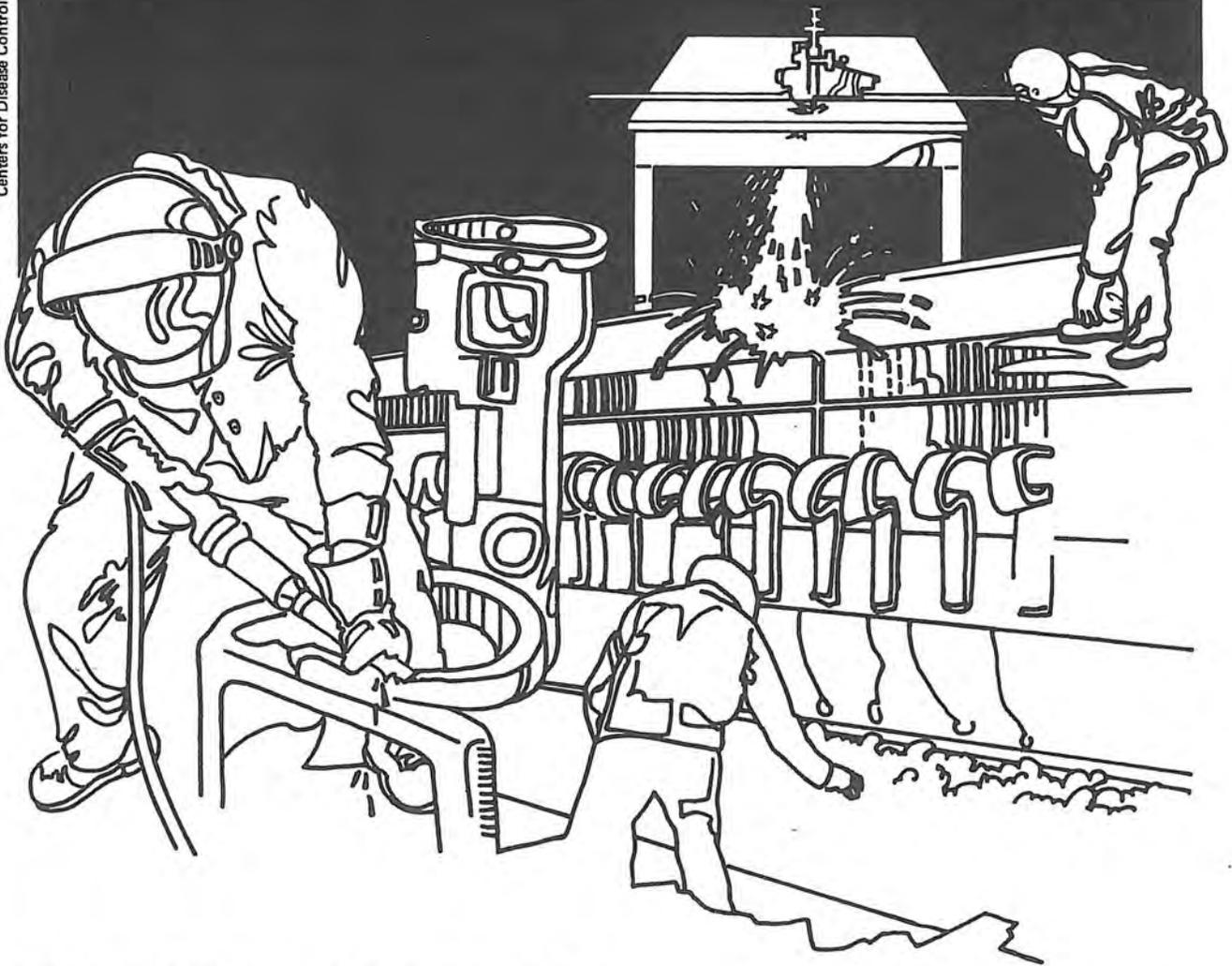


NIOSH



Health Hazard Evaluation Report

HETA 81-126-926
SILVER SYSTEMS LTD.
CHAMBLEE, GEORGIA

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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-126-926
JULY 1981
SILVER SYSTEMS LTD.
CHAMBLEE, GEORGIA

NIOSH INVESTIGATORS:
S. Salisbury, IH

I. SUMMARY

On January 29, 1981, the National Institute for Occupational Safety and Health (NIOSH) conducted a health hazard evaluation at Silver Systems Ltd. (SSL), Chamblee, Georgia, in order to evaluate occupational exposures to hydrogen cyanide (HCN) gas released from a sodium cyanide solution used in the process of recovering silver from exposed photographic and x-ray film.

