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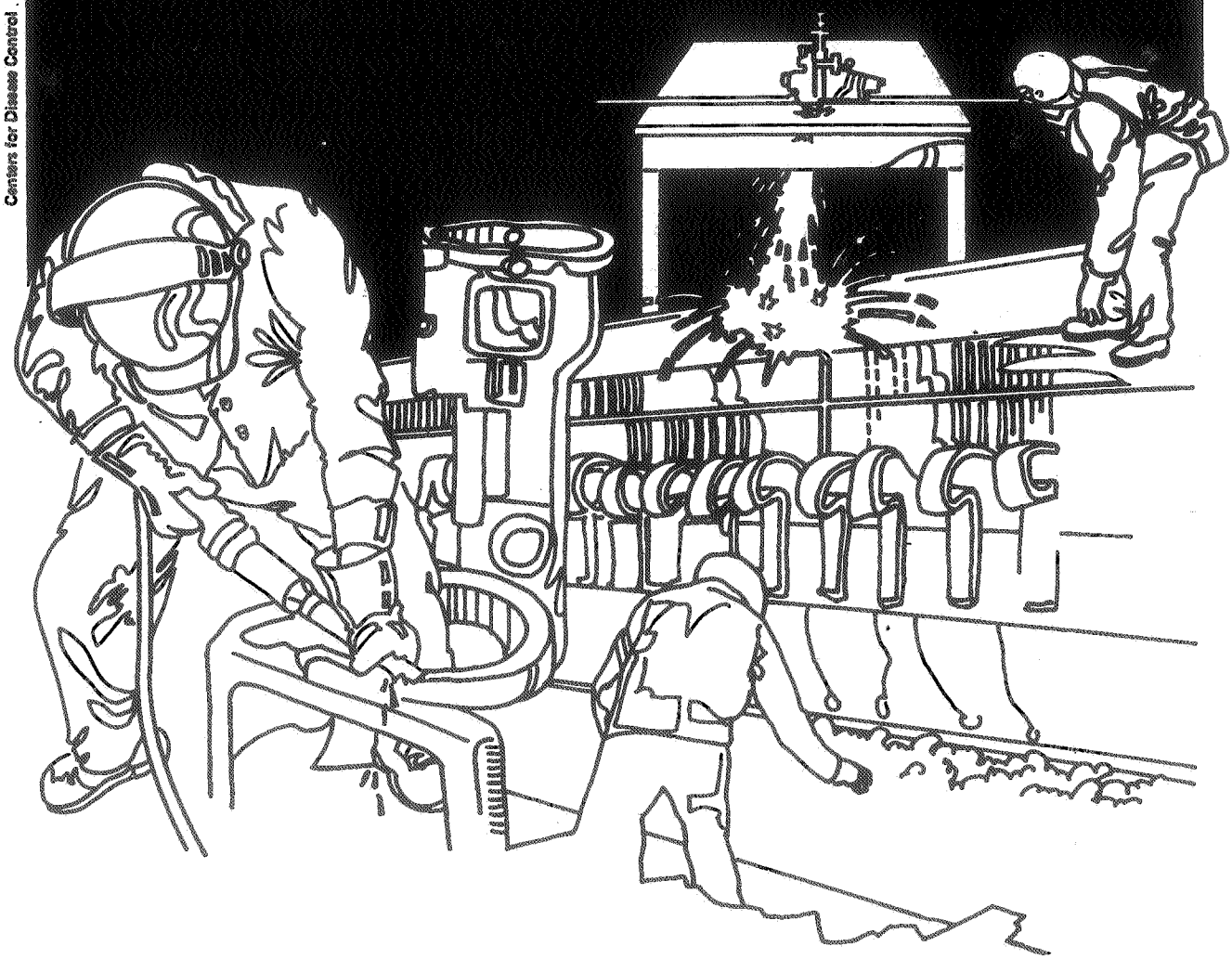

Health Hazard Evaluation Report

HETA 83-164-1377
SIEMENS COMPONENTS, INC.
BROOMFIELD, COLORADO

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.

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SIEMENS COMPONENTS, INC.
BROOMFIELD, COLORADO

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I. SUMMARY

In March 1983, the National Institute for Occupational Safety and Health (NIOSH) received a management request to evaluate worker exposure to etching acids and organic solvents used during semiconductor manufacture at Siemens Components, Inc., Broomfield, Colorado.

