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HETA 94–0191–2670
Bureau of Engraving, Incorporated
Minneapolis, Minnesota

Ann M. Krake, M.S.
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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, technical and consultative assistance 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.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Ann M. Krake and Robert Malkin, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Alan Echt, Elaine Ristinen, Ladina Saluz, and Caroline Serna. Analytical support was provided by Ardith A. Grote of the NIOSH Division of Physical Sciences and Engineering, Dawn M. Ramsey of the NIOSH Division of Biomedical and Behavioral Sciences, and Amy Jo Portlock of Data Chem Laboratories. Desktop publishing was performed by Juanita Nelson.

Copies of this report have been sent to employee and management representatives at the Bureau of Engraving, Inc.; the president of the Graphic Communications International Union, Local 1B; a Ciba Geigy representative; a UCB Radcure, Inc. representative; and the OSHA Regional Office. This report is not copyrighted and may be freely reproduced. Single copies of this report will be available for a period of three years from the date of this report. To expedite your request, include a self-addressed mailing label along with your written request to:

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For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Health Hazard Evaluation Report 94–0191–2670
Bureau of Engraving, Incorporated
Minneapolis, Minnesota
December 1997

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SUMMARY

On March 11, 1994, the National Institute for Occupational Safety and Health (NIOSH) received a request for technical assistance from the Minnesota Department of Labor and Industry, Occupational Safety and Health Division (Minnesota OSHA), in evaluating potential health hazards at the Bureau of Engraving, Incorporated, (BOE) in Minneapolis, Minnesota. A second request for a health hazard evaluation (HHE) at BOE was received by NIOSH on March 28, 1994, from the Graphic Communications International Union (GCIU) Local 1B. Both requests concerned employee exposure to chemicals used in the clean room, including solvents and glycol ethers used with the Ciba Geigy™ coating process. Symptoms reported among clean room employees included difficulty breathing, headaches, skin and eye irritation, and dizziness.

Site visits were conducted in May 1994 and April 1995. Personal breathing zone (PBZ), area, and process air samples were collected for hexane and other hydrocarbons, alcohols, and glycol ethers. Analysis of full–shift PBZ air samples revealed detectable levels of hexane, 1,1,1–trichloroethane, and propylene glycol monomethyl ether acetate (PGMEA), but all concentrations were well below the corresponding occupational exposure criteria. Propylene glycol monomethyl ether (PGME) and ethylene glycol monobutyl ether (EGBE) were not detected.

A medical evaluation was also conducted which consisted of a questionnaire and, because skin exposure was a concern, urine tests for metabolites of 2–ethoxyethanol (EGEE), EGBE, PGME, and PGMEA. All employees working in the clean room were eligible for participation. Twenty–five of the 32 employees answered the questionnaire, and 21 participated in the urine testing. Twenty–nine percent of respondents reported lightheadedness, 25% reported frequent or severe eye irritation, and 21% reported frequent or severe nose irritation while at work. No measurable urinary metabolites of EGEE or EGBE were found in any of the participants; however, one worker, who did not have a measurable PBZ sample for glycol ethers, had urinary metabolites of PGME/PGMEA in one sample.

Airborne exposures to the measured compounds were very low and did not indicate a health hazard during the NIOSH investigation. However, employees are also exposed to compounds, including PGMEA, which have no sampling methods or exposure limits. These compounds are known irritants and could be associated with the undesirable odors and employee discomfort, including respiratory irritation and lightheadedness, reported to NIOSH investigators.

Keywords: SIC 3672 (Printed circuit boards–manufacturing), glycol ethers, solvents, urinary metabolites.

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INTRODUCTION

On March 11, 1994, the National Institute for Occupational Safety and Health (NIOSH) received a request for technical assistance from the Minnesota Department of Labor and Industry, Occupational Safety and Health Division (Minnesota OSHA), in evaluating potential health hazards at the Bureau of Engraving, Incorporated (BOE), in Minneapolis, Minnesota. A second request for a health hazard evaluation (HHE) at BOE was received by NIOSH on March 28, 1994, from the Graphic Communications International Union (GCIU) Local 1B. Both requests concerned employee exposure to chemicals used in the clean room. Symptoms reported among clean room employees included difficulty breathing, headaches, skin and eye irritation, and dizziness.

An initial site visit was conducted in May 1994. NIOSH investigators obtained trade–secret information regarding the composition of one of the products used in the clean room, PF LMB/Probimage 1011®, from the product manufacturer and one of its suppliers. A review of this information revealed that none of the ingredients were regulated, nor were there any sampling methods available for these chemicals. During the second site visit (April 26–29, 1995) air sampling and biological (urine) monitoring were conducted for various other chemicals used in the clean room.