HCN gas concentrations were monitored using Dräger long term detector tubes. The employee assigned to operate the silver recovery process (the barrel man) was exposed to HCN above the NIOSH recommended ceiling limit of 4.5 parts per million (ppm). The large wall fan used to ventilate the work area was pulling HCN contaminated air through other areas of the building occupied by SSL before being exhausted to the outside.

The average full shift personal exposure for the barrel man was 7.7 ppm with a peak exposure of 12.4 ppm detected when loading and unloading film in the stripping tanks. None of the measurements for HCN were above the 8-hour time weighted average federal standard of 10 ppm enforced by the Occupational Safety and Health Administration (OSHA). Routinely exposed employees interviewed had not experienced symptoms of adverse health effects, but these employees had worked at SSL less than two months.

Based on results of atmospheric tests indicating exposure to HCN exceeds the recommended NIOSH exposure criteria, NIOSH has determined that a health hazard does exist for the barrel man when changing film in the barrels. A potential hazard exists for other SSL employees who must work for extended periods in contaminated areas, such as the electronics assembly shop, or the QC office. Improved ventilation by means of a properly designed local exhaust system and interim use of an HCN gas mask for the barrel man have been recommended in this report.

KEYWORDS: SIC 3341, hydrogen cyanide, cyanogram, sodium cyanide, silver recovery

II. INTRODUCTION

On December 22, 1980, NIOSH received a request from the General Manager, Silver Systems Ltd., Chamblee, Georgia, for a health hazard evaluation of working conditions at their plant. The company had been notified by OSHA on November 13, 1980, that an informal complaint had been submitted by the occupants of an adjacent office claiming air contamination from Silver Systems' film stripping operation was causing headaches and throat irritation. An industrial hygiene survey was conducted by NIOSH on January 29, 1981. The purpose of the survey was to evaluate possible exposures to hydrogen cyanide (HCN) gas during the film stripping process and to determine if exposed employees had experienced any symptoms or adverse health effects as a result of that exposure.

III. BACKGROUND

Silver Systems Ltd. manufactures, sells, and services silver recovery units for medical and lithographic film processors. Recovered silver is melted down and sold as slag bars. A percentage of the profits from sale of recovered silver is shared with customers using the SSL unit. SSL has been in business over 7 years and currently operates 8-hour shifts, 2 shifts per day, 7 days a week. SSL is owned and operated by 3 partners. Day shift employees include the General Manager, three service men, the barrel man, a quality control man, and one part-time secretary. One service man and one barrel man work the night shift.

During the past 2-5 years SSL has developed a process for stripping exposed photographic film using a sodium cyanide solution. Silver is recovered from the solution by electrolysis and collected on large stainless steel plates. One employee per shift (the barrel man) is responsible for operating the film stripping and recovery process.

Film brought in from the field is shredded and blown into a holding bin. The shredded film is loaded into perforated 55 gallon drums. The drums are partially submerged in vats (7 each) containing 180 gallons of stripping solution. The solution is water to which approximately 25 lbs. of sodium cyanide powder is added. The pH of the solution is maintained between 9-10 to insure efficient stripping of the film emulsion. The drum or "barrel" is rotated through the solution every few minutes for about two hours. The barrel man removes, rinses, drains and reloads the barrels 4 times during the shift. Stripped film is dumped in large fiber drums which are stored in one corner of the barrel room.

Electroplating current (4 amps) is applied continuously. Anodes and cathodes are large stainless steel plates which hang on the front and back of each vat and also on the rinse tank. Once each shift the barrel man removes and scrapes the silver from the cathode plates with a putty knife.

Ventilation in the barrel room consists of 3 small window fans mounted high on the wall separating the barrel room from the warehouse. Air from the warehouse is pulled into the barrel room through the three small fans and exhausted outside by means of a 6-foot diameter wall fan located at the far end of a corridor running at a right angle and connected to one end of the barrel room (see Figure 1).

