0.0162	General Air
SAMPLE 10 - At control panel.	9:00 AM	3:30 PM	390	2	0.780	1.9	0.0105	General Air
SAMPLE 11 - At operator's desk.	8:50 AM	3:30 PM	400	2	0.800	2.9	0.0147	General Air
SAMPLE 12 - Feed oxide, out-of-doors - 2nd deck.	8:50 AM	3:35 PM	405	2	0.810	5.3	0.0057	General Air

*Sample cassette fell apart at 11:30. Put another complete cassette on man - results indicate total of both filters - 1st filter may have been contaminated.

NOTE: Arsenic analyses were performed using P&CAM 139 and antimony analyses were performed using direct aspiration in the air-acetylene flame of atomic absorption.