

PB91173914



Industrial Hygiene Survey Report of
Arlon Electronic Substrates Division
(formerly Keene Technologies Division, Keene Corporation)
Rancho Cucamonga, California

Survey Conducted by:
Mark F. Boeniger, C.I.H.
John M. Fajen

Dates of Survey:
September 21-23, 1988

Report Written by:
Mark F. Boeniger

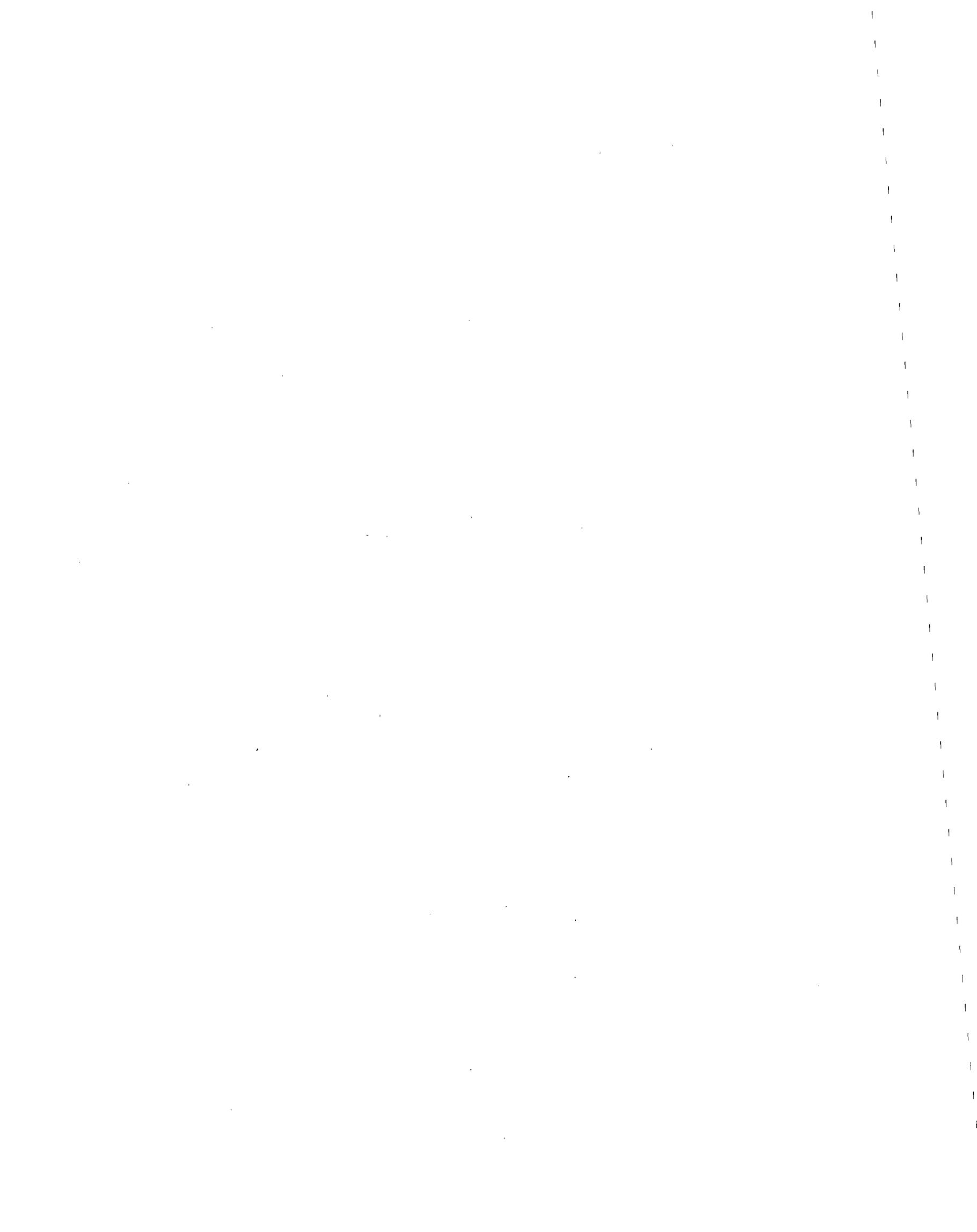
Date of Report:
April 1990

Report Number:
143.24

Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations and Field Studies
Industrywide Studies Branch
Cincinnati, Ohio