An interim report, which included environmental and initial medical findings, was issued on October 27, 1995, pending urine monitoring results. Individual employees received notification of their initial urine monitoring results in July 1995. The final urine monitoring data were received in March 1997, and individual employee notification letters were mailed in April 1997. This report provides the final industrial hygiene and medical sampling results, conclusions, and recommendations.

BACKGROUND

The Bureau of Engraving has manufactured printed circuit boards since 1954 and has occupied its current site since 1981. During the NIOSH site visits, BOE employed a total of nearly 550 employees, 475 of whom were production employees. There were approximately 30 employees who worked in the clean room. The plant operated 24 hours a day, 7 days per week, and there were three 8–hour weekday shifts and two 12–hour weekend shifts. Production in the clean room occurred mostly during the daytime shifts (first, second, and fourth), with clean–up at night during the third and fifth shifts.

The process of concern, according to the HHE request, was a proprietary Ciba Geigy™ process (Ciba process), which was located within the printing area, inside a clean room. The clean room covered 2,000 square feet and had two work areas—wet film, which included the Ciba process, and dry film photoresist (exposing). The Ciba process, which was added to the clean room in the spring of 1993, involves the coating of 18"x24" copper sheets with a trade–secret photo–initiating mixture of polyacrylates in solvent (PF LMB/Probimage 1011®). Coated sheets move via conveyor into a drying oven where they are turned over, coated on the other side, dried in a second oven, and are then ready for imaging. The manufacturer's ventilation specifications for the Ciba process stipulate that all Probimage® equipment be served by a separate heating, ventilating, and air conditioning (HVAC) system, with no recirculation, and a minimum of 15 outside air changes per hour (ACH) within the curtained coater areas. An OSHA inspection conducted in 1993 revealed a disconnected exhaust duct in the ceiling plenum and less than 6 ACH within the curtained coater areas.

Several employees in the clean room reportedly associated the beginning of their symptoms with the start–up of the Ciba process in the clean room. Several employees said that frequent spills, sometimes as many as four or five per day, of the

Probimage® occurred during the start–up of the process. Spill clean–up involved the use of a solvent, propylene glycol monomethyl ether acetate (PGMEA), also the major ingredient of the Probimage® solution. Employees also associated rashes and lightheadedness with the use of Nu–Kleen® film cleaner, which contains hexane (85–95%) and isopropyl alcohol (5–15%), and graphic arts glass cleaner, which contains water (70–75%), ethyl alcohol (10–20%), 2–butoxy ethanol (ethylene glycol monobutyl ether or EGBE) (3.9%), liquified petroleum gas (1–5%), and methyl alcohol (0.8%).

METHODS

Environmental

During the first NIOSH visit (1994), samples of the Probimage® compound were collected and submitted for analysis of volatile organic compounds (VOCs) using a gas chromatograph and mass selective detector (GC–MSD). Based upon these results and the Material Safety Data Sheets (MSDSs) for chemical products used in the clean room, personal breathing zone (PBZ), area, and process air samples were collected for hydrocarbons, alcohols, and several glycol ethers and glycol ether acetates during the second NIOSH visit (April 1995).

Full–shift PBZ samples were collected on 19 employees, representing all 5 clean room shifts and both the wet and dry processes. Task–based PBZ air sampling was also conducted while three employees completed two routine cleaning activities, including the nightly wipe down of the Ciba machine and the weekly, more thorough, cleaning of the Ciba line. Area samples were collected in the co–light, tamarack, and Ciba line catch areas, and during the thorough cleaning of the Ciba line. Process samples were collected in both curtained coater areas of the Ciba line and over the exit of the first drying oven near the turnover machine. All samples were collected using battery–operated personal air sampling pumps drawing air at a measured sampling rate of 50 to 200 milliliters per minute through 150 milligrams (mg) of activated charcoal packed in a glass tube.

Using NIOSH Method 1500 for hydrocarbons, PBZ, area, and process charcoal tube samples were collected and quantitatively analyzed for 1,1,1–trichloroethane (1,1,1–TCE), hexane, mineral spirits, toluene, and benzene.[1] NIOSH Method 1400 was used to collect and quantitatively analyze PBZ, area, and process charcoal tube samples for *sec*–butyl alcohol, ethyl alcohol, and isopropyl alcohol.[2] And, using NIOSH Method 1403, PBZ, area, and process charcoal tube samples were collected and quantitatively analyzed for EGBE and propylene glycol monomethyl ether (PGME).[3] NIOSH Method 1450 was used to collect and analyze PBZ, area, and process charcoal tube samples for *n*–butyl acetate, *sec*–butyl acetate (EGBEA), and PGMEA.[4] (There is no NIOSH method for PGMEA; however, this compound was analyzed using media standards for calibration.) All samples were analyzed by gas chromatography using a flame ionization detector (GC–FID). In addition, 16 thermal desorption tube area air samples were collected using NIOSH Method 2549 for screening of VOCs found in the clean room;[5] each thermal desorption tube contained three beds of sorbent materials–a front layer of Carbopack Y (~90 mg), a middle layer of Carbopack B (~115 mg), and a back section of Carboxen 1003 (~150 mg). These results were used to identify compounds for quantitation from the area air samples.

