

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 NO. 76-46-375

L. L. BEAN, INC.
FREEPORT, MAINE

MARCH 1977

I. TOXICITY DETERMINATION

Exposure to airborne concentrations of benzene, a contaminant in a sole cleaner, in the Making Room are in excess of the recommended environmental criteria. Due to the potential of long term benzene exposure to cause leukemia, recommendations are made in this report to ventilate the operation, and also switch to a solvent which does not contain benzene.

Charcoal tube analysis and detector tube results give different indications of the potential health hazard posed by airborne concentrations of toluene, hexane, and ethyl acetate in the cementing sole operation in the Making Room. Concentrations though, in both cases, are sufficiently close to the environmental criteria that it is judged that modifications should be made in the existing ventilation system.

Because of the toxicity of the thermal decomposition products of nylon and polypropylene and the complaints of mucous membrane irritation by some employees, it is appropriate to ventilate the plastic cord cutting operation.

Exposures of employees to leather, wood, and synthetic rubber dust, chromium residue in leather dust, ammonia, toluene, petroleum naphtha, acetone, isopropyl alcohol, butyl acetate, isobutyl acetate, xylene, and 2-ethoxyethanol (cellosolve) in the other areas of the Manufacturing Building are not believed to pose a health hazard under the conditions observed by the NIOSH industrial hygienist during the visit of November 4 and 5, 1976.

These determinations are based upon measurements of workplace concentrations of airborne contaminants, physical inspection and survey of process operations and control measures, private interviews with exposed employees, and a review of the current knowledge of the toxic effects of the chemicals evaluated.

I. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information 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) L. L. Bean, Inc., Freeport, Maine
- b) U.S. Department of Labor - Region I
- c) NIOSH - Region I

For the purpose of informing the approximately 28 "affected employees" the employer shall promptly "post" for a period of 30 calendar days the 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 the employer, L. L. Bean, Inc., regarding employee exposure to vapors from adhesives and solvents used in the manufacture and repair of boots, shoes, and other leather specialty items. Also stated in the request was that an employee had reported nasal irritation from the dust raised in the cutting of chrome-tanned leather.

IV. HEALTH HAZARD EVALUATION

A. Evaluation Chronology

On May 13, 1976 an initial walk-through survey was conducted by the Regional Program Consultant for NIOSH in Region I. The major, potentially hazardous work areas were identified and most of the chemical products in use in the plant were ascertained. From contacting the manufacturers of the products in question, their composition was determined and the hazardous components were identified through a literature review. On November 3-5, 1976, a NIOSH industrial hygienist conducted an environmental and medical survey of the plant.

B. Description of Process

The production facilities of L. L. Bean, Inc. are primarily engaged in the manufacture of tanned leather consumer items, such as boots, shoes, slippers, luggage, etc., which are subsequently distributed through their retail outlet and mail order business. To a smaller extent, canvas and nylon textiles are also assembled into a finished product.

The entire operation takes place in the Manufacturing Building. Except for the Boot Department, production is conducted in virtually one room. The dimensions of the production area are 104 feet by 250 feet, including the Boot Department which is separated from the main room by a wall on the west side of the building. Access between them is by a main aisle through the wall. The other departments are interspersed throughout the main room separated only by aisles. The references to rooms, e.g., Making Room, in this report are only designations given to different areas by the employer and do not represent actual rooms. The original building was built in the early fifties, but L. L. Bean, Inc. has been in residence only six years. Maintenance, illumination, and housekeeping all appear to be good.

At the time of the survey there were approximately 130 people involved directly in production, divided nearly equally between the sexes. Business is improving and many employees were regularly working overtime and Saturdays. There is only one shift of 8 1/2-hours duration including a one-half hour lunch, a 20-minute morning break, and a 10-minute afternoon break. There is no union or organized employee group.

The manufacturing operation begins with the reception of textile and tanned leather sheets from a supplier. They are then cut into patterns and assembled into the finished product in a multi-step fashion by the use of adhesives or stitching or both. The products are then packaged and stored in a warehouse.

The operations judged to be of potential concern are described below:

1. Cutting Room

In this department there are ten leather cutting presses called clicking machines. Only eight of them were in use at the time of the survey. Oil or chrome-tanned leather sheets are cut into predetermined patterns and then sent on to other departments. The operation involves placement of the leather sheet on a block. A die is then placed on top of the leather and the press is activated, which cuts the appropriate pattern out of the leather.

When cutting plain leather the operation does not appear to be excessively dusty and good housekeeping practices are evident, but one operator out of the eight is assigned almost daily to a particularly dusty operation which was the source of the complaint concerning nasal irritation. This was the cutting of the inner and outer soles for the camp boot. The inner sole of the camp boot is cut from sheepskin which has the wool still

attached to the leather. This is the only operation which involves the cutting of sheepskin and a significant quantity of wool dust is raised and accumulates during the cutting. The operator will spend approximately 5.5 hours per day cutting the inner soles.