In March 1983, a NIOSH industrial hygienist visited the facility and collected personal breathing zone samples for nitric, hydrofluoric, and acetic acids, methanol, isopropanol, 1,1,1-trichloroethane, xylenes, acetone, n-butylacetate, methylene chloride, and trichlorotrifluoroethane (Freon 113). Work practices and engineering controls were observed and employees were interviewed, focusing on health complaints relating to the workplace.

All personal exposures were below recommended occupational exposure limits. Nitric acid exposures ranged from non-detectable to 0.4 mg/m^3 and hydrofluoric acid from non-detectable to 0.5 mg/m^3. Acetic acid exposures were all non-detectable. Organic solvent exposures were as follows: Freon 113, 2 to 417 mg/m^3; 1,1,1-Trichloroethane non-detectable to 124 mg/m^3; xylene, non-detectable to 1 mg/m^3; n-butyl acetate, non-detectable to 1 mg/m^3; acetone, non-detectable to 34 mg/m^3; methylene chloride, non-detectable to 2 mg/m^3; isopropyl alcohol, 2 to 15 mg/m^3; and methyl alcohol, 0.7 to 54 mg/m^3.

Fourteen of approximately 40 employees potentially exposed to acid mists and organic vapors in the Polish/Etch, Diffusion, Clean Room, and Tin Dip areas were interviewed. Although six reported at least one health complaint related to work, three complaints were identified as resulting from one-time, accidential occurrences that had been remedied. The remaining three had either dry throat, difficulty breathing or dry nasal passages. These symptoms may be caused or aggravated by acid or solvent exposures.

Based on environmental data and employee interviews, there does not appear to be a health hazard due to overexposure to acid and organic vapors. The one area where there was a cluster of health complaints should be evaluated on an engineering control and work practice basis to alleviate this problem. Recommendations to eliminate these complaints and improve work practices are presented in Section VII of this report.

KEYWORDS: SIC 3674 (Semiconducters and related devices) organic solvents, semiconductors, acid etching

II. INTRODUCTION

In March 1983, the National Institute for Occupational Safety and Health received a request from the management of Siemens Components, Inc., Broomfield, Colorado, to evaluate worker exposure to acids and organic solvents used in the manufacture of semiconductors. On March 28-30, 1983, an industrial hygienist visited the facility, collected personal breathing zone air samples for airborne contaminants, and interviewed workers.

III. FACILITY AND PROCESS DESCRIPTION

Siemens Components, Incorporated manufactures power semiconductors. This is a non-unionized facility, employing approximately 40 people on first shift in the areas of interest: Polish/Etch, Diffusion, Clean Room, KOH Etch, and Tin Dip. There is no second shift in these areas.

A. Polish/Etch: Silicone wafers are cleaned and polished to remove surface contaminants and crystallographic imperfections. Chemical etching of the wafer also takes place here. In Polish/Etch, potential chemical exposures include hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, acetic acid, sulfuric acid, 1,1,1-trichloroethane, acetone, methanol, and ammonium hydroxide. The acids are used for polishing and etching, generally in mixtures identified as 6:1:1, for example. This denotes the three most commonly used acids as 6 parts nitric: 1 part hydrofluoric: and 1 part acetic.

B. Diffusion: A dopant or impurity source is introduced into the semiconductor to modify its electrical properties. Potential chemical exposures, are to hydrogen peroxide, ammonium hydroxide, Freon 113, methylene chloride, and nitric and hydrofluoric acids.

C. Clean Room: In this area, a photosensitive emulsion is applied to the wafer, which is then exposed to ultraviolet light. Depending on the type of material (called photoresist) used, portions of the wafer are "masked" to produce the desired circuit image on the surface of the wafer. Employees are potentially exposed to n-butyl acetate, hydrofluoric acid, xylene, isopropyl alcohol, methyl alcohol, and hydrogen peroxide.

D. KOH Etch: Potassium hydroxide and methyl alcohol are used to etch and clean wafers in this area.

E. Tin Dip: Metal components of semiconductors are dipped in molten tin to coat them. Freon 113, methyl alcohol, and isopropyl alcohol are used in this area.

IV. EVALUATION DESIGN AND METHODS

Since the request concerned employee exposure to acids and organic solvents, personal breathing zone air samples for those acids and solvents used in the largest quantities were collected.

The following table lists the sampling and analytical descriptions.