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	PB91-173914	
4. Title and Subtitle Industrial Hygiene Survey Report of Arlon Electronic Substrates Division, Rancho Cucamonga, California, Report No. IWS-143-24			5. Report Date 1990/04/00	
7. Author(s) Boeniger, M. F.			8. Performing Organization Rept. No. IWS-143-24	
9. Performing Organization Name and Address Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio			10. Project/Task/Work Unit No. 11. Contract (C) or Grant(G) No. (C) (G)	
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered 14.	
15. Supplementary Notes				
<p>16. Abstract (Limit: 200 words) A walk through survey was conducted at the Arlon Electronic Substrates Division (SIC-3079), Rancho Cucamonga, California in an effort to obtain information on the extent of exposure to 4,4'-methylenedianiline (101779) (MDA) during batch type mixing and during the manufacture and subsequent use of B-stage resin products, to measure the elimination of MDA in the urine of potentially exposed workers, and to identify deficiencies in the handling of MDA. At this facility electrical circuit boards were manufactured. MDA was an ingredient in the resin used to make preimpregnated fiberglass sheets. Personal air concentrations were below the proposed OSHA standard of 5 parts per billion. Widespread contamination of the work surface was noted on wipe sample analysis. Only two of the 52 urine samples taken contained detectable MDA. The author suggests that urine sampling may not be a reliable method for determining exposure levels in such an industry. ←</p>				
<p>17. Document Analysis a. Descriptors</p> <p>b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-Study, IWS-143-24, Region-9, Anilines, Resins, Electronics-industry, Electrical-workers, Adhesives, Occupational-exposure</p> <p>c. COSATI Field/Group</p>				
18. Availability Statement			19. Security Class (This Report)	21. No. of Pages 7
			22. Security Class (This Page)	22. Price



Purpose of Survey:

The purposes of this survey were to
1) obtain information on the extent of exposure to 4,4'-methylenedianiline during batch type mixing and during the manufacture and subsequent use of B-stage resin products, 2) obtain information on the elimination of 4,4'-MDA in the urine of potentially exposed workers, and 3) identify deficiencies in the handling of 4,4'-MDA and to provide recommendations for improving the protection of the workers.

Employee Representatives
Contacted:

Mr. Chet Guiles, Technical Director
Mr. Isidore Romano, Coating Supervisor
and Safety Manager
Mr. Dave Whitcanack, Lamination Supervisor
Mr. Jay Grover, Plant Manufacturing
Manager

Employee Representative
Contacted:

Workers are not in a union.

Standard Industrial Classification

(SIC) Code Number for Plant: 3079 (Miscellaneous Plastic Products)

DISCLAIMER

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

ABSTRACT

An exploratory survey was performed at Arlon ESD, Rancho Cucamonga in order to characterize the extent of employee exposure to 4,4'-methylenedianiline (4,4'-MDA). This facility manufactures electrical circuit boards, of which 4,4'-MDA is an ingredient of the resin used to make preimpregnated fiberglass sheets. Personal and process air, surface wipe, bulk, glove wash, and urine samples were collected for analysis. Personal air concentrations were below the proposed OSHA permissible exposure limit (of 10 ppb) and below the proposed action level (of 5 ppb). Surface wipe samples all contained 4,4'-MDA, and indicated widespread contamination of the work surfaces. In spite of the surface concentrations found, only 2 of 52 urine samples contained detectable analyte. These two samples contained 10 and 70 ppb 4,4'-MDA (LOD = 10 ppb). An integration of the environmental sample results and the urine results suggests that the urine samples may have utility in identifying poor work practices or ineffective glove protection.



INTRODUCTION

Exposure to 4,4'-methylenedianiline (4,4'-MDA) has previously been associated with toxic liver damage, nausea, irritation of mucous membranes, and contact sensitization.⁽¹⁻³⁾ In 1982, the bioassay results from a National Toxicology Program study of 4,4'-MDA supported earlier bioassay findings that 4,4'-MDA is a carcinogen in rats and mice.⁽⁴⁾ There are two epidemiological reports which suggest an increased incidence of cancer in workers.^(5,6) NIOSH researchers have reviewed the available information on 4,4'-MDA and concluded that occupational exposures to 4,4'-MDA should be controlled to the lowest feasible limit.⁽⁷⁾ In July 1987, the Occupational Safety and Health Administration published the recommendations of a mediated rulemaking advisory committee for a health and safety standard for 4,4'-MDA.⁽⁶⁾

This plant was selected for study to obtain information on the extent of worker exposure to 4,4'-MDA in a facility where B-stage prepregs (fiberglass fabric which is preimpregnated with resin) are manufactured and used to make finished products (described in Description of Process). Whereas the initial resin may reportedly contain 6-7 percent 4,4'-MDA, the B-stage resin reportedly contains approximately 2 percent unreacted amine. It is known that this facility is but one of several facilities in the United States that produce circuit boards from 4,4'-MDA containing resin which has been impregnated into fiberglass materials. Additional workers in the U.S. are potentially exposed to 4,4'-MDA in B-stage materials during molding and in lay-up operations within the plastic parts and aerospace industry, respectively.

DESCRIPTION OF PLANT

This facility, constructed in 1984 in a light industrial site, contains 70,000 ft² of floor space and has 30 foot high ceilings. Two low ceilinged enclosed areas have been constructed within the main production area to house the laboratories and clean room production departments (e.g. circuit board construction). The manufacturing area, used for making electronic circuit boards, requires 50,000 ft² of manufacturing space, while the remainder is used to make non-related products. The facility contains a small eating area with vending machines. Offices are located in the front of the building.