Medical

The medical evaluation included a health questionnaire and urine testing for glycol ether metabolites. The questionnaire asked about symptoms at work, including frequent or severe eye irritation, skin irritation, nose irritation, headache, stuffy nose, burning mouth, nausea, sore throat, unusual fatigue, dizziness, lightheadedness, and unusual forgetfulness or confusion. Testing for the urinary metabolites of EGEE (metabolite is ethoxyacetic acid), EGBE (metabolite is butoxyacetic acid), and PGME/PGMEA (metabolite is PGME) was also conducted to assess combined

skin and inhalation exposures to those compounds. (Skin exposure to these compounds was observed during the first NIOSH visit.) EGEE and EGBE metabolites were analyzed by a commercial laboratory using GC–MS. PGME/PGMEA metabolites were analyzed by the NIOSH Division of Biomedical and Behavioral Sciences using solid phase microextraction (SPME), followed by analysis with GC.

The evaluated employees worked in the print and clean coat areas of the clean room. There were approximately 32 employees in those areas; 25 completed the questionnaire and 21 participated in the urine testing. All employees working on the day of the evaluation during the three daytime shifts (first and second shift during the week and fourth shift during the weekend) were eligible for participation in the evaluation. Cleaning of equipment was done on the weekend by a special group of employees, and these workers also were tested. Employees were recruited for participation at the beginning of each shift; those interested in participating signed an informed consent and were administered the questionnaire at a later time, as close to the end of the shift as possible, on the day of urine collection. Urine collection took place at the end of each shift on the fourth day of the work week. One employee who was also involved in cleaning the equipment was sampled after the regular shift and again after cleaning, on two separate days. After collection, urine was frozen with dry ice, shipped to the NIOSH laboratory in Cincinnati, and then, for EGEE and EGBE metabolite analysis, to a commercial laboratory.

EVALUATION CRITERIA

General Guidelines

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),[6] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),[7] and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).[8] In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA–approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criteria. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

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 even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre–existing 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 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.

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 (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short–term.

Approximately half of the chemicals sampled for in the clean room were detected during the second NIOSH evaluation; therefore, health effects information is presented only for those substances that were detected in the air samples. Please see Tables 1 and 2 for the occupational exposure criteria for each of the detected compounds.

Hydrocarbons[9]

Hexane and 1,1,1–TCE are both colorless, volatile liquid solvents and thinners used mainly in the production of tires, glues, and tape (hexane) and as a cleaner (1,1,1–TCE). The primary route of exposure for both chemicals is inhalation; skin absorption can occur but is not considered a primary exposure route in industry. Hexane and 1,1,1–TCE are both upper respiratory irritants which can also cause central nervous system effects, including nausea, dizziness, headache, and confusion. Chronic exposure to hexane can cause peripheral neuropathy (damage to the nerves of the arms, hands, legs, and feet). In studies involving human exposures, hexane caused slight nausea, headache, and irritation of the eyes and throat at 1,500 parts per million (ppm); exposures to concentrations of 1,1,1–TCE approaching 500 ppm caused lightheadedness and impaired equilibrium. As with many organic solvents, skin exposure to hexane and 1,1,1–TCE can result in defatting of the skin, causing dryness, redness, and scaling of exposed areas. Neither chemical has been proven to have carcinogenic or mutagenic effects in humans.

Alcohols[10]

Sec–butyl alcohol (also known as 2–butanol), ethyl alcohol (also known as ethanol), and isopropyl alcohol (also known as isopropanol) are colorless, flammable liquids that are used as industrial solvents. The primary route of exposure in the workplace for each is inhalation; however, ingestion can also be an important route of exposure for isopropanol and ethyl alcohol, which is the alcohol in beer, wine, and liquor. Although workers regularly exposed to 100 ppm of *sec*–butyl alcohol showed no symptoms, acute exposures to higher concentrations cause eye, nose, and throat irritation; headache; nausea; fatigue; and dizziness. Mild skin irritation may occur due to the defatting action of alcohols. Ethyl and isopropyl alcohols are eye and mucous membrane irritants and central nervous system depressants. Human exposure to 5,000 to 10,000 ppm of ethyl alcohol caused short–term eye and nose irritation. Chronic exposure to ethyl alcohol vapors may result in mucous membrane irritation, headache, and lack of concentration; however, there is little systemic toxicity from inhalation of the vapors. Exposure to 400 ppm of isopropyl alcohol caused mild eye, nose, and throat irritation in humans.