Compound	Flow Rate (Lpm)	Reference
Organic solvents (n-butyl acetate, Freon 113, xylenes, acetone, methylene chloride, 1,1,1-trichloroethane)	0.2	P&CAM #127[1]
Alcohols (methyl and isopropyl)	0.2	P&CAM #S59[2]
Organic and Inorganic Acids (acetic, nitric and hydrofluoric)	a-1.0 b-0.2	a-P&CAM #212[3] b-ORBO-53 solid sorbent tube

Acid sampling was performed by two methods for comparison purposes. Simply, the utility of the solid sorbent method was compared to the filter method to determine if it would be an adequate future substitute. Sampling was done for the entire shift.

There had been no indication to management that there were any health problems experienced by the workforce, other than accidential contact with acids. In order to determine if there was any pattern to, or extraordinary, health problems, employees were interviewed at their work station concerning their work and health history.

V. EVALUATION CRITERIA

A. General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These

criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 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) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

B. Specific Substances

1. Hydrofluoric Acid[4,5]. Hydrofluoric acid is the hydrated form of hydrogen fluoride gas. In concentrated form, HF provides an early painful sensation that warns of skin contact. However, in dilute solution, this warning property does not exist, making conscientious handling of HF and potentially HF - contaminated materials important. In either situation, the fluoride ion, F-, may penetrate the skin, leading to the later development of painful, slowly healing ulcers. In addition, excessive absorption and retention of F- in the body may lead to skeletal fluorosis (osteosclerosis or increased bone density). Inhalation of or contact with either HF gas or HF mist causes redness of the skin, and burning and irritation of the nose and eyes.

   NIOSH recommends that exposure to HF be controlled so that no worker is exposed in excess of 2.5 mg/m^3, 10-hour TWA, or 5.0 mg/m^3 measured over any 15 minute period, in order to prevent deleterious health effects resulting from F- deposition. Because of the nonrespiratory (skin and eye irritation) effects, NIOSH recommends that appropriate safe handling practices be required regardless of the air concentration. The OSHA standard for HF is also 2.5 mg/m^3.

2. Acetic Acid[6]. Acetic acid is an eye, skin, and upper respiratory passages irritant. Adherence to the ACGIH and OSHA exposure limit of 25 mg/m^3, 10-hour TWA should prevent these symptoms in all but hypersensitive individuals.

3. Nitric Acid[7]. Exposure to nitric acid mist may result in chronic bronchitis; in severe exposures, a chemical pneumonitis may result. Dental erosion of the front teeth can occur within three months of occupational exposure to levels of acid not reported as causing these symptoms. Liquid nitric acid can cause severe mucous membrane, skin, and eye burns. When nitric acid comes in contact with metal or organic material, oxides of nitrogen, particularly the dioxide, evolve. This oxide appears to be more toxic than the liquid.

   NIOSH recommends a 5 mg/m^3, 10-hour TWA limit, and that, as with HF, appropriate protective measures be used regardless of air concentration. The OSHA standard is 5 mg/m^3, 8-hour TWA.

4. 1,1,1-Trichloroethane[8]. 1,1,1-Trichloroethane, or methyl chloroform, has a strong odor and is mildly irritating. In high concentrations, exposure can result in central nervous system effects (headache, disturbed equilibrium, light-headedness) and cardiovascular effects (reduced peripheral blood flow due to the heart's loss of contracted strength, impaired oxygen consumption) even after short periods of exposure. Hence, NIOSH recommends that exposures be controlled to levels less than 1910 mg/m^3 for any period of time exceeding 15 minutes (a ceiling value). The OSHA standard is 1900 mg/m^3 8-hour TWA.

5. Xylene[9]. Xylene can have a narcotic effect at high concentrations, however, the most commonly reported symptom from industrial exposure has been irritation to the eyes and mucous membranes. Often xylene is contaminated with small amounts of benzene, which has been shown to cause blood changes. NIOSH recommends a 10-hour TWA exposure limit of 435 mg/m^3. The OSHA standard is 710 mg/m^3 8-hour TWA.

6. n-Butyl Acetate[2]. n-Butyl acetate has slight narcotic effects but primarily causes eye and respiratory irritation. The ACGIH recommends exposure be limited to less than 710 mg/m^3, 8-hour TWA to prevent these effects.