When changing film in the barrels the barrel man wore an apron, rubber boots, and protective gloves. No eye protection was worn although goggles were available. Respiratory protection was not used during changeover which requires 30-40 minutes. Scraping Silver from cathode plates is a 30-minute job. With 4 changeovers and cathode scraping, work in the barrel room requires only about 3 hours per shift. At other times the barrel man is free to work in other areas such as the electronics assembly shop or warehouse.

IV. METHODS AND MATERIALS

Atmospheric concentration of HCN gas released from the film stripping process was measured with direct reading Dräger long-term detector tubes. Personal breathing zone samples were taken from the barrel man and QC man. General area samples were taken in the SSL office, warehouse, barrel room, QC office, electronics assembly shop (upstairs in loft), and at the intake of the large wall mounted exhaust fan. This fan discharged air out of an unused loading dock into the parking area in front of the building.

The Dräger long term detector tubes will detect HCN concentrations as low as 1 part per million (ppm) in a 10 liter sample. A known volume of air was pulled through the detector tubes using calibrated air sampling pumps set at a flow rate of approximately 20 cc. of air per minute. Detector tube readings were taken 3-4 times during the shift to determine cumulative time weighted average (TWA) exposure to HCN as well as the 8-hour TWA.

The two people with greatest exposure to the stripping process, the barrel man, and QC man, were interviewed and asked if they had experienced any symptoms of health related problems since working at SSL.

V. EVALUATION CRITERIA

A. Environmental Criteria

The environmental criteria described below are airborne concentrations of substances to which workers may be exposed for eight hours a day, 40 hours per week for a working lifetime without adverse health effects. Because of wide variation in individual susceptibility, a small percentage of workers may experience discomfort from some substances at concentrations at or

below the recommended criteria.¹ The time-weighted average (TWA) exposure refers to the average concentration during a normal 8-hour workday. The ceiling limit is the concentration which should not be exceeded even instantaneously.

The primary sources of environmental evaluation criteria considered for this study were: 1) NIOSH criteria documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) federal occupational health standards.

Environmental Criteria for Hydrogen Cyanide

<u>Ceiling Limit</u>	<u>Short Term Exposure Limit (10 Min.)</u>	<u>8-Hour Time Weighted Average</u>	<u>Source</u>
--	--	10 ppm	OSHA
	4.5 ppm	--	NIOSH
10 ppm	--	--	ACGIH

NOTE: ppm = parts per million parts of air

B. Toxicity

The adverse health effects from excess exposure (exposures to airborne concentrations of hydrogen cyanide above the evaluation criteria) are summarized below:

Hydrogen Cyanide

Hydrogen cyanide is a chemical asphyxiant. It inactivates certain enzymes, the most important being cytochrome oxidase, which are used by the cells of the body for cellular respiration. Although the cells receive an adequate supply of oxygen through the blood stream, they are unable to use this oxygen because the metabolic process has been blocked by the presence of the -CN ion. Inhalation, ingestion, or skin absorption of hydrogen cyanide may be rapidly fatal. Large doses may cause loss of consciousness, respiratory arrest, and death. The liquid and concentrated vapor are adsorbed rapidly through intact skin, but with little or no irritant effects on the skin itself. Lower levels of exposure may cause weakness, headache, confusion, nausea, and vomiting.² A concentration of 270 ppm has long been quoted as being immediately fatal to humans. Other studies have found that 270 ppm is fatal after 6-8 minutes, 181 ppm after 10 minutes, and 135 ppm after 30 minutes.³

In 1948, the ACGIH adopted a TLV for HCN as an 8-hour TWA of 10 ppm.⁴ This TLV was considered to provide a two-fold margin of safety for mild symptoms and a 7-8 fold margin against lethal effects.⁵ The present federal standard enforced by OSHA is also

10 ppm as an 8-hour TWA and is based upon the 1962 ACGIH TLV. In October of 1976 NIOSH recommended to the Department of Labor (OSHA) that occupational exposure to HCN be lowered to 5 mg/M³ (4.5 ppm), determined as a ceiling limit based on a 10 minute sampling period. An increase of subjective symptoms of headache, weakness, changes in taste and smell, irritation of the throat, labored breathing, watery eyes, abdominal colic, chest pain, and nervous instability has been noted among workers having long term low level exposures to HCN below the current OSHA standard of 10 ppm. Enlargement of the thyroid glands and changes in the chemical and cellular composition of the blood of employees exposed to cyanide have also been reported.⁴ The occurrence of symptoms of chronic disease has been reported in electroplating and silver polishing after several years of exposure. Headaches, weakness in arms and legs and thyroid diseases were the most prominent effects noted.⁶ In 1980 the ACGIH adopted 10 ppm as a ceiling limit for HCN thereby recommending that exposures not exceed 10 ppm even instantaneously.¹