In the other two hours he cuts the outer sole of the camp boot. The outer sole is the heaviest leather, approximately 0.3 inches thick, cut in the plant. It is chrome-tanned and is a source of concern because a greater quantity of leather dust is raised during its cutting.

2. Leather Skiving Machines

Four machines that skive (shave) leather into sheets of lesser thickness were observed to be in use in various areas of the Manufacturing Building. There were three types of machines, each applicable to a different type of skiving operation. The skiving machines in general worked by feeding the leather sheet into a rotating blade element, which would shave a layer off of the rough side of the leather. The enclosure of the rotating element was good and force of rotation directed the shaved particles downward into a trap, without the use of exhaust ventilation. In general, little dust was observed to escape in the workroom atmosphere.

3. Making Room

One operator is assigned to this work station, performing basically two tasks. There are two, back to back, locally exhausted benches at which the work is done. The major task of the two is cementing soles to hunting boots. The other is applying dye to leather pieces, and this task is done on the order of once a week.

In the cementing sole task, the employee initially cleans a quantity of soles (enough to fill a wooden rack) with Sole Cleaner #3015. This is performed on a bench off to the side that is not ventilated. Strong organic odors were detected from this operation. On busy days, another employee would be brought over to assist with this phase of the task. The operator would then move the rack next to the ventilated hood and apply all-purpose cement to the cleaned soles and press them against the underside of the boot by hand. The application of the adhesive and the attachment of the sole to the boot would be performed on the ventilated bench, but the operator then has to take the boot and place it on another wooden rack off to his side which is not ventilated. Strong organic odors were being emitted from this drying rack. After filling the drying rack with boots, he would move the rack over to an unventilated press, which firmly secures the sole to the boot. He would then begin the task from the beginning with another rack of soles.

The employee performing the cementing sole task will interrupt his routine about once a week to apply dye to leather pieces. This is done on the other ventilated bench which is exhausted by the same ventilation duct as the cementing sole bench. The application of the leather dye usually takes about four hours to complete. The employee dons gloves and using a sheepskin

applicator applies the dye to the leather by hand on the bench. He then takes the leather piece and places it on a drying rack to his side. A strong organic smell is again emitted from the rack.

4. Intersole Department

The Intersole Department requires the full-time work of only one employee. The work-station consists of a bench into which is built a cement applying machine. The machine feeds glue onto a continuously rotating roller. Leather soles are hand fed to the roller which applies latex cement, and then the soles are stacked off to the side for drying. The operator sits at the bench, with the breathing zone quite close to the source of the air contaminant.

5. Packing Room

One operation in the Packing Room involves the application of latex cement to heel pads. The cement applying machine is not equipped with an automatically rotating roller, but rather the roller sits in a reservoir of cement and the adhesive is applied to the heel pad when the operator rotates it manually. The cement reservoir was well enclosed with only the wetted roller exposed to the atmosphere.

6. Bench Work

Bench work involves a variety of tasks and employs three to four employees each day. Three of the tasks involve exposure to adhesive vapors. The adhesives, latex cement and rubber cement are each used daily for only a 45-minute period. Another adhesive, BeBeTex[®] is used only once every two or three weeks and was not evaluated in this survey.

The rubber cement is hand applied with a brush to grooved soles. Then they are hand pressed together with the stitch-down soles and the pieces are set off to a rack on the side to dry.

The latex cement is applied similarly with a brush to counters and counter pockets and then set off to a rack on the side to dry.

7. Boot Department

In the Boot Department there are two cement applying machines and two to three boot-laying work stations. The cement applying machines apply rubber cement to the uppers of the hunting boot via a rotating element on the machine. The operator holds the boot upper while the machine applies the cement. Occasionally some cement is applied by hand with a brush. Only one cement applying machine was in use at the time of the survey. Strong organic odors were noticed in this area. Sole Cleaner #3015 was used to clean the leather before cementing. Both the cement application and boot-laying operations are full-time procedures. The boot-laying operation takes place on the same bench where the cement applying machine is located. This operation consists of the employee hand pressing

the boot upper to the boot lower and setting them aside on a rack for drying. Personnel would occasionally interchange between working the cement applying machine and boot-laying.

8. Rebuilt Department

The Rebuilt Department consists of two work stations where the boot uppers from old, worn boots are repaired for the customer. In the process of rebuilding the boot upper, a leather softener is sprayed onto the boot from a spray bottle. This may be done one to four times per boot. The spray mist remains in the worker's breathing zone. Also occasional leather patches are applied to the boot using latex cement.

9. Finishing Line

During normal production the Finishing Line will employ one operator approximately four hours per day. At increased production other employees may be called to assist. Occasionally during the day, employees from other departments may use the edge trimmer or buffing machines for short periods.

The Finishing Line consists of five machines: the rough rounder, two heel scours, an edge trimmer, and buffing wheels. All the machines except for the rough rounder are locally exhausted.

