U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT HE 78-68-546

LEAR SIEGLER, INC.
MARBLEHEAD, MASSACHUSETTS

DECEMBER 1978

I. TOXICITY DETERMINATION

It has been determined, based on medical and epidemiological evidence, that a hazard to the health of employees exposed to NIAX® Catalyst ESN existed at Lear Siegler, Inc., Marblehead, Massachusetts. This was determined during the Health Hazard Evaluation conducted by NIOSH on April 4-7, and May 4, 1978.

The evaluation revealed that 50 percent of the employees experienced urological and/or neurological disorders. Many of the affected employees have improved since the usage of the catalyst was terminated and no new cases have been reported since then.

Sexual dysfunctions (decreased ability and frequency) were also reported by 22 percent of the affected employees. Other adverse health effects were reported and though not considered to be due to the catalyst, may have been due to exposures to other chemicals used in the facility.

Environmental sampling, conducted to characterize the airborne contaminants, revealed that acetone, aliphatic hydrocarbons C_9-C_{11}, bis (2(dimethylamino) ethyl) ether (A-99), dimethylaminopropionitrile (DMAPN), methylene chloride, trichloroethane, trichloromethane, trichloroethylene, triethylene diamine (TEDA), toluene diisocyanate (TDI), styrene, quartz and wax particulates were present in the work environment. The TDI concentrations were potentially toxic, and employees reported problems which would be associated with excessive TDI exposure. A potential health hazard also existed for exposures to the C_9-C_{11} aliphatic hydrocarbons. All other exposures were less than the occupational exposure criteria, except that A-99, DMAPN, and TEDA do not have exposure criteria. There were also some unidentifiable substances present.

Recommendations to improve the facility's ventilation and health and safety programs are included in this report to assist in insuring worker health and safety.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

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

Copies of this report have been sent to:

a) Lear Siegler, Inc., Marblehead, Massachusetts 01945
b) Authorized Representatives of Employees, United Auto Workers, Local 1596, Marblehead, Massachusetts 01945
c) United Auto Workers, International Union, Detroit, Michigan
d) U.S. Department of Labor, Region I
e) NIOSH, Region I
f) Division of Occupational Hygiene, Commonwealth of Massachusetts

For the purpose of informing the approximately 231 "affected employees" the employer shall promptly "post" for a period of thirty calendar days, this Determination Report in a prominent place(s) near where exposed employees work.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an 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 National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized employer representative regarding worker exposures to NIAX® Catalyst ESN*, used at Lear Siegler, Inc., Marblehead, Massachusetts.

The request specifically requested a medical evaluation for employees who were experiencing urological problems to ascertain if any adverse health effects had developed and whether or not the ailments were related to exposures to the urethane catalyst which had recently been introduced into production.

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*Union Carbide Corporation Trade Mark

IV. HEALTH HAZARD EVALUATION

A. Facility Description

The main facility is a brick building that is subdivided into three sections and occupies approximately 78,000 square feet. (One of the areas is not currently in use.) The facility was purchased by Lear Siegler in about 1970. The main product is molded flexible polyether urethane* foam seat cushions used primarily in automobiles and pickup trucks.

The facility operates 3 shifts per day, 5 days per week and provides employment for approximately 203 hourly and 28 salaried personnel. Most employees work an eight hour day, forty hour week, but some maintenance is performed on weekends. There are also 11 employees that work at the warehouse, which is located approximately 10 miles away. (See Appendix A for Employee Demographic Data.)

B. Process Description

The facility has two molding lines and the compounding area is situated between them. The majority of the compounding is enclosed in tanks operated by metering pumps. Some chemicals (surfactants) are mixed in open metal containers. The chemical mixtures, both premixed and separate (TDI + polyols + catalysts, fire retardants, etc.), are pumped to a mixing head, where they are briefly foamed (mixed) and poured into open waxed molds. There is a "foam pourer" operating each line who controls the rate and density of foam pouring. Each line has two formulation types. Line one has two "hot" foam formulations referred to as "A" and "B". The "A" formulation utilizes a single amine catalyst and a silica filler. The "B" formulation utilizes a combination of amines and no silica filler, thus it is a lower base density foam. Line two also has two formulations, one hot foam "C" and one high resilient cold foam "D". "C" is similar to "B" in composition except that the water, TDI, amines and surfactants are metered at higher proportions to provide a lower base urethane density. Formula "D" is entirely different except for TDI and the amines.

As the foam is poured into the molds it begins to react exothermically, and a cover lid is put on. The entire mold then proceeds through an oven which ranges in temperature from approximately 300°F at the inlet to 225°F at the outlet. At the discharge end of the oven the mold cover is removed ("coverbreak"), and the cured foam pad removed. The pad is

*Polyether urethanes are generally referred to as flexible polyurethanes and are made with polyols, whereas polyester urethanes are generally referred to as rigid polyurethanes and are made with polyester resins.

placed into a conveyor, and the mold pieces are cleaned of "flash" (excess foam), sprayed with mold-release wax (a wax suspension), and returned to the front of the process. The mold lids return along one side and the mold bottoms along the other side. As the mold bottoms return they are preheated, and on line two, wire or plastic "inserts" are placed into the mold for structural support of the foam product.

The cured pads are placed onto conveyors which lead to the second area called "finishing". Here the pads are trimmed, lightly sanded as needed, repaired, inspected and bagged in bundles for delivery to the warehouse. Scraps are baled into bundles for disposal. Ancillary processes include fibrous glass layup in preparing/repairing molds, machining/tooling, and general maintenance.

There is a cafeteria with vending machines and restroom facilities. Employees receive clean gloves daily upon clocking into work and as needed through the day.

C. Chronology of Events

In August of 1977, a new urethane catalyst (NIAX® Catalyst ESN*) was introduced into the process, and by January 1978 its usage had doubled. During the first two weeks of January, about 6 employees experienced urological problems (the earliest case identified had onset in August/September 1977 and case onsets continued into April 1978), which were thought to be urinary tract infections. Within one week the number had reportedly increased to at least 14 affected employees. Tests given to the employees at a local hospital were negative for evidence of urinary tract infection.

The restrooms were disinfected and the vending machines cleaned as precautionary measures. By the end of the month the company supervisors indicated that some of their employees had improved somewhat. However, by March 1978, the problem had not improved and a complaint was submitted to the Occupational Safety and Health Administration (OSHA). The complaint concerned a mold release wax which had been recently been introduced. An OSHA industrial hygienist began looking into the problem on March 17, 1978. The wax was not considered to be the causative agent of the urinary symptoms and other compounds began to be considered.

On March 27, eleven workers reported to the hospital emergency room with complaints of difficulty initiating urination and a variety of other symptoms related to urination. (Several workers indicated that the

*A product composed of 3-dimethylaminopropionitrile (95 percent) and bis-(2(dimethylamino) ethyl) ether (5 percent).

symptoms had occurred in them and fellow workers over a period of several months but that individual physicians had not been able to identify the source or to determine that it might be occupationally related.) An Occupational Hygiene Physician for the Commonwealth of Massachusetts was notified of the workers' problems. (At about the same time the investigators learned of a similar outbreak among workers at a polyurethane manufacturing plant in Baltimore, Maryland. NIOSH initiated a combined environmental-medical evaluation at the Baltimore facilities on April 7, 1978.[1])

Comparison of the two facilities' chemical usage revealed only three common ingredients, one of which was NIAX® Catalyst ESN. Also a component of "ESN", dimethylaminopropionitrile, was noted to be chemically similar to known neurotoxins.

The company was advised by the Occupational Hygiene Physician to discontinue using the catalyst and to request a NIOSH Health Hazard Evaluation. The substance usage was discontinued on March 28, and the NIOSH regional representative was informed of the problem. That evening a physician working with the Occupational Hygiene Physician reviewed the emergency room records of the eleven affected individuals. The emergency room log was also reviewed for the previous three months to identify other possible cases that might be associated with the problem. The review identified the major presenting symptom as difficulty in initiating urination. (One of the patients seen in the emergency room was noted also to have had an elevated blood anti-nuclear antibody test in November, 1977 while hospitalized shortly after employment at Lear Siegler with an illness attributed to TDI exposure.)

On March 29, the Massachusetts Occupational Hygiene Physician (OHP) interviewed some employees who felt they were affected. These interviews resulted in the identification of two other problems which were possibly related: toxic hepatitis and "spastic colon".

Based on these findings, the decision was made that a full evaluation of individuals at the facility was necessary. Literature searches were initiated for some of the chemicals in use and NIOSH contracted the OHP through the Harvard School of Public Health to conduct the medical evaluations. The NIOSH Region I representative conducted a walk-through survey of the facility on March 30, and a combined NIOSH environmental-medical evaluation began on April 4, 1978. Subsequently, on April 7, 1978, OSHA issued a health hazard alert on the substance, and on May 22, 1978, NIOSH and OSHA issued a joint Current Intelligence Bulletin[2] regarding the possible health hazards associated with NIAX® Catalyst ESN exposure. (Both NIOSH and OSHA had received information that other facilities using the catalyst had an excessive number of employees who had or were experiencing some urological or neurological problems.)

D. Environmental Evaluation

NIOSH industrial hygienists obtained background information from OSHA, management, and labor representatives. Information regarding employee demography, products, raw materials, formulations, usage data and dates, facility and process descriptions, ventilation, health and safety policies, and medical programs were obtained from management. On-site observations of the work place, employee work practices, safety equipment usage and hygiene were made throughout the facility and the warehouse.

Bulk samples of most of the chemicals in use, and those which were recently discontinued, were obtained in glass scintillation vials with Teflon®-lined caps, and samples of the foam product, produced on different dates, were collected in plastic bags.

Photographs of the operations and sketches of the facility were obtained. Qualitative ventilation measurements were made utilizing a Sierra* hot wire anemometer and Gastec* smoke tubes. Quantitative measurements for airborne organic vapor contaminants were made with an Organic Vapor Analyzer (OVA) to facilitate identification/characterization of contaminant generation sources. Swipe samples for surface contamination were obtained with Whatman* filter swipe pads. The samples were placed in glass scintillation vials with Teflon®-lined caps. Relative humidity and temperature measurements were made with a battery operated psychrometer.