Glycol Ethers and Glycol Ether Acetates

Unlike some glycol ethers and their acetates (ethylene oxide–based), EGBE, PGME, and PGMEA have not been found to be human reproductive hazards; in addition, no carcinogenicity studies have been reported for these ethers.[11] The relatively low vapor pressures of EGBE and PGME, compared with other solvents, are such that high air concentrations are unlikely. However, both are absorbed through the skin,[11,12] and for this reason, both routes of exposure should be considered when evaluating employee exposure to glycol ethers and their acetates.

EGBE, also known as 2–butoxyethanol or butyl Cellosolve®, is a colorless liquid with a mild ether odor that is widely used as a solvent and cleaning

agent. Human exposure to 300–600 ppm of the vapor for several hours can cause upper respiratory and mucous membrane irritation and damage to the kidneys and liver.[13] EGBE has been found to cause hematologic (blood cell) changes in rats.[14] PGME, also known as Dowanol® PM, is used as a solvent for coatings and in the solvent–sealing of cellophane. It is low in systemic toxicity but causes irritation of the eyes, nose, and throat, and discomfort with its objectionable odor. At 100 ppm, a transient objectionable odor was reported by human subjects, and at 1000 ppm, irritation of the eyes, nose, and throat occurred, as did signs of central nervous system impairment.[15]

PGMEA, also known as 1–methoxy–2–propyl acetate or methoxypropyl acetate, is used as a photoresist solvent in the printed circuit board industry. It is readily absorbed through the skin and is a central nervous system depressant, and can produce eye, nose, and lung irritation. Upon entering the body, PGMEA is rapidly metabolized to PGME and acetic acid.[11] There are no evaluation criteria established for PGMEA.

PF LMB/Probimage® 1011[16,17]

NIOSH obtained trade–secret information regarding the composition of a clean room product, PF LMB/Probimage 1011®, from the product manufacturer and a supplier. This information revealed that none of the ingredients had OSHA, NIOSH, or ACGIH occupational exposure limits, nor were there any sampling methods available for these compounds. A review of the MSDS and the medical literature indicated that hazard and toxicology data have not been established for many of the ingredients; however, none of the ingredients are listed as carcinogens by OSHA, the National Toxicology Program (NTP), or the International Agency for Research on Cancer (IARC). The primary routes of exposure are listed as skin and inhalation, and the acrylate components are considered to be sensitizers. (Sensitization is an immunologic recognition of the substance that causes some type of reaction, such as dermatitis or asthma, when an individual is exposed to small quantities of that substance). One of the ingredients is a photoinitiator that exhibits a very strong odor when exposed to ultraviolet radiation. And, as previously discussed, PGMEA can cause mild skin, eye, and respiratory irritation, according to the MSDS. Overall, the MSDS for the Probimage® states that this compound can cause allergic skin reactions, headache, nausea, dizziness, and loss of consciousness.

Biological Monitoring

Biological monitoring results may indicate both respiratory uptake and skin absorption and may also be a measure of potential adverse health effects of certain compounds.[18] Biological monitoring may be limited as a direct method for assessing exposure because of the variability of the extent of the skin exposure, the amount taken in through inhalation, which may vary by workload, and excretion rates of the metabolites.[19] It has been estimated that the half lives of EGBE metabolites are about 6 to 9 hours,[20] and the half lives of EGEE metabolites are about 48 hours.[21] There are few studies of the half life of PGME or PGMEA, but in one study, the mean excretion half life of PGME was about 4.4 hours.[22]

The ACGIH has adopted a biological exposure index (BEI) for EGEE of 100 mg/g creatinine.[7] There are no BEIs for PGMEA or EGBE. NIOSH recommends biological monitoring for glycol ether exposure, but provides no specific guidelines for interpreting results. The measured levels, however, can be both an index of glycol ether exposure and an index of potential adverse health effects from this exposure.[18]

RESULTS

Environmental

Results from the first NIOSH visit showed that the major compounds detected at 100°C in the headspace above the Probimage® samples were PGME, PGMEA, and various aliphatic esters, most likely butenedioic acid esters (maleates).

Results from the thermal desorption tube samples collected during the second NIOSH visit showed that the most prevalent compounds detected were PGMEA, hexanes (including methyl pentanes, methylcyclopentane, and *n*–hexane), isopropanol, and PGME. Also present in some of the samples were *sec*–butyl alcohol, EGBE, 1,1,1–TCE, ethyl alcohol, EGBEA, and 2–butenedioic acid alkyl esters. Numerous other compounds detected at lower concentrations included methanol, acetone, various butyl acetates, toluene, aliphatic hydrocarbons, and aliphatic acid esters.