DESCRIPTION OF WORKFORCE

Total employment in this plant is 96, of which 65-70 are in the production departments. The production workforce is predominantly male hispanic. Overall turnover rate is low, with only a 10 percent annual turnover rate in the lower-skilled jobs.

DESCRIPTION OF OPERATIONS

This facility is a major manufacturer of polyimide circuit boards, using a 4,4'-MDA containing resin system. Electrical grade laminates are constructed here from multiple layers of the sheeting ("prepreg") which contains polyimide

resin impregnated into fiberglass cloth. This prepreg is sandwiched between copper sheets. The operations for this process have been termed, in the order of the manufacturing process: mixing, coating, sheeting, coring, lay-up, and laminating.

Mixing

The process of making circuit boards begins by mixing a batch of polyimide resin in a segregated mixing room within the plant. A movable mixing vessel is first loaded with solvents into which resin will be added. The resin is a prepackaged dry powder which contains 4,4'-MDA as one of its ingredients. The resin is received in 25 Kg fiber drums. Up to six drums of resin may be added by the worker by dumping the contents into the mixing vessel. The dumping operation is performed in the center of the room without the benefit of local exhaust ventilation. This is typically a one person task that is performed by a worker from the coating department. The mix is blended with a pneumatic powered propeller blender and is then pumped through pipes to the coating department.

Coating

The coating operation is depicted in Figure 1. The process begins with the continuous feed of rolled fiberglass cloth to a dip tank containing the resin. The amount of resin is regulated by passing the cloth through several adjustable metering bars. Dryer ovens with an internal temperature of 350°-360°F remove the solvents and partially cure the resin to a flexible, yet dry "B-stage" state. "B-stage" cloth is also commonly referred to as "prepreg" which is defined as a glass or other fabric which has been saturated (or im-PREG-nated) with a polyimide, epoxy, or other resin. The coated cloth is finally rolled onto a receiving bar. The coating department operates continuously over three work shifts and typically requires two to three operators. A supervisor works only day shift.

A small laboratory exists in the coating department to perform certain quality control checks on the product. Among these tests are the "burn out" test which entails placing a preweighed square of finished coated cloth into an oven at 1100°F until all the resin is completely burnt off, leaving only the cloth. The resulting smoke released from the cloth escapes when the oven door is opened. Other tests performed here use a lower temperature oven to measure volatiles and a press to determine the resin flow characteristics during the laminating and final curing step. This equipment is located on a bench top under a canopy hood.

Sheeting, Coring, Lay-Up, and Laminating

At this point the prepreg material is ready to be made into finished laminate boards. The operations necessary to accomplish this are performed in a clean room environment. The first operation performed with the prepreg cloth is to cut it from rolls into manageable sheets (termed sheeting). This is usually a one person operation. One type of sheeting machine automatically feeds the prepreg and cuts it at determined lengths. The operator helps stack the sheets as they are received. Alternate sheeting machines can be used and require more handling of the prepreg. Coring is the operation of wiping the

prepreg with a tack cloth and layering it between copper foil sheets. This is a two person operation. Finally, the prepreg and copper foil layers are placed in a press tray and taken outside the clean room where they are loaded in the laminating ovens. The laminating presses apply heat (approximately 425-435°F) under pressure for several hours, which causes the final cure of the prepreg. Typically two or three persons are involved with this operation. When the laminates are cooled and are removed from the laminating press, it is widely believed that they are completely cured and that no 4,4'-MDA remains.

There are additional workers in the laboratories which perform various quality assurance tests on the finished products and which perform various tests on the raw materials. Some of these people have a potential for exposure to 4,4'-MDA during the handling and heating of raw materials and B-stage prepregs.

DESCRIPTION OF PERSONAL PROTECTION

Workers in the coating department are provided nuisance dust masks and latex gloves. Their use is required by the company during the mixing operation since noticeable dust is produced when handling the coating resin. Employees in the coating department are also provided this equipment but their use may not be stressed as much as when preparing a mix.

Personal protection available to the sheeting, coring, and lay-up workers includes a thin vinyl latex glove (surgeons glove), disposable dust respirators, and nylon or tyvek protective suits. Only the gloves and suits are required by company policy to be worn. They are discarded and replaced frequently, about every hour.

DESCRIPTION OF INDUSTRIAL HYGIENE, HOUSEKEEPING, AND MEDICAL PRACTICES

An industrial hygiene evaluation of 4,4'-MDA exposures was performed by a contract consultant (International Technology Corp.) in early 1987. The air samples were collected and analyzed according to a microimpinger and HPLC method developed by Rhone-Poulence Co. (France). Of the samples collected during mixing, in the coating department, and in the sheeting department and elsewhere, 4,4'-MDA was detected only during the mixing operation. The result was about 2 ppb in a 446 minute sample. The limit of detection was about 1 ppb. Wipe samples were only taken inside the test laboratory hood in the coating department. Results of two samples reported 5 and 9 ug/100cm². This is the only known evaluation of assessment of exposure to 4,4'-MDA at this facility.