1. Environmental Sampling

General area and personal samples for qualitative and quantitative assessment of exposures to airborne organic vapor contaminants were taken at both the production facility and the warehouse. Calibrated battery operated MSA* model G and Sipin* personal monitoring pumps were utilized in combination with six different collecting media, including liquid absorbents, solid adsorbents and filter cassettes, to characterize the airborne contaminants.

(The evaluation focused on determining whether or not NIAX® Catalyst ESN and/or its components were present in the workplace. At the time of the survey there were no reported sampling or analytical methods available.)

a. Liquid Absorbent

(1) Modified Marcali Solution

General area samples for TDI were obtained utilizing midget impingers with 15 milliliters (ml) of modified Marcali solution, (sampling data sheet 18,01)[3] and MSA model G sampling pumps operated at air flows of approximately 1.0 liters per minute (lpm). The samples were obtained in the chemical compounding area near the TDI metering pumps and at a TDI spill in a different area.

*Mention of a manufacturer's name does not constitute a NIOSH endorsement.

Personal samples for TDI were obtained utilizing spill-proof impingers containing 15 ml absorption media and MSA pumps operated at air flows of approximately 1.0 lpm. The impingers were pinned to the workers' clothes, on the chest, to simulate their breathing zones. The pumps were hung on belts around their waists and connected to the impinger with tygon® tubing. Samples were obtained of most job classifications throughout the facility.

b. Solid Adsorbents

(1) Charcoal[2]

General area samples for characterization of airborne organic vapors were obtained with 150 milligram (mg) activated charcoal tubes attached to MSA and Sipin pumps operated at air flows of 1.0 and 0.2 lpm, respectively. Some samples were obtained with the charcoal tubes hooked in series. Samples were obtained throughout the facility and warehouse.

Personal samples were also obtained utilizing Sipin pumps operated at air flows of 0.2 and 0.05 lpm. The charcoal tubes were clipped to the workers' collars to simulate their breathing zones. Most job classifications were surveyed.

(2) Silica gel[3]

General area samples for airborne organic amines were obtained with 150 mg silica gel tubes attached to air pumps operated at air flows of 1.0 and 0.2 lpm. Samples were obtained throughout the facility, side by side, with the charcoal samples.

Personal samples were obtained in the same manner as were the charcoal tube personal samples.

(3) Porous Aromatic Polymer

Both general area and personal samples for airborne organic vapors were obtained utilizing 150 mg porous aromatic polymer tubes. The samples were obtained in the same manner as were the charcoal and silica gel samples.

A sample set using each type of solid adsorbent was taken, side by side, in the headspace of both a mixed catalyst and an unmixed NIAX® Catalyst ESN drum to identify off-gases and determine if DMAPN was detectable. (At the time of the sampling there was no reported sampling or analytical method for NIAX® Catalyst ESN or its components.)

(4) Swipe Samples

Swipe samples were taken with Whatman filter swipe pads to determine if any surface contaminants were present.

c. Filters

(1) FWSB Filters

A general area sample for crystalline silica was obtained utilizing a plastic three piece filter cassette with a tared FWSB filter. The sample was taken with a MSA pump operated at an airflow of approximately 1.7 lpm. The sample was located under a sand distribution system used on line #1.

(2) PVC Filters

Personal samples for total particulate (wax particles) were obtained utilizing plastic three-piece filter cassettes with tared PVC filters, with some taken in series with charcoal tubes. MSA pumps were used and were operated at air flows of approximately 1.5 and 1.0 lpm. When both media were used in series, the flow rates were reduced to the 1.0 lpm rate.

The samples were taken at waxing operations where employees complained of upper respiratory tract irritation.

2. Environmental Sample Analyses

a. Liquid absorbents

(1) Samples obtained for TDI were analyzed by a colorimetric method, NIOSH P&CAM #141.[4]

b. Solid Adsorbents

(1) Activated Charcoal Tubes

The charcoal tube samples (plus the front glass-fiber plug) were desorbed in 1.0 ml of carbon disulfide (CS_2) and analyzed by gas chromatography (GC) with a flame ionization detector (FID). The GC columns used were 12- and 20-foot stainless steel, 10 percent SP1000 columns, a 20 foot FFAP column at 80^{o}C and a 6-foot glass UCON column at 100^{o}C.

(2) Silica Gel Tubes

The tubes were desorbed with 0.1 N H_2SO_4, and the pH was adjusted to 9 with KOH. Alequots of the solution were then analyzed by gas chromatography equipped with a nitrogen phosphorous detector. The columns used were 10 foot silanized glass with 10 percent carbowax 20M/2% KOH on 80/100 chromosorb W AW or a 10% UCON 50 HB 5100/2% KOH on 80/100 chromosorb W AW. (It should be noted that significant peaks eluted that were not identifiable but were nitrogen or phosphorous containing compounds.)

(3) Porous Aromatic Polymer Tubes

The samples (including the front plug) were desorbed in 1 ml of a 0.5 percent aqueous cupric chloride in acetone solution* with a two-hour sonification. The solutions were then analyzed by GC using a 6-foot one-fourth-inch glass column containing 4 percent carbowax 20M with 0.8 percent Carbopack B. The GC was run isothermically at 200°C and an 0.1 N KOH solvent flush was run after each sample to prevent column deactivation.

(4) Swipe Samples and Bulk Urethane

The swipe samples were desorbed (extracted) with 2 ml, and bulk samples with 20 ml, of the 0.5 percent aqueous cupric chloride in acetone solution and analyzed the same as in (3).

A polyol-TDI mixture was reacted in the laboratory to simulate production conditions and identify off-gases from the reaction. A set of each type solid adsorbent was used and analyzed as in (3). Mass Spectrometry (MS) was performed on selected samples for identification of unknown eluted compounds. (See Appendix B.) Desorption studies were conducted for some compounds on some of the solid adsorbents. (See Appendix C.)

c. Filter Samples

(1) FWSB

The pre-tared filter was reweighed to an accuracy of 0.01 mg. The filters were then dissolved in tetrahydrofuran and the particulate redeposited on silver membrane filters and analyzed by x-ray diffraction. (NIOSH P&CAM #109).[4]

(2) PVC Filters

The pre-tared filters were reweighed to an accuracy of 0.01 mg. An attempt was made to desorb the wax and analyze it by infrared spectrophotometry; however, it was not soluble in the three solvent systems tried. The wax formed as a suspension rather than a solution.

E. Medical Evaluation

The medical evaluation was made available to all current employees, including management, and was conducted on-site. Management provided the necessary time and space for the evaluation. Written consent forms were signed by all participants prior to evaluation.

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*The analytical method used was supplied by Union Carbide Corporation which had specifically developed it for analysis of the A-99 ether component, bis (2-(dimethylamino) ethyl ether. The method was adaptable for analysis of DMAPN.

Between 8 and 13 days after the catalyst's removal from production, 197 of 230 employees completed a self-administered questionnaire in English or Spanish, consisting of a review of systems, and personal and family history. 210 employees were interviewed by one of eleven physicians with questionnaires concerning genitourinary and neurologic history and symptoms, job description, use of protective equipment and sanitary practices. (Review of company records revealed that 53 persons had left employment in the preceding 8 months, the majority of these having worked more than one month.)

Urinalyses were performed by physicians on the interview day on 197 of the employees, and the same number of venous blood samples were analyzed by a contracted laboratory for complete blood count (CBC) with differential, electrolytes, glucose, blood urea nitrogen (BUN), creatinine, liver function, calcium, uric acid and antinuclear antibody (ANA). Two and one-half weeks after cessation of exposure, five men and three women were referred for neurologic examination, and the following diagnostic tests: cystometro-electromyogram, sacral latency, urecholine stimulation, and sural and peroneal nerve conduction studies.

A re-survey of 100 of the 114 persons with any urinary complaints was conducted 11½ weeks after cessation of exposure by interview in the plant or, for absent employees or those having changed place of employment, by telephone. Medical records were requested for those patients who had consulted physicians.

A case of bladder dysfunction was defined as an employee who had experienced two or more of the following four symptoms: 1) difficulty in initiating urination, 2) need to strain in order to void or maintain a urine stream, 3) decreased force of stream, and 4) increased duration of urination. An employee at risk of bladder dysfunction was defined as one who worked any portion of time in the production or finishing areas. Five persons were excluded from all analysis: an office employee who had developed urinary retention while hospitalized for cardiac catheterization; two whose urine symptoms antedated the use of the suspect chemical, neither of whom were at risk of exposure and the two who lacked initial physician interview. A late-improving case was defined as one who still had urine symptoms at the time of the re-survey.

D. Evaluation Criteria

1. Environmental

The following occupational exposure criteria were used in evaluating the environmental contaminants found at the time of the survey: (1) National Institute for Occupational Safety and Health (NIOSH), Recommended Criteria for Occupational Exposures, (2) American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Substances and Physical Agents in the Workroom Environment and supporting documentation, and (3) U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Standards (29 CFR 1910.1000, Tables Z1, Z2, and Z3).

As the table indicates, there are several substances with no existing occupational exposure criteria or standards.

Substance	Criteria (mg/M³)* NIOSH	ACGIH	OSHA
Acetone	590	2400	2400
Bis(2-(Dimethylamino)ethyl)ether	-	-	-
n-Butyl acetate	-	710	710
Dimethylaminopropionitrile	-	-	-
Methyl Ethyl Ketone	590	590	590
Methylene Chloride	261	360	360
Naphtha distillates (refined petroleum solvent, C_9-C_{11})	350	1350	2000
Dust containing Quartz	-	-[1]	-[2]
Styrene	-	420	420
Toluene	375	375	750
Toluene diisocyanate (TDI)	0.036	0.014[3]	0.14
Total particulates (nuisance dust)	-	10	15
1,1,1-Trichloroethane (methyl chloroform)	1910	1900	1900
Trichloroethylene	134	535	535
Trichloromethane (chloroform)	9.78	50[3]	240
Triethylene Diamine	-	-	-

*Approximate milligrams of substance per cubic meter air

1. Actual exposure criteria based on total mass is calculated by $\frac{30\ mg/M^3}{\%SiO_2+3}$

2. Actual exposure criteria based on total mass is calculated by $\frac{30\ mg/M^3}{\%SiO_2+2}$

3. Recently revised to level indicated

These criteria are designed to protect most workers for an eight to ten hour day, forty-hour week, during a normal working lifetime. However, there are numerous factors that may influence an individual's response to a particular substance, such as age, sex, health status, smoking and alcohol habits, etc. Also, these criteria are based on single substance exposures; thus, effects from exposures to combinations of substances may be additive or synergistic when the substances elicit similar physiological responses.