Full–shift PBZ air sampling results and the respective exposure evaluation criteria are summarized in Table 1. Actual sampling times are shown, and because no exposures occurred outside the sampling periods, all PBZ results (except the Ciba line cleaning) were adjusted to reflect a full 8–hour shift. None of the following substances were detected: benzene, toluene, Stoddard solvent (reported as *n*–decane), EGBEA, or *n*–butyl acetate. Minimum detectable concentrations (MDC) ranged from 0.2 ppm to 0.4 ppm. Concentrations of hexane, 1,1,1–TCE, and PGMEA were all well below their occupational exposure limits. Full–shift PBZ exposures to hexane ranged from less than (<) 0.4 to 8.4 ppm; for 1,1,1–TCE, from <0.2 to 3.9 ppm; for PGMEA, from <0.9 to 2.6 ppm; for *sec*–butyl alcohol, from <1.7 to 5.0 ppm; for ethyl alcohol, from <0.7 to 1.4 ppm; and for isopropyl alcohol, from <1.2 to 3.4 ppm. PGME and EGBE were not detected (MDCs were 0.7 ppm and 0.5 ppm, respectively).

Short–term PBZ and task–based PBZ air sampling results and the respective exposure evaluation criteria are also summarized in Table 1. During the 10–minute wipe–down of the Ciba Geigy machine with PGMEA, an employee's exposure to PGMEA was between the MDC and the minimum quantifiable concentration (MQC). No other compounds were detected (MDCs were less than 33 ppm). During the more thorough cleaning of the Ciba line, which lasted approximately 3½ hours, exposures to PGMEA ranged from 6.5 to 30 ppm, and for ethyl alcohol from <1.3 to 2.2 ppm. No other sampled chemicals were detected.

Area and process air sampling results are summarized in Table 2. Area air concentrations at various locations throughout the clean room during first, second, and third shifts were similar to the PBZ exposures. During the thorough cleaning of the Ciba line, the area air concentration of PGMEA reached 21 ppm inside curtained coater #2. No other chemicals were detected in area samples collected at the Ciba machine, at the Ciba oven #1, or the light table in front of co–light #1.

Analysis of process samples taken at various locations on the operating Ciba line, including curtained coaters #1 and #2, and near the turnover at oven #1, revealed that air concentrations of most compounds were similar to the PBZ concentrations and were well below current occupational exposure limits. Concentrations were highest for all compounds in the curtained coater areas, particularly in curtained coater #2, where the hexane concentration was 3.2 ppm, toluene 0.68 ppm, 1,1,1–TCE 0.68 ppm, *sec*–butyl alcohol 3.2 ppm, and isopropyl alcohol 0.64 ppm. PGME was also detected inside both curtained coater areas and was highest, at 2.6 ppm, inside curtained coater #1. The concentrations of PGMEA, 140 ppm and 105 ppm inside curtained coater #2, were significantly higher than both the PBZ exposures and the area air concentrations measured outside the curtained coater.

Medical

No metabolites of EGEE or EGBE were found in the urine of the 21 participating employees. One employee had measurable levels of PGME in the sample collected after the regular shift. This sample had an estimated PGME concentration of 6.4 milligrams per liter (mg/L) (an estimated concentration is one that was between the analytical limit of detection [LOD] of 5.5 mg/L and the analytical limit of quantitation [LOQ] of 18.3 mg/L).

Employee symptoms are listed in Table 3. The most commonly reported symptom at work was lightheadedness (29% of participants). Other commonly reported symptoms included eye irritation (25%), nose irritation (21%), and severe sore throat (17%). Four employees reported that rashes were associated with contact with the film cleaner, and two reported that lightheadedness was associated with use of the film cleaner and working on the Ciba Geigy line. No other environmental condition was cited by more than one employee as being related to a particular symptom. Other job duties that were associated with symptoms by one worker each included working on the printer, working on the outer layer of the photo resist, and any work with the Ciba process. Since measurable glycol ether metabolites were found in the urine of only one employee, further analysis to relate symptoms to glycol ether exposures could not be done.

Observations

BOE's personal protective equipment guidelines were not comprehensive enough and not reflective of the chemicals or processes currently used in the clean room. To keep lint and dust to a minimum in the clean room, employees are required to wear a long–sleeved 100% polyester gown, booties, and a hair net. Vinyl gloves are supplied, but employees wore them sporadically. When asked on the medical questionnaire "Do you wear protective gloves when you work," 13 of 25 (52%) employees responded "yes," yet most employees complained of frequently spilling PGMEA or film cleaner on their bare hands. Although plastic safety glasses were provided, only the employees responsible for cleaning the Ciba machine were seen wearing them.