7. Acetone[2]. Acetone is considered one of the least toxic of the common solvents, causing only slight irritation at one-fifth the ACGIH TLV of 1780 mg/m^3, 8-hour TWA. The OSHA standard is 2400 mg/m^3, 8-hour TWA.

8. Methylene Chloride[10]. Health effects reported from occupational exposure to methylene chloride include chest pains, heart palpitations, rapid pulse, shortness of breath, tingling in the hands and feet, muscular pains in the arms and legs, headache, and increased fatigue. Methylene chloride is metabolized to carbon monoxide, which interferes with oxygen delivery to the tissues, and results in the symptoms noted. Methylene chloride directly can cause central nervous system effects.

   NIOSH recommends that exposure be limited to less than 260 mg/m^3, 10-hour TWA, if exposure to CO can be limited to 9 ppm, 10-hour TWA. The OSHA standard is 1740 mg/m^3, 8-hour TWA.

9. Freon 113[2]. Freon 113, or trichloro-trifluoroethane, can cause depression of the central nervous system and respiratory tract irritation at high concentrations. Levels reported in industrial exposures have only caused transient throat irritation. Freon 113 is similar to acetone in its low toxicity. ACGIH recommends that exposures not exceed 7600 mg/m^3, 8-hour TWA. The OSHA standard is 7600 mg/m^3, 8-hour TWA.

10. Isopropyl Alcohol[11]. Also known as isopropanol, health effects reported either in experiments or in industry have been few and slight, limited to irritation of the eyes, nose, and throat. The NIOSH recommended criteria is 980 mg/m^3, 10-hour TWA. The OSHA standard is 980 mg/m^3, 8-hour TWA.

11. Methyl Alcohol[12]. Also known as methanol, can be absorbed through the skin as well as absorbed through the lungs. Varying degrees of susceptibility to dermatitis have been reported. Mild eye irritation has also been reported as well as slight loss of vision, which was recoverable. The primary hazard is due to ingestion - methyl alcohol is metabolized to formaldehyde, which can cause blindness and death.

    The NIOSH recommended exposure criteria is 260 mg/m^3, 10-hour TWA. The OSHA standard is 260 mg/m^3, 8-hour TWA.

VI. RESULTS AND DISCUSSION

A. Environmental

Personal air sampling data are presented in Tables I and II. Acid mist data collected by solid sorbent tubes has not been reported due to the low exposure value measured by filter method. Analysis of those few samples that were measurable by filter method indicated comparable values. All values have been corrected to standard conditions of temperature (25°C) and pressure (760 mmHg).

Samples were analyzed for the acids used in greatest quantity. None of the samples exceeded recommended exposure criteria. HF exposures ranged from non-detectable to 0.5 mg/m^3 and nitric acid exposures from non-detectable to 0.4 mg/m^3. All acetic acid exposures were non-detectable. I conclude that the use of hoods and the acid/distilled water rinse arrangement (acid in back, water in front of hood) is, in part, responsible for these low exposure levels. Another factor is the care exercised by the employees in the handling of the acids.

None of the samples for organic solvents exceeded recommended exposure criteria; all were less than 25% of the respective criteria. All personal exposures were below recommended occupational exposure limits. Organic solvent exposures were as follows: Freon 113, 2 to 417 mg/m^3; 1,1,1-Trichloroethane non-detectable to 124 mg/m^3; xylene, non-detectable to 1 mg/m^3; n-butyl acetate, non-detectable to 1 mg/m^3; acetone, non-detectable to 34 mg/m^3; methylene chloride, non-detectable to 2 mg/m^3; isopropyl alcohol, 2 to 15 mg/m^3; and methyl alcohol, 0.7 to 54 mg/m^3. Initially I suspected that the 1,1,1-trichloroethane transfer operation from degreaser to 55 gallon drum in open pans could cause short-term overexposure to the worker assigned to this task. Apparently this is not the case if the transfer is done without mishap. However the potential for spills remains, particularily with the use of open pans.

A sample taken at the parts' exit point from the automatic feed vapor degreaser simulated a worst case exposure potential. This result (955 mg/m^3) was approximately one-half of the full shift exposure criteria. This result does indicate the potential for short-term exposure which could occur if someone were required to perform maintenance at this position during degreaser operation. Generally it appears that work inside the degreaser room would not result in an overexposure; since policy is to not allow this, I recommend that this policy be continued.