2. Medical Criteria

Discussion of the health effects of every substance identified in this survey is beyond the scope of the medical evaluation, which was directed towards employee health problems associated with NIAX® Catalyst ESN exposures; thus, they are not presented in this report. (Included in the Reference Section are sources which can be consulted for health effects information on the substances not discussed here. It should be noted that some of the identified substances have little, if any, health effects reported in the scientific literature.)

a. Toxicity Data

(1) NIAX® Catalyst ESN[5,6]

The catalyst is a light-yellowish, water-soluble liquid mixture containing 3-(dimethylaminopropionitrile (95 percent) and bis(2-(dimethylamino) ethyl) ether. It has an amine-type odor and may contain trace contaminants of acrylonitrile and dimethyl amine.

There is a very limited amount of toxicological information on this urethane catalyst mixture. The only known information available is Union Carbide Corporation's Material Safety Data Sheet and Toxicology Information Sheet. The toxicology data indicate that skin penetration in rabbits is a definite hazard. (LD50= 0.445 mg/kilogram (Kg) body weight). The compound is classified as moderately hazardous in rats via both oral (LD50= 2.46 ml/Kg body weight) and inhalation routes of entry. Skin irritation is listed as a slight hazard and eye injury, to a 15 percent or more solution, a serious hazard. (All data is based on single-exposure animal tests.) The sheet also states that patch testing with human volunteers using cured polyester foams made with the catalyst were not irritating or sensitizing. Other information addressed the properties of the substance and general precautions. (Labels on drums, located at the facilities evaluated, contained less information.)

A preliminary animal study conducted by medical investigators at Harvard School of Public Health revealed the following toxicological action of the catalyst substance. "A 20 percent solution of ESN was administered to rats at a dose of 10 mg/Kg by the intraperitoneal (IP) route (actual dose 2 ml/kg). Several rats were used and the following observations noted: Within 30 to 60 seconds the animal appeared to be depressed, and its stance became low to the tabletop on which it stood; within an additional 15 to 20 seconds clonic convulsions occurred; and within one minute the animal died. A smaller dose of a 20 percent solution, 1 ml/Kg by the IP route, produced depression of activity and apparent right rotation of the body (the animal began to circle its cage). It recovered completely after five to ten minutes.

Further experiments were undertaken with three control rats at two dose levels of ESN (1 ml and 0.5 ml of a 20 percent solution using three rats per dose-level). Gross necropsy of these animals showed a large hematoma of the bladder in the region of the neck of the bladder in the treated rats. The lesion appeared to be on the abdominal side of the bladder and resulted in an apparent division of the bladder into what appeared to be two horns. Depending on the extent of the lesion or erosion the urine was tinged with blood. Whether the urinary output was altered in these latter experiments was not determined since urine was not collected nor volume measured. However, the size of the gross lesions suggests that the potential exists for a mechanical obstruction to occlude the urinary exit from the bladder."[7]

(2) 3-(dimethyl amino) propionitrile[8-28] (DMAPN)

The only known toxicological information available for this substance is the Union Carbide Corporation toxicology sheet. The data, based on single exposure animal studies, indicates that the substance is only a definite hazard to the eyes, via direct contact. The hazards, by route of entry (inhaling, oral, skin contact) are described as moderate to slight. There is, however, information concerning similar propionitriles which are known neurotoxins and can cause skeletal system defects, teratogenesis, and other adverse biological effects.[9] Imino dipropionitriles are used experimentally to cause peripheral neuropathy in rats. Amino acid nitriles, present in certain plants, and particularly in species of sweet peas of the genus Lathyrus, play a role in causing neurolathyrism, a degenerative spinal cord disease related to a diet of such peas. The neurological disorders include clinical descriptions of bowel and bladder dysfunctions, tingling sensations, and impotence.

Osteolathyrism, a syndrome of bone deformity and hind limb paralysis, can be caused by beta-aminopropionitrile (BAPN), In addition, BAPN can cause the syndrome of angiolathyrism, both in young rats and rat fetuses. Feeding BAPN to pregnant rats can result in offspring that are stillborn or that die shortly after birth from aneurysms of great vessels that rupture (e.g. aortic aneurysms). Numerous other adverse effects, including teratogenesis, have also been reported. The effects appear to be associated with an inhibition of the fibroblast cells and collagen and elastin enzymes.

(3) bis(2-(dimethyl amino)ethyl)ether (A99)[29]

Again, the only available information for this substance is Union Carbide's toxicology study sheet. The data indicate that the substance is moderately to slightly hazardous by each route of entry, based on single-exposure animal data.

Both the John Hopkins neurologist and Union Carbide are currently conducting toxicological studies on each of the three substances, and the results will be available at some time in the future.

It should be noted that DMAPN was listed as moderately hazardous, via skin penetration, and the ether as slight to moderately hazardous, but the catalyst mixture as definitely hazardous. The difference in the skin penetration hazard may be that the ether components facilitates or potentiates skin absorption of DMAPN.

(4) Toluene Diisocyanate (TDI)[30-33]

The health effects and properties of this substance are well documented. The substance is a light-yellow liquid and is classified as a Class B poison. It is a strong irritant, especially to the eyes and upper and lower respiratory tract. Acute exposure to the liquid produces chemical burns, and eye contact produces severe conjunctival irritation. Acute exposures can be fatal.

Chronic low level exposures to vapors cause irritation of the eyes, nausea, vomiting, and abdominal pains. Of all the adverse chronic effects, the most notable are those involving the respiratory tract.

(a) Primary Irritancy

At sufficient concentrations of TDI, all exposed individuals are susceptible to effects on the respiratory tract, resulting in a burning sensation in the nose and throat, a choking sensation, dry or productive cough, and general chest pains. These effects are often mistaken for "colds" or upper respiratory tract infection. Exposure to higher concentrations can lead to severe irritation of the respiratory tract, mimicking an asthmatic attack, and may produce a chemical pneumonia. Additional symptoms include headache, sleeplessness, ataxia, and euphoria.

(b) Allergic sensitization

TDI can produce an immunological sensitization and very low concentrations may thus elicit various symptoms. Nocturnal shortness of breath and cough, as well as symptoms and signs of asthma, may appear in sensitized individuals (such asthmatic reactions have been reported to be fatal). A stuffy-headed feeling, similar to hay fever, is often a sign of sensitization.

(c) Accelerated loss of lung function

A third type of respiratory effect, from chronic low level exposure, is that of accelerated loss of lung function in the absence of sensitization.

E. Results and Discussion

1. Environmental

The results of the environmental sampling are contained in Tables I-VII. In general, the results should be considered as the minimum concentrations present because most samples are not full 8-hour samples, and there may be competitive binding of the substances on the media.

Sampling results for airborne TDI (Tables I and II) indicate that exposures were potentially toxic, particularly those at the front of the mold lines. The mold covermen have the highest exposures, as would be expected. (Many employees indicated they were experiencing symptoms which may be related to their TDI exposures.) Measurements for TDI after a spill cleanup also revealed that the decontamination and personal protection procedures were inadequate.

A number of other airborne organic compounds were identified (Tables III-VII), but based on the current existing single substance occupational exposure criteria, only the aliphatic hydrocarbons C_9-C_{11} exposures and one chloroform exposure were excessive on the dates sampled.

The waxing operations, along with the mold cleaners, had the highest exposures to hydrocarbons and the chlorinated compounds. There were high levels, however, detected throughout the production area and certain locations in the finishing area. Many employees complained of the waxing operation, but the wax itself could not be analyzed. Some of the substances do not have exposure criteria; thus, evaluation of these exposures is not certain. There were also exposures to compounds not identifiable but which were nitrogen or phosphorous containing substances. The exposures measured for Triethylene diamine (TEDA) and A-99 are the only human exposure data known to exist. DMAPN was also measured on the first sampling, even though its use was terminated approximately one week before the tests. The second sampling indicated, however, that DMAPN had dissipated, but not the A-99. Both were extractable from the cured product; thus, their presence could be from scraps strewn about the areas. These data would seem to indicate that exposures could have been by either inhalation and/or contact with the cured polyurethane. (The DMAPN and A-99 were also detected as reaction off-gases in a laboratory test simulating the process conditions.)

Readings taken with the OVA revealed that the foam-pouring area has the highest total organic vapor concentrations. This would be expected because the freshly mixed reacting foam is poured into open molds, and then a cover is placed on. Also, purging of the process lines is performed in this area and the purging solvent mixture is poured into a plastic bag-lined container which is not exhaust ventilated.

Observations and qualitative spot check measurements of the ventilation systems indicated that there is an inadequate air flow across the mold-cover station to control the contaminants. This accounts for the operator's excessive exposures. The duct work is also in need of repair and cleaning. In addition, the waxing booths require cleaning, and the facility is in need of additional makeup/dilution ventilation. The fibrous glass layup room needs additional makeup air and the exhaust ventilation redesigned. The facility's housekkeeping also appeared to be inadequate. The lunchroom, however, was well kept and orderly.

2. Medical

The results of the medical evaluation are contained in Tables VIII-XI.

a. Patient Data Base Questionnaire

20 of 36 females (56 percent) at risk and 84 of 130 males (65 percent) at risk were confirmed as cases of bladder dysfunction, a total of 104 in a population of 208, 166 being at risk. Only 3 employees at risk and 3 not at risk thought they had work-related urinary symptoms, but did not meet the criteria of the case definition; 5 of them had one of the 4 defining symptoms. Almost all of the cases, 95 percent, had three or more of the defining symptoms, and 82 percent had all four.