The Finishing Line process starts at the rough rounder, where the operator will usually run through the machine two racks of rough boots. The rough rounder machine cuts the excess sole off of the boot while the operator hand holds the boot. Some synthetic rubber dust is generated. The racks of boots are then moved over to the locally exhausted machines. These machines are all connected to the same ventilation system and the exhaust is regulated to an individual machine by an adjustable blast gate. The operator will run the racks of boots through the operations of scouring, trimming, honing, and buffing in that order. When using a particular machine, the operator will open its blast gate and close the gates of the other machines to maximize the exhaust for the operation he is conducting.

10. Goodyear[®] Stitching

The Goodyear[®] Stitching operation involved the use of a methanol containing thread lubricant. Various parts of a boot are stitched together on a heavy duty machine and the speed of the stitching necessitates the use of a thread lubricant.

In other stitching and vamping operations different types of thread lubricants are in use.

11. Heat Cutting Nylon and Polypropylene Cord

In this operation an employee uses a soldering iron to heat cut sections of polypropylene and nylon cord. An acrid smoke, which was the source of many complaints from employees in the vicinity, results from the cutting.

Polypropylene cord is presently cut each day for approximately one hour/day. Nylon cord is cut only once a week for a one-hour time period.

C. Evaluation Design and Methodology

1. Environmental Samples

a) Cutting Room

A previous extensive survey of 22 shoe factories¹ gave evidence that leather dust levels, generated by cutting machines similar to the ones observed here, were never excessive and did not exceed 10 million particles per cubic foot of air. This concentration is low and compares favorably to the American Conference of Governmental Industrial Hygienists (ACGIH) environmental standard of 30 million particles per cubic foot for nuisance particulates.¹³ It was not expected that high dust levels would be generated by the cutting machines in use at L. L. Bean, Inc., and both the Regional Program Consultant² and the NIOSH industrial hygienist agreed that the leather cutting operation was not excessively dusty. The complaint of nasal irritation due to leather dust did not seem to have a basis in view of the observable low dust levels. Therefore reasons for the irritation were sought in other factors. Sheepskin is cut in the operation that gave rise to the complaint and this leads one to believe that perhaps wool dust is the cause of the irritation.

An alternative explanation could be that much of the leather being cut is chrome-tanned, and chrome salts are irritants. Residual chromium in the leather dust could be the source of the irritation. It was decided to do the bulk of the sampling for total chromium content in the leather dust. The other strategy which appeared fruitless, would be to measure the total leather dust generated by the cutting operations. (As discussed above, the resulting concentrations of total leather dust were expected to be very low and it would not be worthy pursuing this strategy.) It also was decided, though, that the one employee who does the sheepskin and heavy leather cutting would be surveyed in both manners: for total chromium and for total particulates.

Three personal air samples were obtained on leather cutters on Millipore Type AA filters to be analyzed for total chromium content in the leather dust. The leather cutters would cut both oil and chrome-tanned leather as production demanded. Sampling was done for approximately an 8-hour time period to obtain a time-weighted average exposure to chrome in the dust. The flow rate of the pumps was set at 1.7 liters per minute (lpm) and the filter was enclosed in a 3-piece closed-face cassette. Chromium analysis is accomplished in the laboratory by using nitric acid to digest the filter and leather materials. The analyte solution is then aspirated into an atomic absorption spectrophotometer for determination of chromium content.³

The leather cutting operation which was the cause of the nasal irritation was sampled for total airborne dust on a pre-weighed Gelman VM-1 filter. This employee also was monitored for total chromium as discussed above.

This operation involved the cutting of leather and sheepskin and was the only process which evolved relatively large quantities of dust. Personal sampling was done for an 8-hour period with a pump flow rate of 2 lpm. The filter was encased in a 3-piece closed-face cassette. Analysis for total dust was by gravimetric determination.

b) Leather Skiving Machines

As noted in Section IV, B, (2), these machines effectively trapped most of the dust generated, so the decision was made only to survey for the total chromium present in the leather dust exposure. Two personal air samples were obtained on Millipore Type AA filters to be analyzed for total chromium. The Fortuna Leather Splitter machine operator, which handled heavy grades of leather and the smaller Leather Skiver #46, were selected to be surveyed. The sample on the Fortuna Leather Splitter operator was taken for approximately 8 hours at a pump flow rate of 1.2 lpm. The sample on the Leather Skiver #46 operator was taken for approximately 2.5 hours at a pump flow rate of 2 lpm. The latter operator was exposed to both chrome-tanned leather and wool dust, while the former exposure was to chrome-tanned leather dust only.

c) Making Room

Four personal air samples collected on activated charcoal tubes were made to determine employee exposure to organic vapors given off by Sole Cleaner #3015, all-purpose cement, and a leather dye. From information supplied by the manufacturers of the products, the volatile components judged to be most hazardous were analyzed for in the laboratory by gas chromatograph to determine the airborne exposure concentrations. The vapor concentrations that were measured are toluene, hexane, ethyl acetate, acetone, butyl acetate, isobutyl acetate, 2-ethoxy-ethanol (cellosolve), isopropyl alcohol, and xylene. Concentrations of benzene also were analyzed because it is a possible contaminant of solvent mixtures of this nature. Bulk samples of the solvents and adhesives in question were obtained to aid the laboratory in the analysis of the charcoal tubes. All samples were obtained at a flow rate of 50 cc/minute.