Chemical stocking and transferring by the stockroom personnel was thought to have overexposure potential, due to the large volumes of chemicals handled. However, the stockman's exposures were all low on the day of this evaluation.

B. Medical

Fourteen employees were interviewed at their workstations. Six individuals reported at least one health complaint. However, three of these individuals indicated that their symptom occurred either only once as a result of an accidential overexposure to a solvent (lightheadedness), or in the old clean room which no longer exits (headaches), or when she had worked on Etch Through (sore throat).

The remaining three employees reported current health problems which they believe are probably caused by, or aggravated by, conditions at work.

Two employees, one complaining of dry throat and one complaining of difficulty breathing, work in KOH Etch. The remaining employee, who works in Polish/Etch, complained of dry nasal passages.

These symptoms of respiratory distress can be caused by acid or solvent exposure, although, on the days sampled, the environmental evidence does not substantiate this assertion.

VII. RECOMMENDATIONS

A. Establish a Respiratory Protection program as outlined in 21 CFR 1910.134.[13,14] If you are going to provide respirators to employees, then a formal respiratory protection program should be instituted in order to ensure proper selection, fit testing, use, and storage of respirators. Respirator cartridges should not be stored in areas where they can become contaminated. Facial hair often interferes with a proper face-to-mask seal, and does not allow the respirator to provide the degree of protection it can provide.

B. Install exhaust ventilation in the solvent warehouse. This would provide a fail safe method of evacuating the building rapidly in case of a spill rather than relying on open doors and natural dilution ventilation. This ventilation system could be used in emergencies or whenever needed, such as during solvent transfer.

C. Use "closed" containers to transfer degreasing solvents.

D. Re-direct pedestal fans away from the Tin Dip operation. Cross currents interfere with the capture efficiency of local exhaust ventilation.

E. Since two work-related health problems came from the Tin Dip Area (KOH Etch, Station #3), there may be a problem with the exhaust system for this station. The exhaust system should be checked for proper face velocity. Also, the workers' work habits should be reviewed to determine if the manner in which they perform the job can be altered to eliminate the problem.

VIII. REFERENCES

1. National Institute for Occupational Safety and Health. NIOSH manual of analytical methods. Vol 1, 2nd ed. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1977. (DHEW (NIOSH) publication no. 77-157-A).

Table II

Personal Air Sampling Data: Organic Solvents

Siemens Components, Incorporated
Broomfield, Colorado

HETA 83-164
May 28-30, 1983

Sample Location Description	Sampling Duration (min)	Concentrations, in Milligrams Substance/m^3 Air							
		1,1,1-Trichloro-ethane	Xylenes	n-butyl-acetate	Acetone	Methylene Chloride	Freon 113	Isopropyl Alcohol	Methyl Alcohol
Diffusion: transferring 1,1,1-trichloroethane from degreaser	15	124	ND[a]	ND	ND	ND	24	NS[b]	NS
Diffusion: megasonic	438	5	ND	ND	26	1[c]	133	NS	NS
Polish/Etch: etching	399	20	ND	ND	34	ND	43	NS	NS
Polish/Etch: etch-through	335	76	ND	1	8	ND	42	NS	NS
Stock Room: chemical transfer to smaller, portable containers	435	4	0.1	ND	5	2	48	2	0.7[c]
Clean Room: developing wafers	446	ND	1	0.3	6	ND	2	NS	NS
Tin Dip: tin dipping	384	4	ND	ND	5	ND	417	15	54
Tin Dip: KOH etching	393	NS	NS	NS	NS	NS	NS	9	1
Degreaser Room: operating degreaser conveyer line	118	9	ND	ND	4	ND	84	NS	NS
Degreaser Room: exit point of parts from degreaser[d]	118	955	ND	9	4	ND	95	NS	NS
Degreaser Room: exit point of conveyor from room[d]	117	3	ND	ND	4	ND	79	NS	NS
Recommended Exposure Criteria Reference		1910[e] (NIOSH)	435 (NIOSH)	710 (ACGIH)	1780 (ACIGH)	260 (NIOSH)	7600 (ACGIH)	980 (NIOSH)	260 (NIOSH)

a - below analytical limit of detection, 0.01 mg/sample
b - not analyzed for this substance
c - minimum value, breakthrough on sampling media noted
d - area samples, not personal breathing zone
e - ceiling value, not to be exceeded for longer than 15 minutes