Cases were described with acute onset of urinary difficulties, occurring in as little as one day after initial employment. As seen in Table VIII, a prominent complaint was difficulty in initiating urination, with micturition accomplished only by pressing on the lower abdomen, often in conjunction with a Valsalva maneuver. Relaxation of such pressure resulted in cessation of the weak stream that had been induced, and nearly every case (all but 2) noted that the duration of urination was increased, in some individuals to as long as five minutes. Although we did not systematically question the population, several cases volunteered that they lost the urge to urinate, sometimes in conjunction with loss of urethral sensation. Thus, many people would void only once a day or by schedule habit, worried that they ought to be urinating after a six-pack of beer or when arising in the morning. Others described an increase in frequency, and some of those who started with infrequent voiding noted an increase over normal frequency as they improved. The majority described vague abdominal discomfort with or without the identification of a full bladder, and discomfort while urinating became a part of the syndrome for some only as their urinary habits were returning towards normal. Likewise, urethral burning was more likely to occur as cases felt they were improving. Some persons noted that their symptoms improved, at least initially, on weekends, with absenteeism, or during the February blizzard that closed the plant for a week.

There were no significant differences between the proportions of male and female cases experiencing specific urinary symptoms. A greater proportion of women (13 of 20 compared to 34 of 54) complained of urgency. (X^2 = 2.995 not statistically significant $p>.05$.) Two of these women, and one not meeting the case definition, had urinary tract infections documented by culture during a portion of the time in which they had bladder dysfunction. Of interest is that both cases reporting incontinence were male.

In addition to the urinary symptoms, 23 cases complained of sexual difficulties as compared to six non-cases. Decreased libido affected men and women in similar proportion. Two female cases complained of dyspareunia. Ten of the 84 male cases suffered problems with erection and four with ejaculation; the corresponding numbers in non-cases were one and zero of eighty.

With the exception of numbness of the hand or arm affecting 13 cases, there were no neurologic complaints differentiating cases from non-cases. Only small numbers of persons among cases and non-cases suffered weakness, lower extremity numbness, incoordination or cranial nerve symptoms. Three cases and one non-case complained of orthostatic dizziness.

Headache, nausea, anorexia, bloating and diarrhea were complained of more frequently by cases, but in numbers which were not statistically significant; in fact, the first three were more associated with working in the industrial process areas than with having urinary symptoms. There were three cases of hepatitis occurring among bladder cases in the period of interest, but biopsy of one of these persons did not support a toxic etiology. The only complaint of statistical significance apart from the genitourinary and neurologic symptoms above, was that of dry mouth, which affected 20 percent of cases and 22 percent of employees at risk (2 percent not at risk had symptoms; thus, it is a statistically significant finding). This symptom appears associated with exposure to foam production and persisted in similar prevalence on the resurvey.

Little evidence was found for a clinical spectrum of disease afflicting employees other than the bladder dysfunction. Comparing employees at risk with those unexposed to the plant manufacturing areas, there was only one symptom, anorexia, significant at the .05 level, present in 11 percent of the manufacturing population and in none of the remaining employees. Given the number of comparisons tested this finding is probably not significant. As expected with toluene di-isocyanate exposure, there was a high prevalence of respiratory complaints, especially for wheezing in increasing prevalence correlated with seniority for the population at risk. Also of interest, 14 of 151 persons at risk complained of chest colds occurring more often than once a month, whereas none of the 39 employees not at risk had this tendency.

Of the 104 cases, four women and 10 men continued to have symptoms, albeit milder, nearly 3 months after exposure was presumed to have ceased. These 14 late-improvers ranged from 21 to 54 years in age, with a mean of 36 years, and were a significantly older group than the other cases, who ranged from 20 to 65 with a mean of 32 years. They tended to have more seniority with 64 percent of them having worked more than 3 years prior to the period of interest, whereas only 35 percent of the other cases had such experience. The late improvers were different from the other cases in a few ways: all of them suffered dysuria and a greater proportion, 3 percent had increased frequency in addition to decreased frequency during part of their course. They were more likely to complain of urgency, 10 of the 14, but this was significant only at the .055 level and may be misleading since two of the women had documented urinary tract infections (UTI's) during a small portion of their course. Half of the late improvers complained of sexual dysfunction, with one having problems with erection, two with ejaculation, and the remainder with decreased libido. Apart from genito-urinary symptoms, late improvers clearly differentiated themselves from other cases in complaining of nausea (6/13 vs 10/83) and tinnitus (4/13 vs 6/83); this group also had three of 13 members complaining of pain on bowel movements compared to 4 of 83 (difference not significant); 6 of 13 suffering headaches (17/85) and 3 of 4 reported increased vaginal discharge. Of the 14, 8 had declared no improvement when interviewed in April, and three had agreed to neuro-urologic tests at that time. One other of this group, a 42-year-old, had required suprapubic cystostomy in February for two liter urinary retention, and was still unable to empty his bladder completely four months after leaving work at the time of operation.

Only one other case underwent surgery. A 58 year old was treated with a transurethral prostatectomy for acute urinary retention in December. In addition to the two surgery cases, two additional persons were cystoscoped, and none had evidence of structural abnormality to explain their symptoms. In total, at least 45 cases consulted physicians for their urinary symptoms, 16 more than once. Women were more likely to see a physician (14 of 19 as compared to 31 of 70), and were more likely to be catheterized (4 of 14 vs 6 of 31); men, on the other hand, were twice as likely to report their urine symptoms to the employer. 42 employees did so, with the first reports as early as August, 1977 (35/84 men, 4/19 women, 3 non-cases).

There were no differences between cases, other employees or late-improvers in the incidence of genito-urinary symptoms diagnosed prior to the period of interest. Nor were there differences among these groups in the few persons taking medication for diabetes, sedation, sleep, hypertension, or upper respiratory symptoms. Regular alcohol consumption did not differentiate cases from other employees, but cases were possibly more likely to be smokers (63/104 vs 49/104, $p = .08$).

b. Laboratory Data

Eighteen percent of the cases and eight percent of other employees had microscopic hematuria ($p = .07$), despite significantly greater epithelial cell contamination among non-cases. Glucosuria, proteinuria and pyuria occurred in very small similar numbers in cases, non-cases, those at risk, those not at risk, and in late improvers.

With the exception of albumin, whose mean value was slightly higher among cases, there were no significant differences from the blood parameters of non-cases. However, several tests differentiated those at risk (in manufacturing) from those not at risk, even though all mean values were within the normal ranges. The population at risk had lower mean hemoglobin (14.42 vs 15.49), RBC count and hematocrit, and higher liver enzymes: SGPT (15.0 vs 10.9), SGOT (31 vs 21.7), LDH (208 vs 197), alkaline phosphatase (74 vs 65). Of less clear meaning, those at risk also had higher albumin (4.74 vs 4.62), higher phosphate (3.58 vs 3.18), higher sodium (144.1 vs 142.2), higher chloride (103.0 vs 101.8), and lower potassium (4.08 vs 4.26).

When the population at risk was examined by work location the four liver function tests noted above were further elevated for those in foam production (SGPT 17.2; SGOT 32.6; LDH 21.0; alkaline phosphatase 79.5). There were no significant differences in urea nitrogen, creatinine, uric acid, calcium, glucose, iron or antinuclear antibody among cases and non-cases nor among those at risk and not. Only two cases had elevated random glucose; 158 and 174, and neither of these were glycosuric. Late improvers could not be differentiated from other cases on any parameter.

Of the eight persons referred for neurologic and urologic testing, four men and one woman lacked the bladder detrusor reflex despite adequate rectal sphincter relaxation, and several had increased polyphasic potentials compatible with denervation. Only one of four tested had a response to urecholine administered intramuscularly. Two of the four men and a woman who had a normally reflexive bladder had a high sensory threshold for bladder filling. Sacral latency time was prolonged in two of the four males with areflexive bladders and in a third male with a normal detrusor reflex. The most seriously affected of these three complained of difficulties with ejaculation (premature in one case, unspecified in the other), as well as testicular discomfort. Only one male had evidence of urinary retention, and he had all other bladder abnormalities as well; he was the only person with an elevated random glucose of 158 and subsequently had a normal glucose tolerance test.

Neurologic symptoms were not helpful in identifying individuals with peripheral nerve abnormalities. Of the 4 males and 2 females who were thought to have some sensory impairment in the distal lower extremities on clinical exam, only two men had prolonged conduction and low amplitude on sural nerve study. One of these two, a 26 year old, was hyporeflexive as well, and had distal muscle wasting in the feet, an increased latency and decreased amplitude on peroneal nerve conduction study. These two with sensory nerve conduction abnormalities also had impaired bladder sensation, areflexic bladders, denervation potentials and prolonged sacral latencies; they continued to have some urinary symptoms at the time of the resurvey two months after study.

3. Epidemiology

The first case was in August 1977 in a female mold cleaner and wax sprayer on Line 1, a job close to the area in which hot cured foam is removed from the mold. (Figure I shows the progress of epidemic curve for cases over the preceeding 9 months.)

As seen in Table IX, the highest rate of bladder dysfunction occurred among production assembly line workers, closely followed by those involved in cleanup and tasks characteristic of new employees in general service. These tasks include work in the finishing area where employees also have a high incidence of urinary symptoms. Supervisory and equipment maintenance personnel in the production and finishing areas were affected in lower proportion. There were no cases of bladder problems among employees who worked exclusively in the adjoining offices and laboratories, in the warehouse several miles distant where the finished foam is stored in the polyethylene bags, or in maintenance shop outside of the production area. Within the production and finishing areas, there were no striking differences in attack rates for the various job descriptions although the number of workers holding any particular job title on the production line might be small. There was only one job among those at risk of the bladder syndrome in which there were no affected workers. This work (wire salvage from scrapped foam) was done in an area physically removed from the main production area. In contrast, 100 percent of the other wire salvage workers developed bladder dysfunction.