One personal sample was obtained on an employee just cleaning soles. Thus an evaluation of this task alone, involving the use of Sole Cleaner #3015 and performed at an unventilated bench, was possible without the exposure being masked by the exposures to other substances during other parts of the operation. The sample was for a 1.5 hour period.

Another personal sample was obtained during the cementing sole task, involving exposure only to all-purpose cement. This task was done at the ventilated bench, and it will be possible to evaluate this phase of the operation. The sample was obtained over a 2 hour period.

A personal sample was obtained on the entire operation as normally performed from cleaning the soles to applying the adhesive. Thus the integrated operation could be evaluated as a whole. This sample was taken over a 3.5 hour period.

A final personal sample was obtained during the application of dye to the leather pieces. Inadvertently the employee also performed the sole cleaning and cement applying tasks while wearing the same charcoal tube. Thus exposures to all these materials were evaluated. This sample was obtained over a 3 hour period.

Drager detector tubes also were used to obtain an immediate, albeit not as accurate, assessment of this employee's exposure to acetone, ethyl acetate, and toluene. The samples were all taken in proximity of the employee's breathing zone as the operation was performed. Detector tube samples represent spot measurements and do not give an evaluation of time-weighted exposures as do charcoal tube samples.

Sampling with the acetone sensitive detector tube was done while the employee was using Sole Cleaner #3015. Ethyl acetate and toluene sensitive detector tubes were used while the employee was applying all-purpose cement to the soles. The toluene sensitive detector tubes are NIOSH certified for an accuracy of ± 35 at one-half the exposure limit and ± 25 percent at one to five times the exposure limit.

d) Intersole Department

From information supplied by the manufacturer of the latex cement, the most hazardous components are judged to be petroleum naphtha, ammonia, and toluene. Benzene was thought to be a likely contaminant of the adhesive mixture. A bulk sample of the cement was acquired to assist the laboratory in the determination.

Exposure to petroleum naphtha, toluene, and benzene was measured by drawing air through an activated charcoal tube at a flow rate of 50 cc/minute for three hours. The personal sample was analyzed in the laboratory by the gas chromatographic method.

Two personal samples for ammonia were obtained by drawing air through an impinger containing absorbant solution.³ A 1-hour sample was obtained at a flow rate of 1.7 lpm and a 1.5-hour sample was obtained at a flow rate of 1.2 lpm.

Drager detector tubes were also used for an immediate assessment of exposure to toluene, benzene, and ammonia. All three tubes are NIOSH certified.

e) Packing Room

Exposure to latex cement was evaluated by obtaining one personal sample for ammonia with an impinger and one personal sample for naphtha, toluene, and benzene with an activated charcoal tube. NIOSH certified (Drager) detector tubes were used for an immediate evaluation of exposure to ammonia and toluene.

f) Bench Work

Exposure to latex cement was measured by a personal sample for ammonia with an impinger. Exposure to toluene, naphtha, and benzene was not evaluated, but was thought to be low, based upon the results of detector tube measurements for toluene and ammonia at the operation.

From information supplied by the manufacturer, petroleum naphtha and isopropyl alcohol were judged to be the components in the rubber cement most likely to present a problem. A personal sample for isopropyl alcohol and naphtha was acquired by drawing air through an activated charcoal tube and later analyzed in the laboratory by gas chromatography. A bulk sample of the cement was obtained to aid the laboratory in analysis.

g) Boot Department

Two personal samples were obtained on the employees who operated the cement application machine. This involved exposure to the rubber cement and Sole Cleaner #3015. One personal sample was acquired from a boot-layer, involving essentially exposure to vapors from the rubber cement. The samples were collected on an activated charcoal tube and later analyzed in the laboratory for naphtha, isopropyl alcohol, and acetone.

h) Rebuilt Department

From the manufacturer, a listing of the components of the leather softener was obtained and isopropyl alcohol was considered to be the only component of industrial hygiene importance. One personal sample was obtained and the activated charcoal tube was analyzed for exposure to isopropyl alcohol, petroleum naphtha, and toluene. The latter two being suspect because of the occasional use of latex cement.

i) Finishing Line

Synthetic rubber dust from the cutting, scouring, honing, and buffing operations is the only expected exposure on the Finishing Line. A personal sample was obtained by drawing air at a rate of 1.6 lpm through a pre-weighed Gelman VM-1 filter and then a determination of the total particulate collected by gravimetric measurement in the laboratory. The sample was collected for 8 hours to determine a time-weighted average exposure.

j) Goodyear® Stitching

The methanol contained in the thread lubricant was the only expected source of airborne exposure for this operation. Drager detector tubes for alcohol were used to evaluate the exposure.

k) Heat Cutting Nylon and Polypropylene Cord

The NIOSH industrial hygienist was not prepared to sample for the pyrolysis products of nylon and polypropylene as it was not mentioned in the request or in subsequent telephone calls. Since this procedure occurred at the most for an hour per day, the recommendations noted in Section F(3) of this report should be adequate to solve the problem.