VI. RESULTS

Results of air samples taken indicate the barrel man was exposed to HCN at levels exceeding the recommended NIOSH 10-minute ceiling limit of 4.5 ppm. Four out of 5 areas monitored were contaminated with HCN, especially during the beginning of the shift. The average full shift exposure for the barrel man was 7.7 ppm. During the first barrel changeover his exposure averaged 12.4 ppm. This high concentration early in the shift was also reflected in area samples which ranged from 8-12 ppm during the morning hours. Average HCN levels declined throughout the remainder of the day shift, although higher readings were observed during and immediately following barrel change over. The results as discussed above are presented in the attached table.

Although NIOSH's recommended limits were frequently exceeded, the concentration averages for full-shift exposures were below the 8-hour OSHA standard of 10 ppm. It is possible that HCN levels build up at night and decrease during the day. The most significant exposure period is during the first barrel changeover. All areas contaminated were downwind from the barrel area. The large 6 ft. dia. exhaust fan was pulling contaminated air through these areas prior to being exhausted to the outside. The sample taken from near the melting furnace was located approximately 10 feet in front of this exhaust fan intake.

The barrel man employed by SSL only 1 month had not experienced adverse health effects from his exposure except on one occasion during cleanup when "he suddenly felt sleepy". The QC man had not experienced any symptoms but had also worked at SSL for only 1 month. SSL reported that a former employee had quit the barrel job because of low tolerance to the smell of the vapors from the vats and stripped film. No clear description of symptoms experienced by this worker was available.

VII. DISCUSSION

The sodium cyanide used by SSL is supplied by the Ashland Chemical Company under the trade name Cyanogram. The product is labeled as 99% sodium cyanide. The label also contained a warning that the product "may be fatal if swallowed or inhaled" and that "contact with acids or weak alkalies liberates poisonous gas". The label also recommends having a "cyanide first aid kit on hand" and provides instructions for administering an antidote (inhalation of amyl nitrite).

In contrast to the excellent information provided on the product label, the Material Safety Data Sheet (MSDS) from the supplier was misleading and did not adequately address the potential hazard for exposure to HCN as a result of product decomposition. The MSDS refers to hazardous decomposition products as "cyanide fumes, etc". This statement may have led employees at SSL to believe that the "dust, fume, and mist respirator", worn when mixing Cyanogram with water, would also provide adequate protection against HCN, which is a gas, not a fume. The MSDS in Section VIII does recommend the use of self containing breathing apparatus to avoid overexposure.

The MSDS also stated in Section II - Hazardous Components, that the product was greater than 95% sodium cyanide and that no TLV had been established. This statement is false. Although there is no specific TLV for sodium cyanide, there is a TLV and an OSHA standard for cyanides (5 mg/M^3). Under Section V - Health Hazard Data, First aid procedures make no mention of administering an amyl nitrite as a temporary antidote for treatment against effects of acute overexposure to HCN.

Although SSL had requested the supplier provide technical assistance and recommendations for safe use of Cyanogram, the information was not accurate, and as a result, SSL employees had not been adequately protected. The information on the product label clearly states that Cyanogram may release HCN gas when in contact with weak alkalies. The pH of the cyanide solution in the film stripping vats at SSL has a pH between 9-10 (a weak alkali).

VIII. CONCLUSION

Atmospheric samples have demonstrated a potential HCN exposure hazard does exist. Adequate local exhaust ventilation is needed to properly control this hazard. Although SSL employees apparently are not exposed to HCN gas at concentrations above the OSHA standard (10 ppm as 8-hour TWA), a properly designed ventilation system should be installed. Contaminated air should not be pulled through the building and discharged directly onto the parking lot. The present ventilation system used by SSL violates the basic design principle of industrial ventilation and should be replaced with a properly designed local exhaust system.