Housekeeping in this facility appeared excellent, this being a product-related aspect of quality assurance. The facility has an in-house vacuuming system for the coating and sheeting-coring departments for removing accumulated dust. This is used at least daily. Workers servicing the vacuuming system reportedly wear disposable dust masks and nylon jackets to protect themselves from the dust. In the coating department, thorough cleaning is performed by wiping down surfaces with tack rags and by solvent mopping of the floors. A mixture of acetone and n-methyl pyrrolidine is used when mopping.

Workers in the coating department are provided fresh work clothes each day which are professionally laundered. Safety shoes and safety glasses are provided annually or as needed. The finishing department workers must wear nylon or Tyvek lab coats and hair nets when working in the clean rooms. Workers in both the coating and finishing departments are provided a locker for their personal clothing. The lockers for the coating department are located in the mixing area, while the lockers for the finishing department workers are located in a hall area between laboratories.

All workers are provided an initial employment physical. In addition, the coating department workers have recently been offered medical examinations that include blood and urine analysis. This examination is performed at the nearby Haven Medical Hospital. The last exam was provided 1-1/2 years ago.

DESCRIPTION OF VENTILATION CONTROLS

The mixing room is provided with several floor and mid-height exhaust air orifices to remove solvent vapors, and probably to some extent, airborne particulates. No local exhaust to control particulates during the dumping of dry resin is provided.

There are several local exhaust hoods located within the coater machine. A slot hood located along the length of the resin reservoir had a measured face velocity of 15 fpm at the slot opening. The resin reservoir opening is 15" wide. No air flow was measured at the dryer opening where the impregnated cloth enters the dryer while a 40 fpm flow rate was measured entering the dryer at the exit opening. A vacuum exhaust contacts the width of the prepreg sheet prior to being rolled up. This is to remove loose particulates from the surface of the sheet. Fresh make-up air is provided to this room by overhead plenums. In the nearby quality assurance laboratory, a canopy hood is situated about five feet above two electric bench top ovens, which are not locally exhausted.

SURVEY PROCEDURES

Fourteen personal breathing zone air samples were collected on the coater and finishing department workers. In addition, six stationary air samples were collected. All air samples were collected on 37 mm acid-treated glass fiber filters, assembled with a paper o-ring support pad in a three piece cassette. Sampling was performed open-faced at a sampling flow rate of 2.5 liters per minute. Analysis was performed by a method developed within NIOSH (Memo to Director, DPSE, NIOSH, Method Development for 4,4'-Methylenedianiline. Sequence #4752. IWSB-85-544. November 3, 1986). This procedure involves use of a high performance liquid chromatograph (HPLC) for separation of the analyte while an ultraviolet (UV) detector and electrochemical detector (ECD) are attached in series to monitor each chromatographic run. The UV detector is set at 254 nm wavelength. The sample filters are eluted from the acid-treated glass fiber filters with 4 mL 0.1 N potassium hydroxide in methanol. The base eluent converts all the salts of 4,4'-MDA back to the free amine. A direct injection of the eluent is made into the HPLC. Analyte

recovery of spiked samples, samples spiked and stored for one month, and samples spiked with air drawn through has previously been performed. Recovery ranged from 94.5% at 3712 ng per filter to 77.8% at 9 ng per filter. Using a linear regression analysis of the calibration curve, an analytical Limit of Quantitation (LOQ) of 5.9 ng per mL and a Limit of Detection (LOD) of 1.8 ng per mL were established. This method provides a detection limit of about 1 part per trillion, provided that a 1000 liter air sample is collected.

Wipe samples were collected on various work surfaces using dry cotton gauze pads. Samples were immediately placed in 10 mL of 0.1N methanolic potassium hydroxide solution to stabilize the 4,4'-MDA. Analyte recovery and long-term and stability studies have shown the extraction efficiency is greater than 90 percent and stability is essentially unchanged when the analyte is in solution. Analysis was performed using the same analytical set-up described for air sample analysis.

Workers were instructed to collect a 4-hour timed urine void at the end of the work shift, 4-hours after leaving work, and approximately an 8-hour timed sample upon awakening in the morning for each of three days. Each worker was given a 500 mL high-density polyethylene bottle to use to collect each of these samples. The urine volume was approximately determined by weighing the bottles. In addition, the refractive index was determined, before freezing the samples with dry-ice, with an optical refractometer. An aliquot of 50 mL was transferred to a 60 mL HDPE leak proof bottle for later analysis of 4,4'-MDA. Additional 30 mL samples were taken in the event that confirmation would be required by mass-spectrometry. Creatinine content was determined by an automated procedure using a modified Jaffe reaction, upon arrival at the NIOSH laboratory.