2. Ventilation

A Sierra Air Velocity Meter was used to evaluate the local exhaust systems in use. On the Finishing Line the capture velocity of the hoods on the buffing wheels, edge trimmer, and two heel scourers were measured when the

blast gates to other machines were closed. This situation represents the usual conditions of work, where the operator will close the blast gates to the other machines while using one of them.

The exhaust system for the Making Room consisted of two hoods, back to back, connected to the same 14.5 inch exhaust duct. Each hood has one exhaust slot, drawing air from the surface of the partially enclosed work bench. The effective dimensions of the exhaust slot is 7 by 36 inches. Each slot could be closed increasing ventilation to the opposite bench. When the operator was using one bench he would close the slot of the other, thus creating a greater exhaust. A smoke tube was used to study the exhaust pattern of the hood, and the capture velocities of the hoods also were measured.

3. Medical Survey

During the survey it was determined that 28 employees had possible exposures to dusts and vapors. A cross section of the employees in the heaviest areas of exposure (19 people) were administered a non-directed medical questionnaire by the industrial hygienist. The plant's OSHA Form 102 for the past two years were reviewed.

D. Evaluation Criteria

1. Toxicological Considerations

a) Leather Dust

The toxicological characteristics of leather dust are presently ill-defined and it is usually considered a nuisance particulate in terms of its control and regulation.^{1,4} Nuisance particulates are controlled to prevent mechanical irritation of the respiratory tract and eyes. They do not cause noticeable scarring of lung tissue or other pathological changes as a result of inhalation. Leather dust has been observed to be mildly irritant to the skin and mucous membranes.¹ Occasionally, workers may become sensitized to leather proteins or perhaps to residual chromate from the tanning process,⁵ and develop allergic reactions such as hives, sinus congestion, or asthma.

Two epidemiologic studies on leather workers in England^{6,7} suggest that leather dust or some component of it may be more serious than a nuisance particulate. The studies demonstrated a high incidence of nasal cancer among leather workers, particularly those involved in the more dusty operations of cutting, trimming, or scouring the leather. The individuals in the study who were diagnosed as having nasal cancer had been employed for a long time and had worked in the factories back when conditions had been extremely dusty and housekeeping was poor. It is not known whether the etiologic (cancer-causing) agent is still present in the generally improved work environment. The authors speculated that the etiologic agent could be the leather itself, or some added factor such as residual chromate in the leather from the tanning process or molds and fungi growing on the leathers.

Chromium compounds are strongly irritant to the mucosal membranes⁸ and the chromium residing in the leather after tanning can be hypothesized to be a cause of leather dust irritation and possibly the cancer found in the English studies. Chromium compounds usually exist in two valence states, chromium (VI) or chromium (III). Chromium (VI) compounds are by far the more serious from toxicological considerations. Some have been indicted as being carcinogenic to the lung and all of them being strong irritants and skin sensitizers.^{5,8} Chromium (III) compounds have not been shown to be carcinogenic, but are irritants. The question of their being skin sensitizers is in doubt at the moment.⁸ Chromium (VI) compounds are used in the tanning process, but theoretically during tanning they are transformed to chromium (III) in chemical combination with the leather proteins.⁵ It has been suggested that a small amount of chromium (VI) may remain untransformed in the leather and be a source of trouble, but most of the chromium residue is expected to be in the trivalent (III) form.

In view of the English epidemiological studies and the toxicology of chromium, it is concluded that no standard can yet be set for airborne concentrations of leather dust, and that the nuisance dust standard may not apply. Airborne levels of leather dust should be kept as low as possible.

b) Wool Dust

A literature search of occupational experiences with wool dust turned up little. Sheep's wool is a mild primary irritant and on occasion has caused sensitization with skin dermatitis or respiratory tract congestion as a result.⁹ Chromium (VI) compounds are also sometimes used as a fixative for wool attached to sheep's skin, but again most of the chromium should be transformed into the less toxic trivalent form.⁵

c) Synthetic Rubber Dust

Synthetic rubbers are polymers that are in general relatively biologically inert.¹⁰ As such the dusts resulting from their grinding should be regulated as nuisance particulates, until evidence is presented to the contrary.

d) Ammonia

Ammonia is primarily a strong irritant gas. Moderate concentrations of the gas will be absorbed strongly by the first moist membranes contacted, and in humans this will result in irritation and burning to the eyes, nose, and throat.¹¹ Higher concentrations will penetrate more deeply into the human respiratory system and irritation and inflammatory changes to the lungs can result. Irreversible damage to eye sight and chronic lung disease may be the expression of very high exposure to ammonia gas.