The suspect catalyst was introduced on assembly line 1 in August 1977 and was used inconsistently until introduced on assembly line 2 as well in late December; total monthly consumption of the catalyst is graphically presented in Figure I. Heavy use of the catalyst in October was succeeded by a several-fold increase in cases in November among assembly line workers. The cases in the finishing-area job categories lagged behind the November increase in production worker cases, and new cases occurred despite reduction of catalyst use in November. Figure II demonstrates that the cases in the finishing area job categories lagged behind the November increase in production worker cases, and new cases occurred despite reduction of catalyst usage in November. Of note, all employees were required to work a sixty-hour week from September to Thanksgiving and for three weeks in February. In February, the New England blizzard closed the plant for one week and there was a decrease in the number of new cases in February, despite the steadily increasing production of catalyst-containing products. The amount of catalyst used in each assembly line per month is not available, but the amount of catalyst-containing polyurethane foam produced and shipped by each line was available for representative time periods, as shown in Table X. Line 1 workers produced 2/3 again as much as line 2 workers over a longer time period. Nearly 3 times as much catalyst-containing foam produced on line 1 was scrapped as on line 2.

As shown in Figure III, there were cases of bladder dysfunction among line 2 workers in the three months prior to the introduction of the catalyst on their line, and the percentage of workers affected on line 1 and 2 was virtually the same despite differences in production. Of the 8 late improving cases in the production area, 5 worked exclusively on line 2, and 3 worked a portion of time on both lines 1 and 2.

The proportions of persons at risk developing bladder dysfunction differed significantly among the three shifts ($p = .017$), second shift workers being affected in highest proportion, as shown in Figure IV. In addition to having a higher attack rate, second shift workers were more likely to have persistent symptoms, 19 percent of second shift cases being late improvers, accounting for 57 percent of the 14 late-improving cases. In comparison, only 5 of 34 first shift cases and 1 of 28 third shift cases have had symptoms persisting at the time of resurvey.

The shifts differed in several respects. Second shift workers experienced the plant at its dirtiest, since cleanup of the production area during the day and evening was deferred to the graveyard shift. Second and third shifts produced more foam, as shown in Table X, and less of it proportionally was scrapped, since production innovation and tests were done on the first shift. Table XI shows that second shift workers had the lowest rate of absenteeism over the period in question, and hence, as a group, may have had more exposure to the agent. Counterbalancing the absenteeism, however, was a lower rate of overtime paid to second shift employees compared to equivalent amounts for first and third shift workers. There were no differences among shifts in the use of protective equipment, exposure to chemical spills, or personal sanitary practices. Although ventilation in the winter months may have differed among shifts, this could not be substantiated.

As would be expected, the third shift had the highest turnover rate and the first shift the lowest. Seniority was not correlated with bladder dysfunction. Within any particular shift, the attack rate of those with greater than 3 years seniority was not significantly lower than that of employees hired within the last three years, and hence the trend for more senior workers to have a lower incidence of symptoms is largely explained by the differential distribution of persons with seniority in the first shift. In addition, turnover was higher among the job categories with a high incidence of bladder dysfunction than among supervisory and skilled personnel, who had lower attack rates and more seniority. Hence, seniority, per se, seems to have had no effect on the likelihood of bladder dysfunction.

Among the population at risk, handling foam products did not predispose to having bladder symptoms. There were cases among persons who only incidentally came in contact with foam or chemical compounds, for example, among electricians, among assembly line workers who put structural screens and wires in empty molds prior to foam pouring and among cover men and cover cleaners, the latter two groups being in close proximity to hot production processes. Cases were significantly more likely to have worn the cotton gloves provided compared to others at risk, probably reflecting dirtier work.

The wearing of aprons had no effect on the occurrence of the syndrome, nor did the report of spilling chemicals frequently. There were no statistical differences between cases and non-cases in the population at risk in hand washing before eating, location of eating, or showering after work. There were no differences between late improvers and other cases in any of the above parameters.

Two mold cleaners developed bladder dysfunction only one and three days after being employed. Four other new employees developed symptoms after 1, 1.5, 2 and 3 weeks of employment respectively. Once bladder dysfunction developed, no improvement was noted prior to the month when catalyst use was stopped by 85 percent of cases. However, within ten days of catalyst removal, 21 percent (21/98) were back to normal and 51 percent (50/98) were definitely improved within a month of removal. All but 8 cases reported improvement if not resolution, and these reported onset of improvement in the second month after cessation of catalyst use.

The cases with persisting urinary symptoms at the time of resurvey three months after exposure cessation could not be differentiated from other cases by month of onset of improvement, 12 of 14 having begun improvement by at least one month post exposure, and the remainder within two months. Nor was there a preponderance of the late improvers among specific job areas or categories.

IV. CONCLUSIONS/RECOMMENDATIONS

A. Conclusions

Based on the results of medical and environmental evaluations and comprehensive literature searches, it was determined that NIAX® Catalyst ESN was the probable causative agent of employee urological and neurological disorders and possibly the sexual dysfunctions, too. The specific substance which probably elicited the toxic effects was the dimethyl aminopropionitrile component. Further toxicological testing is underway, but the results were not available for this report. The evaluation revealed other health complaints which may be the result of occupational exposures. However, this study was not designed to determine the causes of those effects.

The majority of affected employees are improving since the ESN usage was discontinued.

B. Recommendations

1. Good personal hygiene and work practices should be observed by all employees. Washing of hands before smoking, eating and drinking will help reduce possible contamination. Food, drinks, and cigarettes should not be kept at work locations or near the production area.

2. Management is encouraged to continue developing detailed written health and safety programs and instruct all employees of the hazards associated with the chemicals used in the facility and the proper usage of personal protective equipment.

a. Materials for neutralization and adsorption of chemical spills (i.e. TDI) and proper safety equipment should be located near the compound area and specific emergency/cleanup written procedures should be developed, taught the employees and reviewed periodically. Emphasis should be placed on personal protection, limitation of the protection, proper use, maintenance, cleaning and storage of safety equipment used for spills and emergencies. All employees should be instructed in the hazards of the chemicals in use.

b. The ventilation systems should be cleaned and maintained regularly. The local exhaust systems at the pouring area should be extended horizontally a couple more feet to be across from the pouring operator, thus providing for better capture of the vapors which come off the foam poured into waste barrels during switch over/purging. This will also help control mist generation in the pouring process, which was detected as polymerized urethane film on the bottom of the impingers used for personal monitoring of the operator.

c. The air intakes for the "push air" blown across the mold lines at the foamer station should be located remotely from the process area to prevent recirculating contaminants across the back of the covermen and pouring operator. The pipe connections could be directed to a more suitable area for intake air.

d. Impervious plastic/rubber aprons should be provided the compounder, pouring operators, covermen and waxers. They should also wear chemical safety goggles and impervious gloves. (Cotton liners could be used inside the gloves but should be changed as often as desired to keep hands dry and clean.)

e. The exhaust stacks on the roof for the waxing booths should be extended to help reduce recirculating the contaminants back into the facility.

f. Locker facilities should be located in a clean, quiet area and employees encouraged to change into separate work clothes daily. Clean work jumpsuits could be provided the workers daily to encourage personal hygiene and good work practices.

g. The ventilation in the fibrous glass layup operations should be redesigned to be more effective. Make-up air could be provided through louvers in the shop door bottoms.

3. Complete sets of Material Safety Data sheets and supplemental toxicology information on each substance should be acquired and maintained and first-aid procedures outlined.

4. The preplacement and periodic medical evaluation program, as outlined in the NIOSH Criteria Document for TDI, should be followed. Of particular importance are the following:

a. Medical history - paying particular attention to any respiratory symptoms and allergies.

b. 14" X 17" chest roentgenogram.

c. White blood cell count with differential and absolute eosiniphil counts.

d. Pulmonary function testing which includes forced vital capacity (FVC) and forced expiratory volume at one second (FEV).

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Table I

Results of Air Sampling for Toluene Diisocyanate

Lear Siegler, Inc.
Marblehead, Massachusetts

April 4 & 6, 1978

HHE 78-68

Environmental Conditions: Indoors, Temperature 71-73^{o}F, R.H. = 30%, Time 1857-1900

Sample Number	Time	Description	Results (mg/M^3)* Total TDI[1]	TWA[2]
TDI-1	1631 - 2225	Personal Sample (P.S.) Foamer Operator Line #1	0.048	0.035
TDI-2	1620 - 2230	P.S. Foamer Operator Line #2	0.057	0.044
TDI-3	1620 - 1905	P.S. Break and Coverman Line #2	0.075	0.026
TDI-4	1633 - 1903	P.S. Break and Coverman Line #1	0.084	0.026
TDI-25	2311 - 0425	P.S. Foamer Operator Line #1	0.031	0.02
TDI-102	2305 - 0420	P.S. Coverman Line #1	0.16	0.11
TDI-103	2317 - 0620	P.S. Foamer Operator Line #2	0.073	0.064
TDI-104A	2320 - 0215	P.S. Break and Coverman Line #2	0.096	0.049
TDI-104B	0216 - 0635	P.S. Break and Coverman Line #2	0.025	
TDI-200	2340 - 0315	P.S. Trimmer Line #2	0.007	0.006
TDI-201	2327 - 0623	P.S. Compounder	0.01	0.009
TDI-202	2346 - 0620	P.S. Janitor	N.D.[3]	
TDI-300	0802 - 1050	P.S. Waxer Line #1	0.009	0.003
TDI-301	0726 - 1051	P.S. Wireman Line #2	N.D.[3]	
TDI-Spill	1740 - 1803	Spill Area after cleanup at Water Fountain	.514	

*Approximate milligrams of substance per cubic meter air
1. Toluene Diisocyanate Concentration for sample period.
2. Calculated 8-hour Time Weighted Average based on sample period assuming no other exposure time.
3. Not Detected - The limit of detection for these samples was 0.2 micrograms per milliliter of absorption solution

The NIOSH Recommended Criteria for Occupational Exposure to TDI is 0.036 mg/M^3 as on 8-hour TWA daily exposure or 0.14 mg/M^3 as a twenty minute ceiling.