Analysis of the urine samples for 4,4'-MDA was performed by a method developed at NIOSH. First, 50 mL of urine was subjected to alkaline hydrolysis at 80°C for 2 hours. This step converts the acetylated and conjugated 4,4'-MDA to the free amine. A C18 Sep-Pak solid sorbent tube was then used to separate and collect the free amine in the urine. The amine was eluted from the Sep-Pak with 10 mL benzene and collected. This eluent was taken to dryness under a stream of nitrogen and gentle heat. The residue was redissolved in 1N potassium hydroxide in methanol, allowed to sit overnight, and filtered through a 0.45-um filter. Detection and quantitation of 4,4'-MDA was performed on a HPLC equipped with a Waters 440 ultra-violet detector set at 245 nm, and a Coulochem 5100 electrochemical detector, connected in series. The mobile phase was isocratic with 70:30 (v/v) 0.1N aqueous sodium acetate-acetonitrile. The flow rate was 1.0 mL/min. Injection volume was 25 uL. Laboratory evaluations of the method over a concentration range of 2 to 100 ug/L were performed. The LOD and LOQ for the UV and ECD detectors were similar - LOD 10-30 ug/L and LOQ 30-80 ug/L, respectively. If a sample was found positive for 4,4'-MDA by either UV or EC detection, it was reanalyzed.

RESULTS

The results from the analysis of the air samples are reported in Table 1. All personal sampling results were well below the proposed OSHA PEL of 81 ug/m³ or 10 ppb in air for 4,4'-MDA. The highest sample results were collected on coating department workers who had prepared and mixed dry resin with solvents in the mixing room. This is clearly a dusty operation, but requires only about 30 minutes to complete. The air concentrations measured during a 8-hour and 3-hour time period were 2 and 1 ppb, respectively. It is interesting that in the case of the first result a double batch of resin was prepared, whereas a single batch was prepared in the latter case. The coating department workers had measureable exposures to 4, 0.2, 0.4, and 0.04 ppb 4,4'-MDA. The last two samples represent normal operations but were abbreviated due to an equipment malfunction which caused the coating operation to be closed down for repair. All finishing workers (i.e., those involved in sheeting, coring, and lay-up) were all determined to have exposures values of less than or equal to 1 ppb.

Several stationary air samples were collected at specific process points to determine if elevated air concentration of 4,4'-MDA were associated with certain processes. An air sample located above the resin tub in the coater department measured 0.2 ppb of 4,4'-MDA. This result is not different from the ambient concentration measured on workers in this department, indicating that this is not an important contributor to the overall room concentrations. Another sampler located at the output opening of the heating tower measured an average 2 ppb 4,4'-MDA, suggesting that this is a potential contributor to the general room air concentration. Two samplers placed near the hot air annealing gun behind the trimmer blade measured an average of 7 and 33 ppb 4,4'-MDA, indicating that this is a potentially important source of room air contamination. Two samplers attached on the final press cure indicate that air concentrations of 4,4'-MDA during this operation are about 1 ppb.

Fourteen surface wipe samples were taken throughout the process to determine the extent of surface contamination with 4,4'-MDA. All sample results indicated detectable amounts, ranging from 0.4 ug per 100 cm² area to 1200 ug per 100 cm² area. Some considerably high concentrations were found outside the coater unit and in the coater laboratory. However, the highest concentration was measured in settled dust collected in the sheeting room. This dust had accumulated over a period of less than a day. The prepreg sheet itself is known to contain a few percent unreacted 4,4'-MDA. A dry wipe sample of this material, as it is used in the finishing departments, contained a concentration of 4,4'-MDA corresponding to 118 ug per 100 cm².

A bulk sample of the dry resin mix that is used to formulate the liquid resin was analyzed after extraction with 10 mL of methanolic KOH. The analysis result indicates that the resin mix contains 11.5 percent 4,4'-MDA on a weight basis. A sample of the partially cured prepreg that was obtained in the coating department was similarly determined to contain 6.4% 4,4'-MDA on a resin basis or 3.9% 4,4'-MDA on a total basis (resin plus cloth).

A latex glove which had been worn by a coring worker for approximately 25 minutes was obtained and both the inside and outside were rinsed with 25 ml of methanolic KOH. The analysis of these rinses indicated 61 and 77 ug 4,4'-MDA on the inside and outside, respectively, of the glove. Another heavy utility glove which had been worn by a coating department worker when mixing resin was similarly rinsed. This glove has reportedly been used for about three weeks and contained a small hole. The analytical result indicated 580 ug of 4,4'-MDA rinsed from the inside of this glove. The use of a methanolic solvent reagent to rinse these gloves was selected because 4,4'-MDA is highly soluble in methanol while methanol has minimal permeability through most synthetic glove materials, thus only the surface contaminants on the glove are extracted.(9)

The urine analysis revealed that only 2 of 52 urine samples contained detectable quantities of 4,4'-MDA. The first positive urine sample was collected from the mixer operator from whom a heavy utility glove had been obtained at the end of the survey and was found upon analysis to contain significant amounts of 4,4'-MDA. This glove had been worn by this worker during the survey when mixing batches of resin. The positive urine sample was collected at home between 5-7:30 p.m. and contained 70 ppb 4,4'-MDA. This sample had a specific gravity of 1.036 and a calculated urine flow rate of 0.51 mL/hour, indicating that it was normal in these respects. Unfortunately, the previous collection void was not obtained from this worker and the following void probably was incomplete, but was nevertheless less than the minimum volume required for analysis.