IX. RECOMMENDATIONS

1. Film stripping tanks should be equipped with lateral draft local exhaust hoods vented to the outside by ducting contaminated air up through the roof (see Figure 1). Based on NIOSH guidelines for exhaust ventilating open surface tanks a minimum capture velocity of 50 feet per minute (fpm) is required for controlling HCN gas released from the cyanide solution. To maintain this capture velocity for tanks having a width to length ratio from 0.5-0.99, an exhaust volume of 90 cubic feet per minute (cfm) per square foot of tank area is required.⁷
2. The barrel man should wear proper respiratory protection when changing film in barrels. A full facepiece gas mask equipped with canister specific for HCN should be used until proper local exhaust systems are installed.
3. A cyanide exposure treatment kit should be procured by SSL and at least 2 people on each shift should be trained in the proper administration of the amyl nitrite antidote.
4. All SSL personnel should be made aware of the hazards associated with exposures to HCN and should be instructed to alert SSL management immediately if exposure symptoms are noted.

Comment:

Following the NIOSH survey, SSL has taken steps to have a proper local exhaust ventilation system installed in the barrel room. In the interim the barrel man has been provided a full facepiece HCN gas mask to be worn during barrel changeover.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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XI. DISTRIBUTION AND AVAILABILITY

Copies of this report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After ninety (90) days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from the NIOSH Publications Office at the Cincinnati, Ohio address.

Copies of this report have been sent to:

- a) Silver Systems Ltd.
- b) U.S. Department of Labor, Region IV
- c) NIOSH Region IV
- d) Designated State Agencies

For the purpose of informing the approximately 8 "affected employees", the employer will promptly "post" this report for a period of thirty (30) calendar days in a prominent place(s) near where the affected employees work.

XII. REFERENCES

1. "Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1980", American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio.
2. Occupational Diseases, A Guide to Their Recognition, Revised Edition, DHEW (NIOSH) Publication No. 77-181, June 1977.
3. Proctor, N.H., J.P. Hughes, Chemical Hazards of the Work Place, J.P. Lippincott Co., New York, pp 287-289, 1978.
4. Criteria for a Recommended Standard, Occupational Exposure to Hydrogen Cyanide and Cyanide Salts, DHEW (NIOSH) Publication No. 77-108, Cincinnati, Ohio, NIOSH, 1976.
5. "Documentation of the Threshold Limit Values, Supplements for Those Substances Added or Changed Since 1971", American Conference of Industrial Hygienists (ACGIH) 3rd. Edition, Cincinnati, Ohio, ACGIH, 1971.
6. Encyclopaedia of Occupational Health and Safety, International Labour Office, Geneva, Switzerland, McGraw-Hill Book Company, New York, pp 352-355, 1972.
7. Recommended Industrial Ventilation Guidelines, DHEW (NIOSH) Publication No. 76-162, Cincinnati, Ohio, NIOSH, 1976.

SILVER SYSTEMS LTD.
 CHAMBLEE, GEORGIA
 HETA 81-126

HYDROGEN CYANIDE CONCENTRATIONS
 January 29, 1981

<u>Job/Location</u>	<u>Sampling Period</u>	<u>Concentration</u> (ppm)	<u>Cumulative TWA</u> (ppm)
Barrel man (personal exp.)	9:14am-10:40am	12.4	12.4
"	10:40am-12:10pm	3.3	7.6
"	12:10pm-1:40pm	9.6	8.2
"	1:40pm-2:02pm	3.5	7.7
Barrel area on tank No. 1	9:45am-10:40am	9.0	9.0
"	10:40am-12:10pm	4.9	6.4
"	12:10pm-1:40pm	5.3	6.0
"	1:40pm-4:05pm	3.6	5.1
On melting furnace	9:58am-10:40am	11.5	11.5
"	10:40am-12:10pm	5.8	7.6
"	12:10pm-1:40pm	6.2	7.1
"	1:40pm-4:05pm	5.2	6.4
Shop (upstairs)	11:02am-12:10pm	12.0	12.0
"	12:10pm-1:40pm	4.5	9.7
"	1:40pm-4:05pm	2.5	4.7
QC Office	11:15am-12:10pm	8.0	8.0
"	12:10pm-1:40pm	5.9	6.8
"	1:40pm-4:05pm	2.6	4.8
QC man (personal exp.)	11:19am-12:10pm	4.0	4.0
"	12:10pm-1:40pm	4.6	4.4
"	1:40pm-4:05pm	1.8	3.2
Office	11:08pm-4:08pm	0.8	0.8