ɹble II

Results of Air Sampling for Toluene Diisocyanate

Lear Siegler, Inc.
Marblehead, Massachusetts

May 4, 1978

HHE 78-68

Environmental Conditions: Indoors, Temperature 63-65°F, R.H. = 30%, Time 0745

Sample Number	Time	Description	Results (mg/M^3)*	
			Total TDI[1]	TWA[2]
TDI-1	1255 - 1500	Personal Sample (P.S.) Coverman Line #1	0.23	0.06
TDI-2	1300 - 1500	P.S. Foamer Line #2	0.15	0.04
TDI-3	1302 - 1500	P.S. Coverman Line #2	0.04	0.01
TDI-4	1500 - 2256	P.S. Foamer Line #2	0.04	0.04
TDI-5A	1505 - 1755	P.S. Coverman Line #2	0.22	0.08
TDI-6	1537 - 2255	P.S. Foamer Line #1	0.08	0.07
TDI-7A	1522 - 1810	P.S. Coverman - Breakerman Line #1	0.08	0.03
TDI-7B	1810 - 2255	P.S. "	0.01	
TDI-8A	1524 - 2101	P.S. Breakerman - Coverman Line #1	0.01	0.03
TDI-8B	2103 - 2255	P.S. " "	0.10	
TDI-9	1528 - 1930	General Area Compounding	0.10	
TDI-12	2130 - 2257	P.S. Coverman Line #2	0.04	0.01
TDI-20	1807 - 2100	P.S. Coverman Line #2	0.10	0.04

*Approximate milligrams of substance per cubic meter air
1. Toluene diisocyanate concentration based on sample period.
2. Calculated 8-hour Time Weighted Average exposure based on sample period and assuming no other exposure time.
The NIOSH Recommended Standard for Occupational Exposure to TDI is 0.036 mg/M^3 as an 8-hour TWA daily exposure or 0.14 mg/M^3 as a twenty minute ceiling.

Table III

Results of Air Sampling for Organic Vapors

Lear Siegler, Inc.
Marblehead, Massachusetts

April 4 - 5, 1976
HE 78-68

Environmental Conditions: Indoors, Temperature 71-73°F, R.H. = 30%, Time 1857-1900

Sample No.	Time	Description	Results (mg/M³)*						
			Acetone	AH[1]	MC[2]	Styrene	TCM[3]	TCE[4]	TCEE[5]
CT-1A & CT-1B**	1559-2221	General Area (G.A.) Compounding	--	107	--	--	1.2	1.7	1.7
CT-3	1845-2227	Personal Sample (P.S.) Covermen Line #2	--	220	--	--	2.3	23	4.6
CT-4	1847-2237	P.S. Mold Cleaner Line #1	--	447	--	--	2.2	13	6.4
CT-5	1900-2235	P.S. Mold Cleaner Line #2	--	546	--	--	2.4	7.1	2.4
CT-7A & CT-7B**	1603-2225	G.A. Finishing	--	85	--	--	4.2	64	4.2
CT-61	2252-0640	G.A. Compounding	--	61	--	--	N.D.***	0.43	0.43
CT-200[6]	2340-0315	P.S. Gluer Line #2 Finishing	--	83	--	--	2.1	79	2.1
CT-201[6]	2327-0623	P.S. Compounder	--	341	--	--	2.4	24	2.4
CT-202	2330-0620	P.S. Janitor	--	189	--	--	4.0	25	8.0
CT-203**	2330-0623	P.S. Waxer Line #2	--	435	--	--	2.9	17	7.8
CT-204	0322-0710	P.S. Wireman Line #2	--	368	--	--	2.0	16	4.0
CT-302	0710-0731	P.S. Waxer Line #1	--	750	--	--	23	45	N.D.***
CT-300**	0715-1025	G.A. Fiberglass Layup Room	32	26	70	50	--	18	--

* Approximate milligrams per cubic meter air
** Values must be taken as minimum concentration present due to possible breakthrough on backup section
*** Not Detected: The limit of quantification for these samples was 0.05 mg/sample
1. Aliphatic Hydrocarbons
2. Methylene Chloride
3. Trichloromethane (Chloroform)
4. 1,1,1-Trichloroethane
5. Tetrachloroethylene
6. Pump failed

Table

RESULTS OF AIR SAMPLING FOR ORGANIC VAPORS

Lear Siegler, Inc.
Marblehead, Massachusetts

April 4-5, 1978

HE 78-68

Environmental Conditions: Indoors, Temperature 71°-73°, R.H. ≈30%, Time 1857-1900

Sample No.	Time	Description	Results mg/M³		
			A-99[1]	DMAPN[2]	TEDA[3]
PP-100	0820-0923	Bulk Air-ESN Drum Headspace	58**	205**	-
PP-101	0926-1020	Bulk Air-Mixed Catalyst with ESN Drum Headspace	26***	329***	-
PP-1	1559-2221	General Air(G.A.) Compounding	0.14	0.11	-
PP-7	1603-2225	G.A. Finishing	0.30	0.11	
SG-1	1559-2221	G.A. Compounding	-	-	0.45
SG-7	1604-2225	G.A. Finishing	-	-	0.61
SG-12	1731-1736	TDI spill area	-	-	N.D.[4]
SG-23	0927-1020	Bulk Air Mixed Catalyst with ESN	-	-	0.56
SG-24	0715-1025	G.A. fiberglass layup room	-	-	N.D.
SG-25	2307-0615	Personal sample (P.S.) line #1 foam operator	-	-	0.44
SG-26	0820-0923	Bulk Air ESN Drum Headspace	-	-	N.D.
SG-28	1620-2230	P.S. line #2 foamer operator	-	-	0.66
SG-29	1640-2226	P.S. line #1 foamer operator	-	-	0.49
SG-30	0737-1054	P.S. baler operator	-	-	1.1

* approximate milligrams of substance per cubic meter air
** minimum concentration due to possible breakthrough
*** sample "wet" may have sucked up liquid during sampling

1. bis (2-(dimethylamino)ethyl) ether
2. dimethylamine propionitrile
3. triethylene diamine
4. not detected - the limit of quantification was 4 micrograms per sample

. ıe V

Results of Air Sampling for Organic Vapors

Lear Siegler, Inc.
Marblehead, Massachusetts

May 4, 1978

HE 78-68

Environmental Conditions: Indoors, Temperature 63-65°F, R.H. = 30%, Time 0745

Sample No.	Time	Description	Results (mg/M³)* A99[1]	DMAPN[2]	TED[3]
PP-10	0725 - 1418	General Area (G.A.) Compounding Production Department	0.48	N.D.**	0.15
PP-11	0727 - 1416	G.A. Finishing Department	0.49	N.D.**	0.12
PP-13	0845 - 1359	G.A. Warehouse	N.D.***	N.D.**	0.06
PP-12	0845 - 1359	Personal Sample (P.S.) Warehouseman	N.D.***	N.D.**	N.D.**
PP-101	0710 - 1419	P.S. Line #2 Trimmer Finishing Department	0.54	N.D.**	0.43
PP-100	0719 - 1419	P.S. Line #1 Patch and Repair Finishing Department	0.50	N.D.**	0.50
PP-102	0723 - 1416	P.S. Line #1 Bagger " "	N.D.***	N.D.**	N.D.**
PP-103	0713 - 1422	P.S. Line #2 Trimmer " "	N.D.***	N.D.**	N.D.**
PP-105	0705 - 1426	P.S. Compounder Production Department	0.53	N.D.**	0.53
PP-106	0819 - 1439	P.S. Mold Unloader Line #1	0.65	N.D.**	0.52
PP-108	1550 - 2225	P.S. Line #1 Finishing Department	0.38	N.D.**	0.50

*Approximate milligrams of substance per cubic meter air

**Not Detected: Triethylenediamine and DMAPN had the same GC retention time, since TED was confirmed on PP-101, the compound was calculated at TED for each sample. The limit of detection was 0.02 mg/sample

***Background interferences were observed from other small peaks thus value must be considered as high. The detection limit for these samples was 0.02 mg/sample

1. Bis(2-(dimethylamino)ethyl)ether
2 Dimethylaminopropionitrile
3. Triethylene Diamine

Table VI

Results of Air Sampling for Airborne Contaminants

Lear Siegler, Inc.
Marblehead, Massachusetts

May 4, 1978

HE 78-68

Environmental Conditions - Indoors, Temperature 63-65°F, R.H. = 30%, Time - 0745

Sample No.	Time	Description	AN[1]	BA[2]	MEK[3]	MC[4]	STY[5]	QUA[6]	CRB[7]	TP[8]	PN[9]
			Results (mg/M³)*								
CT-44	1530-2236	Personal Sample (P.S.) Wireman Line #2	--	--	--	--	--	--	--	--	230
PVC-43	1532-2240	P.S. Wireman Line #2	--	--	--	--	--	--	--	1.74	--
CT-47	0710-1430	P.S. Lids Line #1	--	--	--	--	--	--	--	--	290
PVC-47	" "	P.S. Waxer Lids Line #1	--	--	--	--	--	--	--	.14	--
CT-48	1521-2241	P.S. Waxer Bottoms Line #1	--	--	--	--	--	--	--	--	130
PVC-44	1535-2239	P.S. Waxer Bottoms Line #1	--	--	--	--	--	--	--	.22	--
CT-49	0705-1432	P.S. Wireman Line #2	--	--	--	--	--	--	--	--	300
PVC-49	0706-1432	" " " "	--	--	--	--	--	--	--	.33	--
CT-50	0715-1435	P.S. Waxer Bottoms Line #2	--	--	--	--	--	--	--	--	330
PVC-50	" "	" " " "	--	--	--	--	--	--	--	.23	--
PVC-48	1520-2241	P.S. Waxer Bottoms Line #1	--	--	--	--	--	--	--	.41	--
PVC-45	0718-1438	P.S. Waxer Lids Line #2	--	--	--	--	--	--	--	3.15	--
CT-1**	1510-2245	P.S. Compounder	N.D.[10]	N.D.[11]	N.D.[10]	2.6	N.D.[10]	--	--	--	+[14]
CT-3	2050-2225	General Area (G.A.) Compounding	N.D.[10]	N.D.[11]	N.D.[10]	6.5	N.D.[10]	--	--	--	--
CT-4	2230-2247	G.A. - Shop Area	N.D.[10]	N.D.[11]	N.D.[10]	1.1	.39	--	--	--	--
FNSB-1446	0824-1439	G.A. Line #1 Across from Foamer Operator Below Sand Distributor	--	--	--	--	--	24[12]	N.D.[13]	.25	--