The second positive urine sample was collected by a sheet cutter while at work between 10:00 a.m. and 2:00 p.m. Neither his previous sample, nor the sample collected afterwards, contained detectable 4,4'-MDA. However, the analytical result for that sample of 10 ppb was at the least detectable limit.

CONCLUSIONS AND DISCUSSION

A comprehensive survey of the presence and extent of exposure to 4,4'-MDA was performed in the Arlon ESD plant where electronic circuit boards are produced. A total of 14 surface wipe samples, 2 bulk samples, 3 glove rinse samples, 20 air samples, and 52 urine samples were collected.

The analytical results from bulk resin and prepreg samples indicate that these materials may contain more 4,4'-MDA than previously believed. The resin was assayed at over 11 percent 4,4'-MDA, while the manufacturer reports 6-7 percent 4,4'-MDA. The prepreg was assayed at over 6 percent 4,4'-MDA, whereas the company believed that the prepreg contains only about 2 percent unreacted amine. Differences in extraction and/or analytical methods may account for this discrepancy.

Trace concentrations of 4,4'-MDA were detected in all surface wipe samples indicating widespread contamination of the work areas throughout the circuit board manufacturing operations. Visually, housekeeping in this facility appeared exemplary. Such surface contamination presents a potential for

repeated skin contact by the workers, requiring good work and personal hygiene practices, and adequate personal protection. Generally speaking, the potential for exposure to 4,4'-MDA and other amines through skin contact is believed to be much higher than through inhalation.

In spite of the detectable concentrations of 4,4'-MDA in all the wipe samples collected, including glove wash samples, it was found in only 2 of 52 urine samples. The analytical limit of detection was 10 ppb, and if a lower sensitivity was available during this analytical run, perhaps the incidence of detectable samples would have been greater. At present, there is insufficient information for establishing an acceptable amount of 4,4'-MDA in urine. The highest personal air concentration measured was 4 ppb, which is below both the proposed OSHA permissible exposure limit of 10 ppb, and the proposed action level of 5 ppb (8-hr. TWA).

RECOMMENDATIONS

As stated in the Introduction section, NIOSH has reviewed the available information on 4,4'-MDA and concluded that occupational exposures to 4,4'-MDA should be controlled to the lowest feasible limit.⁽⁵⁾ Although the methods used in this survey provides limits of detection which are extremely low, the detection of 4,4'-MDA in the air, on surfaces, and in some urine voids warrants the following recommendations.

(1) Dry cleanup in the mixing and formulating department should be performed with a high efficiency vacuum (using a HEPA filter) followed by washing with a dilute acidic solution. When these vacuums are emptied, appropriate precautions should be taken to prevent respiratory and skin exposure. Dry sweeping should not be used unless absolutely necessary and only when personal protection is worn to prevent inhalation of airborne dust.

(2) All concrete surfaces should be sealed with an impervious coating to facilitate decontamination procedures.^(9,10)

(3) Workers in this department should shower after the work shift ends to remove dust containing 4,4'-MDA from their skin.

(4) The company's practice of issuing laundered work clothes to the coating department workers should be continued. However, extraction of the clothing to check the extent of decontamination should be performed.

(5) The change room should be moved from the mixing room or segregated as a clean area, free from chemical contamination.

(6) Repeated use of gloves after being in contact with 4,4'-MDA is strongly discouraged since permeation continues to occur after the gloves are used and thus these gloves represent a recurring source of exposure every time they are reworn.⁽¹¹⁾

(7) Because of the trace concentration of 4,4'-MDA found throughout the process operations and inside the thin latex gloves, all workers should wear a glove which is more resistant to permeation. Gloves made of polyvinyl chloride or natural latex rubber have been shown to be most resistant to dilute concentrations of 4,4'-MDA. These may be used in combination with thin cotton gloves if necessary. As usual, used gloves should be discarded at frequent intervals.

(8) Finally, the finishing workers should not be allowed to wear their street clothes at work.