Qualitative analysis of the Ciba process local exhaust ventilation indicated that when visible test powder was released approximately 6" away at different angles to each inlet, the ventilation appeared to adequately capture the powder. Area air samples taken outside the curtained coaters showed that PGMEA was not detected or was present in low concentrations ($\leq$ 4.2 ppm) outside the curtains. Some of the PGMEA detected outside the curtain is likely due to employees moving in and out of the curtained areas and/or solvent evaporation. Several empty five–gallon Probimage® containers were observed behind the end of the Ciba line near an employee workstation, where they were left to drain; solvent vapors, including PGMEA, could evaporate and volatilize into the work area increasing the air concentration of the solvents.

The only available eyewash station in the clean room is located against a wall between the beginning of the Ciba line and the film spotter's station, behind a stack of boxes and some chemical carts. This station would be difficult to reach by an employee in need of it.

DISCUSSION AND CONCLUSIONS

The sampling results indicated that none of the sampled chemicals were detected at concentrations exceeding OSHA or NIOSH occupational exposure limits, and therefore, an inhalation health hazard to those compounds did not exist at the time of the second NIOSH visit. However, workers were also exposed to known irritants that have no sampling methods or exposure limits and which could be associated with undesirable odors, employee discomfort, and symptoms, including upper respiratory irritation and lightheadedness. In addition, the findings reported here indicate clean room conditions only on the days of the NIOSH survey; during the start–up phase of the Ciba line in 1993 and during spill clean–ups, ambient levels of solvents could have been higher.

One employee had measurable levels of urinary PGME, indicating exposure to PGME and/or PGMEA. There are no standards for interpreting urinary levels of this metabolite, but it has been estimated that a PGME air concentration of 101 ppm would be associated with a urinary metabolite concentration between 10 and 31 mg/L PGME, assuming inhalation exposure only (no skin absorption).[23] During the NIOSH site visit, the

highest PGMEA concentration detected, 30 ppm, was in a PBZ short–term task sample collected during cleaning but, skin exposure, which is the major route of glycol ether exposure, was also observed.

Employee complaints of lightheadedness, upper respiratory irritation, and rashes may stem from a variety of factors. As mentioned in the Evaluation Criteria section, a small percentage of people may experience adverse health effects even though chemical exposures are below relevant exposure limits. Exposures to mixtures of irritating chemicals may cause more discomfort than exposure to a comparable amount of a single irritant. Employees may also experience health effects as a result of skin exposure. In addition, some specific exposures could not be measured.

RECOMMENDATIONS

The following recommendations are offered to further minimize exposures to the chemicals used in the clean room:

Administrative:

✦ An effective hazard communication program is essential to a healthy work environment, and information and training are critical elements of the program. If employees express concerns about not understanding hazards in their workplace, then the program is not effective. Each employee should be educated on the potential hazards of the chemicals they work with and the appropriate methods for controlling exposures. Workers should be aware of the significance of each chemical MSDS, including how to access an MSDS should the need arise. Employees should be encouraged to report any injuries or illnesses to their immediate supervisor, who should take appropriate action to get medical help for the employee.

✦ BOE should consider implementing joint labor/management safety and health teams to improve communication between employees and management regarding working conditions. These teams could also be used to direct future investigations to those areas or processes where employee health complaints or illnesses are reported.

Personal protective equipment:

✦ Use of chemically–impermeable, elbow–length gloves and clothing should be used when there is a potential for splashing or skin exposure to any of the clean room chemicals. The polyester gowns currently worn by employees are not impervious to these chemicals. Because employees potentially work with a mix of compounds, consultation with glove and chemical manufacturers for appropriate glove materials is recommended. Appropriate glove choices can also be found in the *Quick Selection Guide to Chemical Protective Clothing* by Krister Forsberg and S. Z. Mansdorf.[24] Degradation of the glove material occurs due to continuous use and exposure to chemical substances, and depending on the mix of chemicals used, gloves should periodically be discarded and replaced with new gloves.

Workplace:

✦ If skin or eye exposure to any of the clean room chemicals occurs, skin should be rinsed immediately with soap and water, and eyes should be rinsed immediately at the eyewash station.

✦ The eyewash station should be made easily accessible to all employees by moving all the carts and boxes away from that area. Installing a new eyewash station in the center of the clean room would also provide increased accessibility for every employee.

✦ All clean room employees should remove their gowns and wash their hands and face before eating, drinking, smoking, or using toilet facilities. Soiled clothing should be removed promptly and washed thoroughly before re–use.