e) Benzene

Benzene is no longer used as a primary solvent as was once common in the shoe industry¹, but it still may be present as a contaminant in solvent and adhesive mixtures. As a volatile, it vaporizes and poses a health hazard risk to the workers using the solvent contaminated with benzene. In a review of the research on benzene hazards, NIOSH¹² has determined that benzene's most hazardous effect is on the blood-forming systems of man. Blood abnormalities, such as aplastic anemia, occur in worker populations exposed. In those workers afflicted with chronic benzene poisoning

headaches and extreme fatigue were prominent signs. From several epidemiologic studies, it has been shown that exposed workers also are subject to an increased risk of cancer, specifically acute and chronic leukemia. These can result from low-level, long term exposure to benzene. NIOSH now recommends that benzene be controlled as a carcinogen, and concentrations in the air be kept as low as possible.

f) Hexane

Hexane is an aliphatic hydrocarbon in common use as a solvent, either alone or in mixtures. Originally, environmental control of hexane was designed to prevent its irritant and narcotic effects on exposed workers.¹³ Hexane vapors would irritate the eyes and respiratory tract. The narcotic effects would be a depression of the central nervous system resulting in headaches, dizziness, and giddiness at relatively low concentrations and progressing to convulsions and death at very high concentrations.

Recent clinical studies in Japan and the United States have presented evidence that exposure to hexane may cause peripheral neuropathy in some exposed workers.¹⁴ The neuropathy takes the form of a distal motor and sensory disorder, characterized primarily by weakness and sensory changes in distal portions of the extremities. This evidence has forced re-evaluation of the toxicity of hexane and it is thought that airborne levels should be kept as low as is practical, until the situation is clarified.

As an organic solvent, hexane has the ability to dehydrate and defat the skin upon contact. Repeated and/or prolonged contact with liquid hexane solvents can cause irritation and redness of the affected skin, which can progress to dermatitis. Precautions should be taken to avoid skin contact.

g) Irritant Hydrocarbon Solvents: Petroleum Naphtha, Isopropyl Alcohol, Acetone, Ethyl Acetate, Butyl Acetate, Isobutyl Acetate, and 2-Ethoxy-ethanol (cellosolve)

These hydrocarbon solvents all share the characteristic of having the environmental standards relating to them designed to control the irritation to the mucous membranes of the eyes, nose, and throat.^{13,15,16} Mucous membrane irritation is the predominant feature of relatively low-level exposure to these solvents. As the airborne concentrations increase, the narcotic effects on people become more pronounced. Headaches, fatigue, giddiness, dizziness, and loss of muscular coordination are some of the more noticeably narcotic influences. High concentrations can cause coma and death. The toxicity and irritancy of the different solvents vary according to their biologic activity and thus the environmental standards reflect the differences between them.

These organic solvents share the property of being able to dehydrate and defat the skin upon liquid contact. Thus as noted before, repeated and/or prolonged contact with the skin can cause irritation and redness, which

can progress to a severe dermatitis. Isopropyl alcohol is the least likely to cause skin irritation among all the solvents listed, but significant quantities of the alcohol can be absorbed directly through the skin into the blood¹⁶, so even in this case precautions should be taken to minimize skin contact.

The toxicity of petroleum naphtha, or petroleum distillates in general, varies according to the percentages of high boiling hydrocarbons and aromatic hydrocarbons present in the mixture. These hydrocarbons both increase the toxicity of the "naphtha" mixture. The percentages vary between the manufacturers of "naphtha" and there is no standardization. There were four brands of petroleum naphtha involved in this survey and they are all different in their composition. Some situations surveyed in this study involved exposures to two different brands of naphtha simultaneously. The analytical laboratory was not able to provide a break-down of composition of the naphthas involved, because of the complexities of the solvent mixtures and exposures. The laboratory was only able to report total peaks from the gas chromatograph and measure them as total naphtha. Thus a determination of true toxicity of the naphtha mixture is not possible, because the composition and relative percentages are not known. To evaluate the petroleum naphthas in this study, it was decided to apply the Occupational Safety and Health Administration (OSHA) standard for petroleum distillates to the different exposures that were measured. The OSHA standard of 2000 milligrams of contaminant/cubic meter of air (2000 mg/M³), can be found in the Code of Federal Regulations, (29 CFR 1910.1000) Table Z-1.¹⁷ This standard is applicable to a wide range of petroleum distillates, and the safety margin is sufficient to protect against any serious hazards to the worker. The standard is an 8-hour, time-weighted average (TWA), which allows excursions above and below, as long as the average exposure for the entire work-day does not exceed it.

h) Aromatic Hydrocarbon Solvents: Toluene and Xylene

These two aromatic hydrocarbon solvents have in general more pronounced narcotic effects than the aliphatic hydrocarbons.^{18,19} This depression of the central nervous system can cause dizziness, fatigue, loss of coordination, headaches, mental confusion, nausea, and a loss of appetite. These hazardous symptoms become manifest at the same or only slightly higher concentrations than the irritant symptoms appear. The aromatic solvents have the ability to cause irritation in the mucous membranes of the eye, nose, and throat at concentrations just greater than 200 ppm.

Absorption of these solvents through the skin and into the blood is a cause for concern and skin contact should be minimized.

i) Thermal Decomposition Products of Nylon and Polypropylene

Both nylon and polypropylene plastics are reported to give off toxic decomposition products upon heating under laboratory conditions.^{20,21} The exact constituents of the decomposition products and their properties vary upon two major factors: the availability of oxygen to the plastic upon vaporization and the temperature of the process.