REFERENCES

1. Dunn, G.W. and S.S. Guriguis: Methylene Dianiline (MDA) as a Occupational Health Problem: A Suggested Time-Weighted Average Exposure Level and Medical Program. *Arh. Hyg. Rada Toksikol.* 30:639-645, 1979.
2. McGill, D. and J. Motto: An Industrial Outbreak of Toxic Hepatitis due to Methylene Dianiline. *N. Eng. J. Med.* 296:278-282, 1974.
3. American Conference of Governmental Industrial Hygienists, Documentation of the Threshold Limit Values, P.O. Box 1937, Cincinnati, Ohio.
4. Draft Report. NTP Technical Report on the Carcinogenesis Bioassay of 4,4'-Methylene Dianiline Dihydrochloride in F384/N Rats and B6C3F/N Mice. NTP Publication No. 82-2504, 1982.
5. World Health Organization, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Supplement 7, pp.248, 1987. Lyon, France.
6. NIOSH, Health Hazard Evaluation Report 82-146-1388 of the Boeing Vertol Company, Philadelphia, Pennsylvania. Cincinnati, Ohio, 1982.
7. NIOSH, Current Intelligence Bulletin #47, 4,4'-Methylenedianiline (MDA) (Revised) July 25, 1986. Cincinnati, Ohio.
8. Federal Register, 29 CFR Part 1910. Health and Safety Standards; Methylenedianiline (MDA) Mediated Rulemaking Advisory Committee Recommendations. Thursday, July 16, 1987, pp. 26776-26903.
9. Schoch, D.H., L.K. Tersegno, J.E. Winter, D.G. Bush, and R.L. James: Testing of "Impervious" Gloves for Permeation by Organic Solvents. Presented at the American Industrial Hygiene Conference, June 6-11, 1982.
- 10 Weeks, R.W. B.J. Dean and S.K. Yasuda: Detection Limits of Chemical Spot Tests toward Certain Carcinogens on Metal, Painted, and Concrete Surfaces. *Anal. Chem.* 48:2227-2232, 1976.
11. Weeks, R.W. and B.J. Dean: Decontamination of Aromatic Amine Cancer-Suspect Agents on Concrete, Metal or Painted Surfaces. *Am. Ind. Hyg. Assoc. J.* 39:758-762, 1978.
12. Weeks, R.W. and B.J. Dean: Permeation of Methanolic Aromatic Amine Solutions through Commercially Available Glove Materials. *Am. Ind. Hyg. Assoc. J.* 38:721-725, 1977.
13. Environmental Protection Agency: Dermal Absorption of ¹⁴C-Labeled 4,4'-Methylenedianiline in Rats, Guinea Pigs, and Monkeys. Office of Toxic Substances, Washington, D.C. EPA-560/5-86-011, 1986.

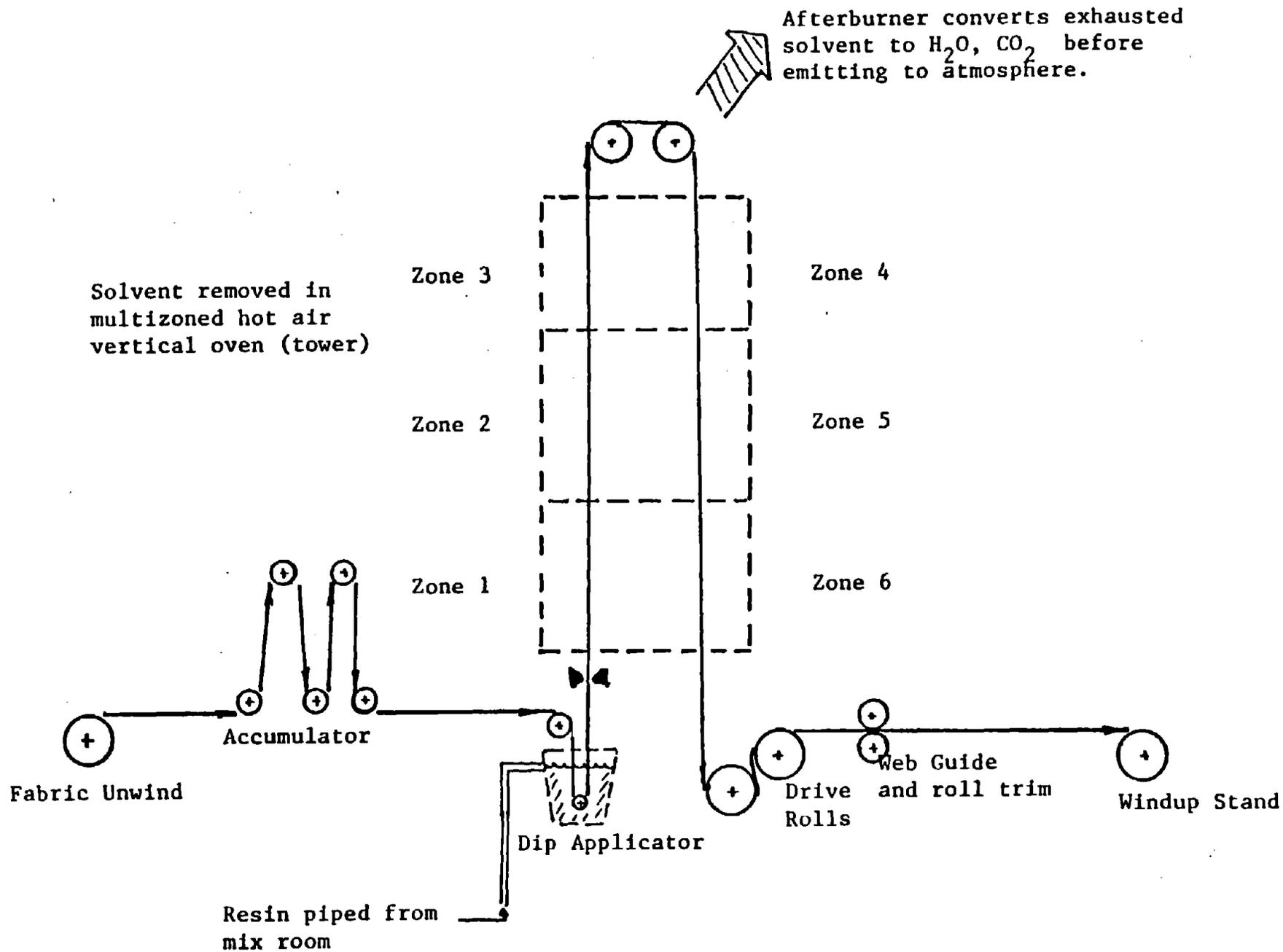


Figure 1 - Typical Prepreg Treater Schematic

Table 1
 Air Sampling Results
 4,4'-Methylenedianiline
 Arlon ESD
 Rancho Cucamonga, California
 September 21-23, 1988