ppm = parts per million

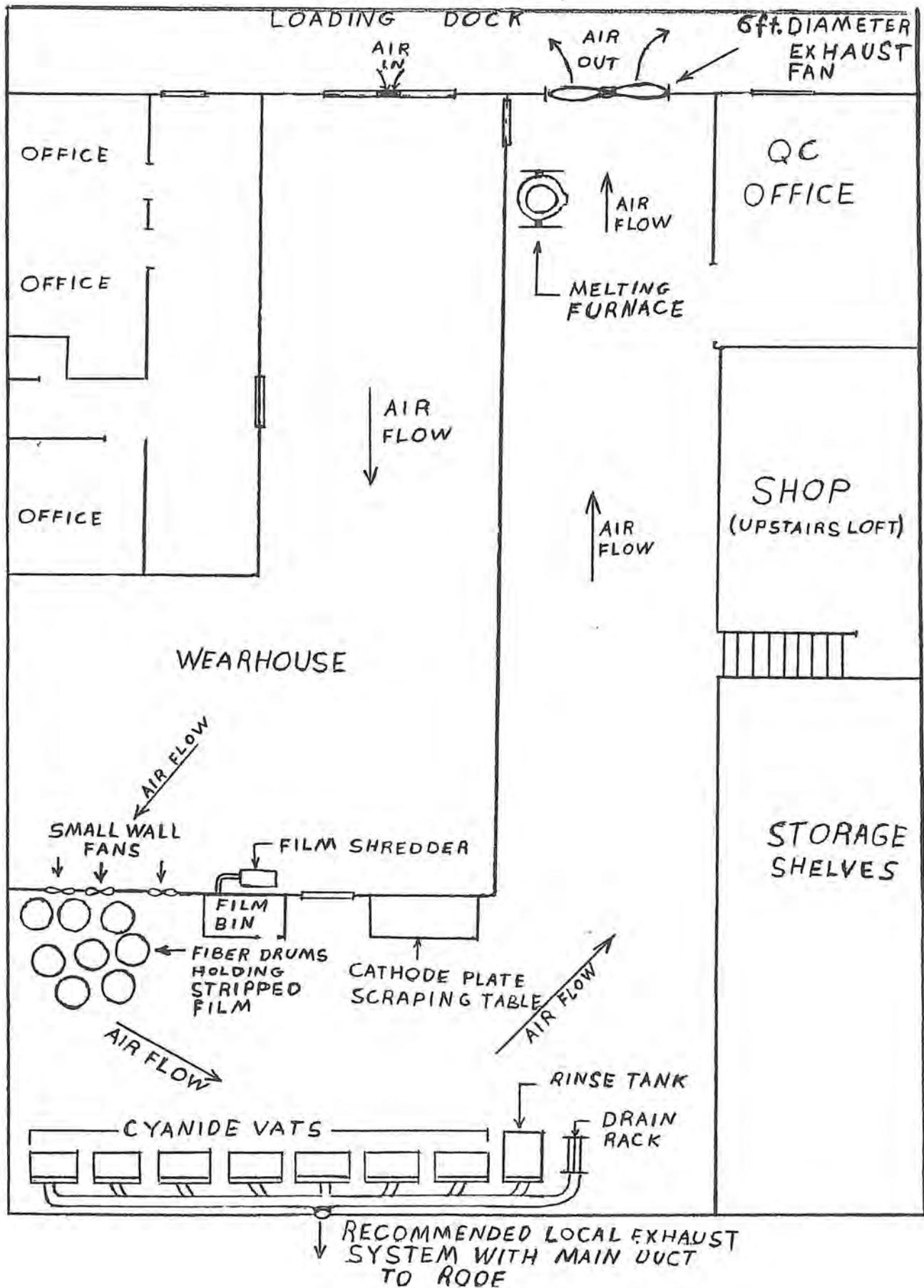
TWA = time weighted average concentration

OSHA standard = 10 ppm (TWA) for full 8-hour shift

NIOSH recommended limit = 5 mg/M³ (4.5 ppm) as ceiling limit (10 min.)

Note: All concentrations were measured using DRAGER long term detector tubes.

FIGURE 1
 SILVER SYSTEMS LTD.
 FLOOR PLAN WITH
 CURRENT AIR FLOW PATTERN AND RECOMMENDED LOCAL EXHAUST SYSTEM



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