*Approximate milligrams substance per cubic meter air
**Significant unknowns eluted but were not identified

1. Acrylonitrile
2. Butyl Acetate
3. Methyl ethyl ketone
4. Methylene chloride
5. Styrene
6. Quartz
7. Cristobalite
8. Total particulate
9. Painters Naphtha (Naphtha distillates)
10. Non-detectable - Limit of quantification was .01 milligrams substance per sample.
11. Non-detectable - Limit of quantification was 0.6 milligrams substance per sample.
12. Due to an unknown interference the secondary quartz diffraction line was used for quantification of sample
13. Non-detectable - Limit of quantification was .03 milligrams of substance per sample.
14. Substance present, not quantitated

ıable VII

Results of Samples taken for NIAX ESN Components
Lear Siegler, Inc.
Marblehead, Massachusetts

April 4, 1978
Environmental Conditions; Indoors, Temperature 67^{o}-70^{o} F, R.H.≈30-35%

Sample No.	Description	Results (mg/Sample)* A99[1]	DMAPN[2]
SS-1	Mixed Catalyst Drum Top	0.02**	N.D.**
SS-2	Conveyor Belt-Finishing Department	N.D.**	N.D.**
SS-3	Process Equipment-Production Area	N.D.**	N.D.**
SS-4	" "	N.D.**	N.D.**
FS	Seat cushion produced on March 21, 1978	+[3]	+[3]
Lab Generated	Reacted in Laboratory to simulate production conditions	+[3]	+[3]

May 4, 1978

Sample No.	Time	Description	A99[1]	DMAPN[2]	TED[4]
SS-1	0915	Line #2 Conveyor Pad Takeoff-Production	<0.02	<0.02	--
SS-2	0920	Line #2 Conveyor (Before Rollers)-Finishing	<0.02	<0.02	--
SS-3	0922	Line #2 Rollers - Finishing	<0.02	<0.02	--
SS-4	0925	Line #1 Conveyor- "	<0.02	<0.02	--
SS-5	0930	Line #1 Rollers - "	<0.02	<0.02	--
SS-6	1045	Compounding Mixing Drum	0.26	<0.02	0.26
SS-7	1045	Stirring Rod in Mixing Drum	0.10	<0.02	0.14

* Approximate milligrams of substance per filter
** Not Detected: The limit of detection for these samples was 0.01 milligrams per sample

1. Bis(2-(Dimethyl Amino)ethyl) ether
2. Dimethylaminopropionitrile
3. Detected via Extraction - not quantitated.
4. Triethylene Diamine

Table VIII

MEDICAL RESULTS

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

URINARY COMPLAINTS

SYMPTOMS	CASES	NON-CASES
Increased Duration	102/104	1/104
Hesitance	98/104	0/104
Need to Strain	98/104	0/104
Decreased Stream	94/104	4/104
Subjective Retention	70/102	4/104
Dysuria	70/104	13/104
Abdominal Discomfort	61/103	6/104
Urgency	47/104	3/104
Decreased Frequency	47/104	1/104
Increased Frequency [1]	44/104	23/104
Urethral Discharge	19/84	2/80
Nocturia	15/104	10/104
Gross Hematuria	12/104	4/104

[1] Includes 9 cases reporting decreased frequency as well.

Table IX

ATTACK RATES IN DIFFERENT WORK CLASSIFICATIONS
(See Text for Case Definition)
Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

WORK CLASSIFICATION	MALE CASES / MALE EMPLOYEES	FEMALE CASES / FEMALE EMPLOYEES	ATTACK RATE
AT RISK			
Production	49/70	3/5	69.3%
Finishing	14/21	16/29	60.0%
Miscellaneous at Risk*	12/19	1/1	65.0%
Plant Engineers/ Electricians	4/9	0/0	44.4%
Supervisory at Risk	5/11	0/1	41.7%
Total at Risk	84/130	20/36	62.7%
NOT AT RISK			
Miscellaneous / ** Outside Plant	0/14	0/2	0
Maintenance/*** Outside Plant	0/13	0/0	0
Office Workers/ Truckdrivers	0/7	0/6	0
Total Not at Risk	0/34	0/8	0
TOTAL EMPLOYEES	84/164	20/44	50.0%

* Includes general service, janitors, housekeepers, lab utility and wire salvage on defunct line

** Includes stitchers, receivers, loaders, lab and process technicians, warehouse

*** Includes mold lay up and maintenance, tooling, auto mechanic

Table X

Catalyst Containing Foam Produced and Scrapped for Line and Shift

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

Produced - March 13 - 29

	Shift 1	Shift 2	Shift 3	Total
Line 1	51,394	52,769	57,619	161,782
Line 2	30,050	30,960	35,470	96,480
Total	81,444	83,729	93,089	258,262

Scrapped in February and March

	Shift 1	Shift 2	Shift 3	Total
Line 1	18,420	13,777	16,563	48,760
Line 2	7,210	4,305	6,195	17,710
Total	25,630	18,082	22,758	66,470

Table XI

Absenteeism Among Employees in Production Work

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

	December	January	February	March	Total
SHIFT 1					
Percent Absent*	5.3	8.0	5.1**	4.1	5.5
Average Present/Day	46.0	43.3	47.9	47.6	46.3
SHIFT 2					
Percent Absent*	3.9	5.2	6.7**	4.2	4.8
Average Present/Day	43.9	44.3	43.5	43.7	43.7
SHIFT 3					
Percent Absent*	8.6	9.3	6.4**	9.2	8.5
Average Present/Day	41.8	43.1	48.4	46.7	44.9
TOTAL					
Percent Absent*	5.9	7.5	6.0**	5.9	

* Percent Absent = Number of persons absent x number of days of absence/ Total Person Days