✦ To reduce solvent evaporation in the clean room, empty Probimage® containers should be removed immediately to a well–ventilated area outside the clean room and away from any workstations.

✦ The clean room HVAC system should be checked periodically to ensure that the correct amount of fresh air is being supplied and that air changes per hour are within specifications for the Ciba Geigy process.

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Table 1
Personal Breathing Zone Air Sampling Results
Bureau of Engraving, Incorporated
HETA 94–0191
April 26–30, 1995

Job or Activity	Sampling Time (minutes)*	Concentration, expressed in parts per million (ppm)					
		Hexane	1,1,1– TCE	PGMEA	*sec*–butyl alcohol	Ethyl alcohol	Isopropyl alcohol
First Shift							
Ciba line‡	396	NS	NS	NS	ND	ND	ND
Co–light #2, inner layer printing	369	4.4	1.6	1.7	1.4	ND	2.1
Ciba line catcher	378	NS	NS	NS	2.8	ND	2.7
Co–light #1, nearest Ciba line	380	(0.28)	ND	(0.42)	NS	NS	NS
Assistant supervisor	379	1.7	0.82	(0.40)	ND	ND	ND
Tamarack (dry film)	361	3.7	2.2	ND	1.04	ND	(0.86)
STEL–cleaning Ciba line with PMA‡	9	ND	ND	(3.2)	ND	ND	ND
Second Shift							
Co–light #6, outer layer printing	402	8.4	3.9	ND	5.0	ND	3.4
Film spotting	411	2.4	1.2	ND	1.7	ND	1.2
Ciba line catcher	395	0.74	0.50	0.96	NS	NS	NS
Co–light #1 (nearest Ciba line)	402	4.7	2.2	0.56	2.0	(0.51)	1.5
Co–light #2, inner layer printing	391	7.2	3.2	(0.42)	ND	1.4	NS
Tamarack (dry film)	412	5.03	2.4	ND	1.8	ND	1.2
Tamarack	374	4.2	2.1	ND	(1.5)	ND	1.3
Supervisor	338	0.80	0.53	0.92	(0.17)	ND	(0.17)

Table 1 continued on next page...

Table 1 *(continued)*
Personal Breathing Zone Air Sampling Results
Bureau of Engraving, Incorporated
HETA 94–0191
April 26–30, 1995

Job or Activity		Sampling Time (minutes)*	Concentration, expressed in parts per million (ppm)					
			Hexane	1,1,1– TCE	PGMEA	*sec*–butyl alcohol	Ethyl alcohol	Isopropyl alcohol
Third Shift								
Co–light #2, inner layer printing		450	8.4	3.7	(0.43)	3.0	(0.27)	2.2
Co–light #1 (nearest Ciba line)		448	4.0	1.8	(0.96)	NS	NS	NS
Odd jobs (all over clean room)		449	1.2	0.69	(0.40)	(0.41)	ND	(0.41)
Tamarack		442	2.7	1.3	ND	ND	ND	(0.84)
Ciba line catcher		440	NS	NS	NS	ND	ND	ND
Fifth Shift†								
Ciba line catcher		293	(0.27)	(0.18)	2.6	ND	ND	ND
Film spotting		304	1.0	0.58	ND	(0.69)	ND	(0.85)
Tamarack		339	6.4	2.8	(0.40)	1.8	(0.33)	1.6
Ciba line cleaning (Task sample)	Employee #1	203	ND	ND	30	ND	2.2	ND
	Employee #2	205	ND	ND	6.5	ND	1.6	ND
NIOSH REL – TWA/STEL (S) or CEILING (C)			50	350/350 (C)	None§	100/150 (S)	1,000	400/500 (S)
OSHA PEL – TWA			500	350	None§	150	1,000	400
ACGIH TLV – TWA/STEL			50	350/450	None§	100	1,000	400/500

Comments:

* Actual sampling times are shown, but because no exposures occurred outside the sampling periods, all results (except the Ciba line cleaning) were adjusted to reflect a full 8–hour shift.

† The first two job descriptions are second shift employees working with the fifth shift employee, until the Ciba line was shut down at midnight.

‡ Indicates that one employee completed both jobs.

§ Indicates no established criteria.

NIOSH ceiling limits are exposures that are assessed as a 15–minute TWA exposure that shall not be exceeded at any time during a workday.

NIOSH Short Term Exposure Limit (STEL) is the 15–minute TWA exposure that shall not be exceeded at any time during the workday.

American Conference of Governmental Industrial Hygienists Short Term Exposure Limit (ACGIH STEL) is defined as a 15–minute TWA exposure which should not be exceeded at any time during a workday even if the 8–hour TWA is within the TLV–TWA.