Personal Samples

Sample Number	Job Description	Sample Duration ¹	Air Concentration (ug/m ³)	ppb	8-Hr. TWA ppb ²	Comments
K-6	mixer	491	13	2.0	2	mixed double load
K-49	mixer	167	6.5	1.1	0.3	mixed single load
K-3	Coater	486	30	4.0	4.0	included 90 minutes work outside
K-2	Coater	489	2	0.2	0.2	sampler damaged
K-16	Coater	167	4	0.4	0.2	mechanical breakdown prevented operation for 5 hours
K-17	Coater	152	0.3	0.04	0.01	mechanical breakdown prevented operation for 5 hours
K-1	Cutting	494	7	0.9	0.9	cutting prepreg
K-7	Cutting	512	8.5	1.0	1.0	operated Seybold stack cutter
K-18	Cutting	410	4.5	0.4	0.3	
K-19	Cutter	498	0.2	0.02	0.02	
K-5	Lay-up	480	0.2	0.02	0.02	
K-12	Lay-up	470	1.3	0.2	0.2	
K-4	Coaring	360	0.3	0.04	0.03	worker wore nuisance dust mask
K-25	Coaring	509	2.2	0.3	0.3	

¹ Sample duration in minutes

² Where the 8-hr. TWA is less than the measured concentration, it was assumed that exposure during the unsampled time was essentially zero.

Table 1 (continued)
 Air Sample Results
 4,4'-Methylenedianiline

Area Samples

Sample Number	Job Description	Sample Duration	Air Concentration (ug/m ³) ppb		Comments
K-14	Coater Machine	451	2	0.2	inside hood above coater resin tub
K-13	Coater Machine	420	59	7	above heat gun behind trimmer
K-24	Coater Machine	205	268	33	above heat gun behind trimmer
K-44	Coater Machine	204	16	2	outtake opening below heaters coils
K-15	Final Cure Oven	378	0.1	0.01	attached to press plates
K-26	Final Cure Oven	346	0.1	0.01	attached to press plates

Table 2
 Surface Wipe and Bulk Sample Results
 4,4'-Methylenedianiline
 Arlon ESD
 Rancho Cucamonga, California
 September 21-23, 1988

Wipe Samples¹

Sample Number	Surface Area (cm ²)	Analytical Result (ug)	Location/Description
W-1	100	0.5	R & D Lab Hood-batch preparation room/back panel under hood.
W-2	100	23	R & D Lab - batch preparation room/steel bench top.
W-3	NA ²	5	Mixing Room/ door handle leading to coating room.
W-12	100	172	Coating Room/ outside surface of coater on upper level.
W-4	100	19	Coating Lab/ bench top under hood
W-5	100	18	Coating Lab/ bench top under hood
W-6	100	101	Coating Lab/ top of psi hydrolic press
W-7	100	28	Coating Lab/ outside front of lab hood
W-9	100	55	Coating Lab/ outside front of lab hood
W-8	100	168	Coating Lab/ top of First Aid box on wall
W-10	100	118	Sheeting Room/ wipe of prepreg
W-11	100	0.4	Curing Press Oven wipe of metal plate in oven near the end of a curing cycle.
W-13	100	1200	Sheeting Room/ window sill ledge
W-14	100	122	Sheeting Room/ top of Seybold cutter

1. All wipes were performed with dry gauze. A 100 cm² surface area is equivalent to about a 4 x 4 inch square area.
2. Area too small or irregular to estimate surface area.

Table 2 (continued)
Surface Wipe and Bulk Sample Results
4,4'-Methylenedianiline
Arlon ESD
Rancho Cucamonga, California
September 21-23, 1988

Bulk Samples

Sample Number	Analytical Result (ug)	Description/Comments
B-3	71,500	0.623 grams of Keramide 601A. Contains 11.5 % 4,4'-MDA by weight.
B-2	9,830	0.2532 gram piece of prepreg containing 60.6% resin Contains 6.4 % 4,4'-MDA by resin content; 3.9 % by total weight.
B-4	61	25 mL methanolic KOH rinse of inside of surgical glove used by sheeting worker for about 20 minutes.
B-5	77	25 mL methanolic KOH rinse of outside of surgical glove used by sheeting worker for about 20 minutes.
B-6	580	25 mL methanolic KOH rinse of inside of synthetic work glove worn by mixing operator for about 3 weeks.