** Excluding February Blizzard

Figures 1 and 2

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

FIGURE I

EPIDEMIC CURVE OF BLADDER SYNDROME CASES COMPARED WITH CATALYST CONSUMPTION

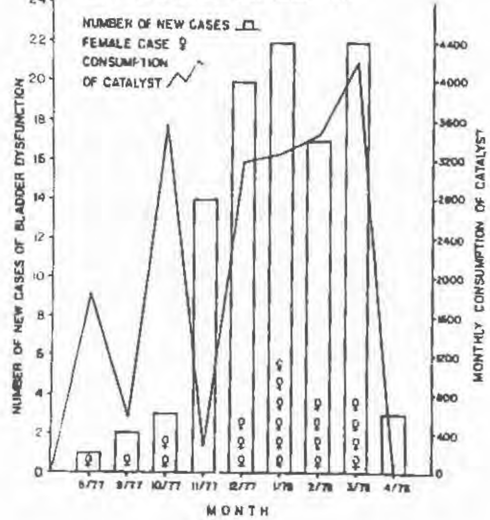

FIGURE 2

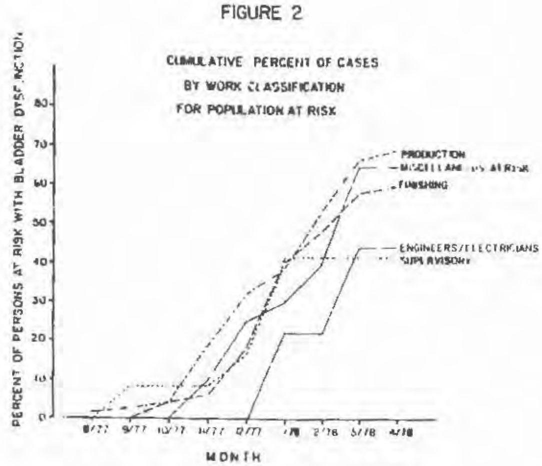

Figure 3

Cumulative Cases of Bladder Syndrome as Percent of Workers on Line

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68

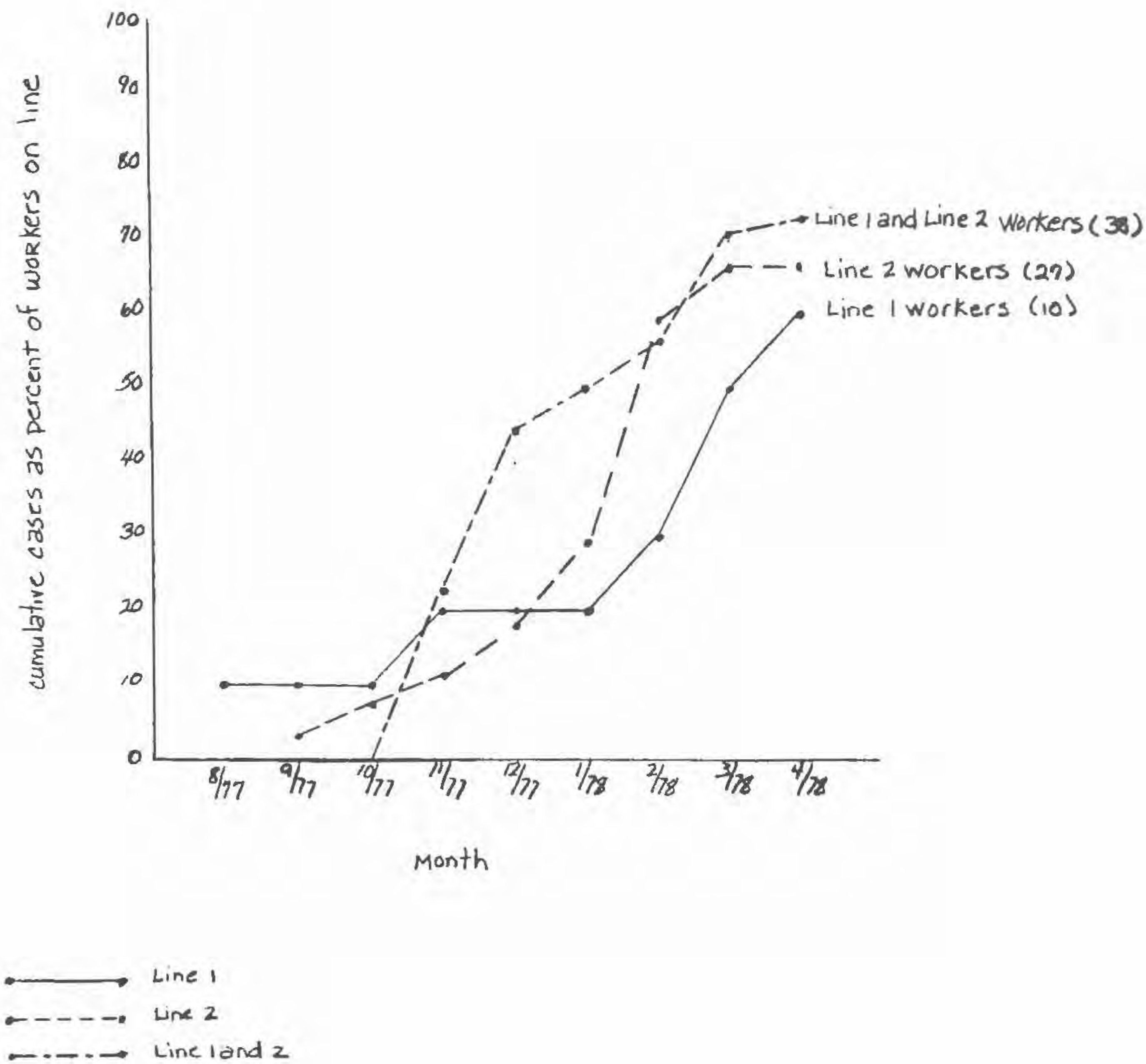

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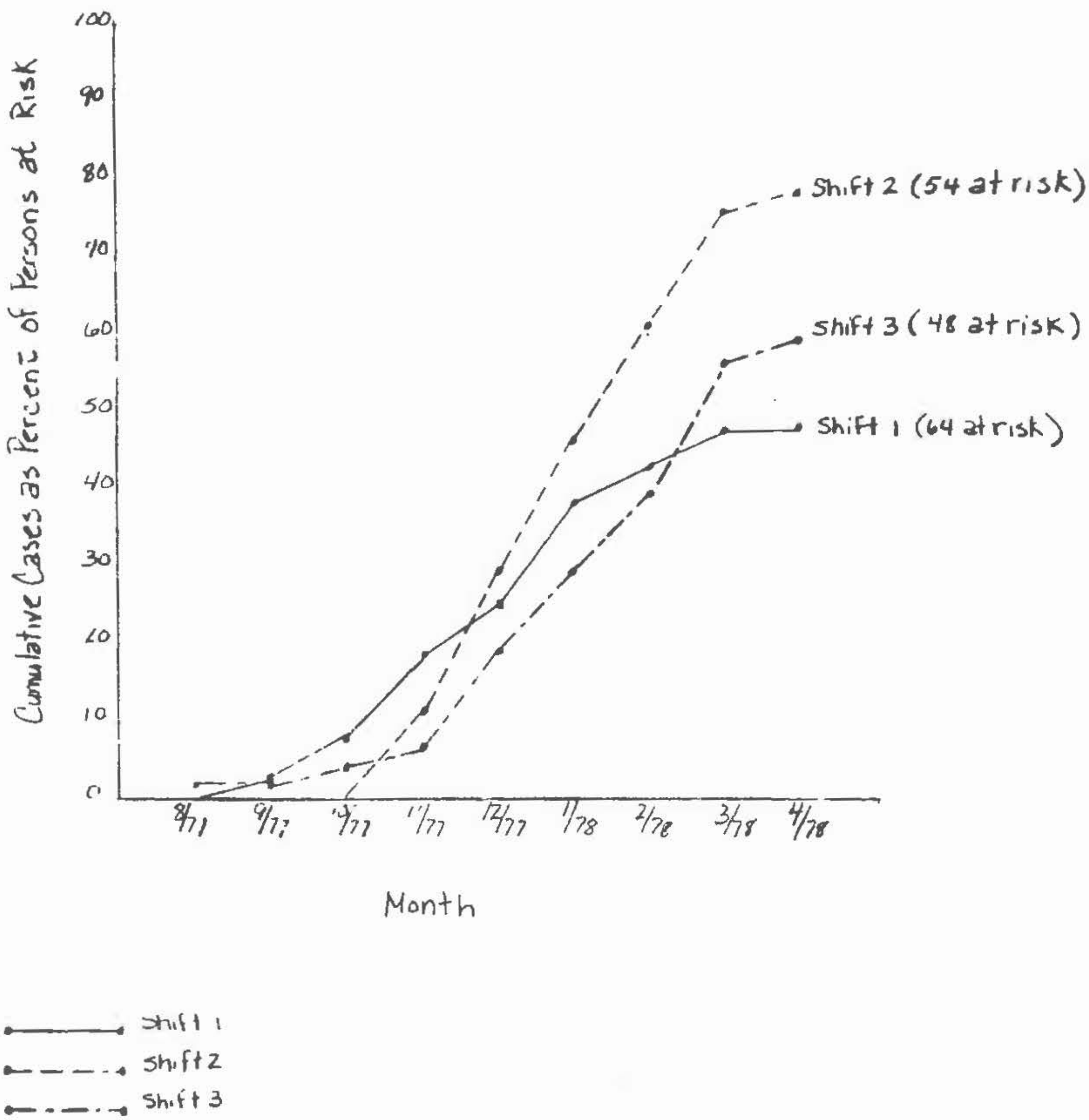
Figure 4

Cumulative Cases of Bladder Syndrome as Percent for Population at Risk

Lear Siegler, Inc.
Marblehead, Massachusetts
April 1978

HE 78-68



APPENDIX A

Employee Demography Data

Lear Siegler, Inc.

HE 78-68

	HOURLY WORKERS									SALARIED WORKERS				
	PRODUCTION [1]		FINISH [2]		MAINTENANCE [3]		WAREHOUSE [4]		TOTAL	SUPERVISORS		OFFICE		TOTAL
SHIFT	M	F	M	F	M	F	M	F		M	F	M	F	
1	33	4	10	17	18	0	10	0	92	5	0	9	8	22
2	33	2	11	8	3	0	0	0	57	2	1	0	0	3
3	32	1	11	8	2	0	0	0	54	3	0	0	0	3
									203					28

Grand Total 231

Area	Job Classification
1. Production	Compound, Operators, Utility, Coverman, Moldcleaners, Springer, Netters, Foam Puller, Pad Puller, Baler Janitor
2. Finishing	Inspect, Patch, Repair, Trim, Bag, Shippers, Wire salvager, Etc.
3. Maintenance	Electricians, Mechanics, Layup, Etc.
4. Warehouse	Loaders, Unloaders, Truck Drivers, Etc.

APPENDIX B

Compounds Identified by Gas Chromotography/Mass Spectrometry

Lear Siegler, Inc.
Marblehead, Massachusetts
HE 78-68

Field No.	Compounds Identified
Bulk DMAPN	(Run to obtain mass spectrum for comparison)
Bulk A99	" " " " " " "
Bulk Isophoronediamine	" " " " " " "
CT-1A(Front)	Aliphatic hydrocarbons (C_9 - C_{11}), chloroform
CT-1A(Back)	1,1,1 trichloroethane, trichloroethylene, aliphatic hydrocarbons (C_9 - C_{11})
CT-1B(Front)	1,1,1 trichloroethane, chloroform, trichloroethylene, aliphatic hydrocarbons (C_9 - C_{11})
CT-7A(Front)	1,1,1 trichloroethane, chloroform, trichloroethylene, aliphatic hydrocarbons (C_9 - C_{11})
CT-100	DMAPN, A-99
CT-101(Front & back)	Toluene, DMAPN (3 smaller unidentified peaks).
PP101(wet)	Isophorone diamine, DMAPN, A99, Dipropylene glycol, triethylene diamine
Wax bulk (CS_2 extract)	Aliphatic hydrocarbons (C_9 - C_{11}) Aromatics (small amounts of molecular weights 120, 134)
Resin bulk (CS_2 extract)	Styrene, phthallic anhydride, N,N diethyl aniline (trace), phthalates, substituted phthallic anhydrides (small amounts)
Hardener bulk (CS_2 extract)	MEK, Methyl ethyl ketone peroxide, dimethyl phthalate, 2 small unknowns.
Mold release bulk (CS_2 extract)	Isopropanol

Appendix C

DESORPTION EFFICIENCY STUDIES

Lear Siegler Inc.
Marblehead, Massachusetts
HE 78-68

Charcoal Tubes - Carbon Disulfide

Compound	No. of Samples	mg Spiked on Tube	Average Desorption(%)	Range(%)
DMAPN[1]	4	2.6	94	92-97
DMAPN[1]	4	0.03	58	57-59
A-99*[2]	4	2.7	58	53-64
A-99[2]	4	0.03	Not Detected	

*Peak tails on GC column used for sample analyses.

Porous Aromatic Polymer - Aq.$CuCl_2$ - Acetone

Compound	No. of Samples	mg Spiked on Tube	Average Desorption(%)	Range(%)
DMAPN[1]	3	0.02	92	90-94
DMAPN[1]	4	0.04	96	92-98
A-99**[2]	4	0.02	81	70-92
A-99[2]	4	0.05	93	91-96

**Low amount close to detection limit of method (10-20 μg)

1. Dimethyl-amino propionitrile
2. Bis(2-(Dimethylamino)ethyl)ether