Minimum detectable concentrations (MDCs) for the full–shift samples assume an average sampling time of 380 minutes and range from 0.2–1.7 ppm for all substances; MDCs for the task sample assume an average sampling time of 200 minutes and range from 0.5–3.3 ppm for all substances; MDCs for the STEL assume an average sampling time of 9 minutes and range from 15–86 ppm.

( ) Numbers in parentheses indicate measured concentrations below the minimum quantifiable concentration (MQC) but above the MDC. Values below the MQC lack the usual precision compared with those above the MQC, and therefore must be considered estimates.

Abbreviations:

1,1,1–TCE = 1,1,1–Trichloroethane
NS = No sample collected
PGMEA/PMA = Propylene glycol monoethyl ether acetate
ND = Not detected (below the MDC)

Table 2
Area and Process Air Sampling Results
Bureau of Engraving, Incorporated
HETA 94–0191
April 26–30, 1995

Sample location	Sampling Time (minutes)	Concentration, expressed in parts per million (ppm)						
		Hexane	1,1,1– TCE	PGMEA	*sec*–butyl alcohol	Ethyl alcohol	Isopropyl alcohol	PGME
First Shift								
AREA–Middle of clean room	374	(0.36)	(0.27)	(0.76)	(0.17)	ND	(0.07)	ND
PROCESS–Curtained coater #2	395	(2.6)	(0.26)	140	3.2	ND	(0.21)	(1.7)
PROCESS–Oven #1 turnover	385	(0.31)	ND	(0.89)	ND	ND	ND	ND
Second Shift								
AREA–Dry film	160	6.7	3.5	ND	3.2	ND	2.8	NS
PROCESS–Curtained coater #1	398	NS	NS	NS	2.0	ND	(0.21)	2.6
PROCESS–Curtained coater #2	161	3.2	(0.68)	105	(0.51)	ND	(0.64)	(0.90)
Third Shift and Fifth Shift								
AREA–Between the tamaracks	422	1.9	0.98	(0.64)	ND	ND	(0.70)	ND
AREA–Ciba catch area	425	(0.62)	(0.40)	4.2	ND	ND	ND	ND
AREA–Co–light area	424	1.8	0.67	1.0	ND	ND	ND	ND
Ciba Line Cleaning								
AREA–Co–light #1	214	ND	ND	ND	ND	ND	ND	ND
AREA–Curtained coater #2	190	ND	ND	21	ND	ND	ND	ND
AREA–Oven #1 turnover	216	ND	ND	ND	ND	ND	ND	ND
NIOSH REL–TWA/STEL (S) or CEILING (C)		50	350/350 (C)	None[§]	100/150 (S)	1,000	400/500 (S)	100/150(S)
OSHA PEL – TWA		500	350	None[§]	150	1,000	400	None[§]
ACGIH TLV – TWA/STEL		50	350/450	None[§]	100	1,000	400/500	100/150

Comments:

[§] Indicates no established criteria.

NIOSH ceiling limits are exposures that are assessed as a 15–minute TWA exposure that shall not be exceeded at any time during a workday.

NIOSH Short Term Exposure Limit (STEL) is the 15–minute TWA exposure that shall not be exceeded at any time during the workday.

American Conference of Governmental Industrial Hygienists Short Term Exposure Limit (ACGIH STEL) is defined as a 15–minute TWA exposure which should not be exceeded at any time during a workday even if the 8–hour TWA is within the TLV–TWA.

Minimum detectable concentrations (MDCs) for the area and process samples assume an average sampling time of 350 minutes and range from 0.23–1.0 ppm for all substances; MDCs for the area Ciba line cleaning air samples assume an average sampling time of 207 minutes and range from 0.5–3.3 ppm for all substances.

( ) Numbers in parentheses indicate measured concentrations below the minimum quantifiable concentration (MQC) but above the MDC. Values below the MQC lack the usual precision compared with those above the MQC, and therefore must be considered estimates.

Abbreviations:

1,1,1–TCE = 1,1,1–Trichloroethane
NS = No sample collected
PGMEA/PMA = Propylene glycol monoethyl ether acetate
ND = Not detected (below the MDC)

Table 3
Percentage of 24 Employees Reporting Symptoms
Bureau of Engraving, Incorporated
HETA 94–0191
April 26–30, 1995

SYMPTOM	PERCENT	SYMPTOM	PERCENT
Lightheadedness	29	Frequent or severe headaches	13
Frequent or severe eye irritation	25	Unusual fatigue	8
Frequent or severe nose irritation (burning, sores, or bleeding)	21	Unusual forgetfulness or confusion	4
Frequent or severe sore throat	17	Burning mouth	4
Frequent or severe dizziness	13	Nausea	0

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