For polypropylene it has been reported in the literature that a series of low boiling point alkane and alkene hydrocarbons^{20,21} plus acrolein and phenol,²¹ are all possible thermal decomposition products under laboratory conditions. These hydrocarbons have all the irritant and narcotic properties that were discussed earlier. In the laboratory it has been reported^{20,21} that nylon may thermally degrade releasing carbon monoxide, ammonia, hydrogen cyanide, nitric oxide, and nitrogen containing hydrocarbons. These gases and vapors are also irritating, narcotic,²¹ and/or toxic to various body organs. In an actual industrial situation though,²¹ most of these gases have not been found in any significant quantities and no health effects have been reported. The process at L. L. Bean though differs significantly from this other NIOSH study in that the temperature and process holding time vary considerably between them. It would not be safe to extrapolate the results from this study to the operation at L. L. Bean.

Since no air measurements were obtained at the heat cutting of the plastic cord operation, it is not known which gases and vapors were actually released into the environment at L. L. Bean. Therefore, an accurate assessment of the problem is not possible. Considering the small size of the operation, it is only expected that small quantities of irritating contaminants would be released. This is substantiated by the complaints of surrounding employees. Extended exposure to irritating contaminants can aggravate and sometimes initiate sinus and respiratory conditions.

2. Relevant Environmental Standards

Airborne exposure limits intended to protect the health of workers have been recommended or promulgated by several sources. The concentrations listed are established at levels to which a worker may be occupationally exposed over an 8-hour day, 40-hours per week, for a normal working lifetime and suffer no impairment in health. These limits represent the average exposure concentration for the work day (8-hour TWA) unless otherwise noted.

For this investigation, the criteria used were selected from three sources:

- a) NIOSH Recommended Standards - airborne exposure limits which NIOSH has recommended to OSHA for occupational health standards.
- b) ACGIH Threshold Limit Values (TLV's) - guidelines for airborne exposures recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for 1976.
- c) OSHA Standards - the air contaminant standards enforced by the U.S. Department of Labor as found in the Code of Federal Regulations, (29 CFR 1910.1000), July 1, 1975. These standards are the only legal ones, but are not as inclusive or up to date as those recommended by NIOSH or the ACGIH, and are not cited where the other sources provide better criteria.

<u>Source</u>	<u>Substance</u>	<u>Standard (8-hour TWA, unless otherwise noted)</u>
-	Leather and Wool Dusts	No standard set at present. Airborne levels should be kept as low as possible.
OSHA	Total Chromium	0.5 mg/M ³ (a)
ACGIH	Synthetic Rubber Dust as a Nuisance Particulate	10 mg/M ³
ACGIH	Hexane	100 ppm(b)
NIOSH	Ammonia	50 ppm*
NIOSH	Benzene	1 ppm* ₃
OSHA	Petroleum Distillates (Naphtha)	2000 mg/M ³
OSHA	Acetone	1000 ppm
ACGIH	2-Ethoxy-ethanol (Cellosolve)	100 ppm
OSHA	Isopropyl Alcohol	400 ppm
OSHA	Butyl Acetate	150 ppm
OSHA	Isobutyl Acetate	150 ppm
OSHA	Ethyl Acetate	400 ppm
NIOSH	Toluene	100 ppm
OSHA	Xylene	100 ppm

(a) mg/M³ - approximate milligrams of contaminant per cubic meter of air sampled

(b) ppm - parts of contaminant per million parts of contaminated air

* - a ceiling limit not to be exceeded except due to the limitations of the analytic measuring method

In addition to the criteria listed above, it is necessary to compute a formula in the instances where there is a mixture of air contaminants in a single exposure. The formula applies only when the air contaminants involved have the same physiological effect on the human body. The equivalent exposure of the mixture is computed as follows:

$$Em = \frac{C1}{L1} + \frac{C2}{L2} + \dots + \frac{Cn}{Ln}$$

% of Permissible Exposure for the Mixture = Em X 100

Where: Em is the equivalent exposure for the mixture
C is the concentration of a particular contaminant
L is the exposure limit for that contaminant as found in the table above.

If the value of E_m exceeds the number one, then the equivalent exposure limit for that mixture has been exceeded. This means the exposure is in violation of the law and/or health standards, even though the individual substances may not be in excess of their own limit. The percent of permissible exposure expresses E_m in convenient percentage terms, where 100% means the 8-hour TWA for the mixture of contaminants.

3. Ventilation Standards

The following criteria, taken from the ACGIH Industrial Ventilation Manual,²² was used in evaluation of the local exhaust systems:

RANGE OF CAPTURE VELOCITIES

Condition of Dispersion of Contaminant	Examples	Capture Velocity, fpm
Released with practically no velocity into quiet air.	Evaporation from tanks; degreasing, etc.	50-100
Released at low velocity into moderately still air.	Spray booths; intermittent container filling; low speed conveyor transfers; welding; plating; pickling	100-200
Active generation into zone of rapid air motion	Spray painting in shallow booths; barrel filling; conveyor loading; crushers	200-500
Released at high initial velocity into zone of very rapid air motion.	Grinding; abrasive blasting, tumbling	500-2000

In each category above, a range of capture velocity is shown. The proper choice of values depends on several factors:

<u>Lower End of Range</u>	<u>Upper End of Range</u>
1. Room air currents minimal or favorable to capture.	1. Disturbing room air currents.
2. Contaminants of low toxicity or of nuisance value only.	2. Contaminants of high toxicity.
3. Intermittent, low production.	3. High production, heavy use.
4. Large hood—large air mass in motion.	4. Small hood—local control only.

E. Results

1. Exposure to Particulates

The results of the analysis for total particulates in the Cutting Department and the Finishing Line are depicted in Table I.

The composition of the particulates in the leather cutting process was assumed to be almost entirely wool and leather dust, as that was the only material being handled in the area. The concentration of 0.54 mg/M^3 of dust in the breathing zone is low. It is only 5 percent of the nuisance particulate standard of the ACGIH, but as discussed in Section D(1) a of this report the nuisance particulate standard may not apply to this exposure. This sample was obtained at the dustiest operation in the leather cutting group. It was where the heaviest leather and the only wool/sheepskin was being cut, and the exposure here was visually observed to far exceed that

at the other cutting and skiving operations. Dust levels in the vicinity of the leather cutting and skiving machines have been reported by others to be low. These investigators were using the nuisance particulate standard of the ACGIH and their sample concentrations were in a range from 3 percent to 30 percent of it. Since they reported no ill effects from this range of concentrations and the English epidemiological studies^{6,7} were performed on workers exposed to dust levels grossly higher than those found in the modern industry (although no air concentrations were obtained) it cannot be concluded at this time that the air concentration measured at this work station is excessive. As with any suspect carcinogen, air concentrations should be kept as low as possible.

Since the Finishing Line Operator cuts, scours, grinds, and buffs synthetic rubber soles, it is assumed that the major particulate on his sample would be synthetic rubber. It was found that the breathing zone concentration of dust was quite low, 3 percent of the standard.

The results of the analysis for total chromium exposure from the leather dust aerosols are shown in Table II. The total chromium exposure to the employees from the dusts generated during the leather cutting and skiving operations range from 0.0007 to 0.003 mg/M³, well below the criteria of 0.5 mg/M³. It can reasonably be concluded that the chromium exposure from the leather dust is within safe levels. If we assume that some chromium VI residue may be a portion of the total chromium exposure, it is only expected to be a small fraction thereof. This fraction would be unlikely to exceed the chromium VI standard of .001 mg/M³.

2. Exposure to Adhesives, Solvents, and Dyes

In the Intersole Department, Rebuilt Department, Bench Work, and Packing Room the same latex cement was in use and potentially exposed employees to ammonia, toluene, benzene, and naphtha. Working in the Rebuilt Department involved simultaneous exposure to the latex cement plus a leather stretcher which reportedly contained acetone and isopropyl alcohol. The results from analysis of impinger tubes for ammonia and charcoal tubes for hydrocarbons, plus results from direct-reading detector tubes, are all reported in Table III.

The breathing zone concentrations of ammonia released from the latex cement are all very low when either measured by detector tube or the impingers. Values range from none detectable to 3 ppm. There is one disturbing element in that the lab reported that a blind blank impinger sample contained 90 times the lower limit of detection of ammonia. This was the greatest quantity of ammonia detected in any of the samples. There is a possibility that the impinger samples were accidentally mixed and what is reported as a blind blank is actually a sample. Since the determined concentration would be no more than 5 ppm (calculated by using an average sample volume), whereas the standard is 50 ppm (ceiling value), there is no danger to the employees from excess exposure to ammonia.

The reported values for breathing zone concentrations of toluene, benzene, and petroleum naphtha for those working with the latex cement are also within safe limits. No benzene was detected in any of the samples. The concentrations of toluene ranged from none detected to just 14 percent of the standard. The concentrations of petroleum naphtha were slightly higher ranging from 370 to 972 mg/M³, but this is low when compared to a standard of 2000 mg/M³. In the Rebuilt Department there was a simultaneous exposure to both the latex cement and the leather stretcher, so in addition to toluene, benzene, and naphtha, the vapors of acetone and isopropyl alcohol were also analyzed. No acetone was detected, but isopropyl alcohol was detected in a small amount, 12.2 ppm.

Since these samples represent multiple exposures to different hydrocarbon solvents, all of which have additive irritant and narcotic properties, it is necessary to calculate equivalent exposure of the mixture as a whole. The column in Table III, "% of Permissible Exposure for the Mixture", expresses this concept in convenient percentage terms. Ammonia is not added in calculating the equivalent exposure because its physiological effects are not narcotic as are those of the hydrocarbons. The low concentrations of ammonia detected would not have much effect on the reported permissible exposures anyway. The calculated permissible exposures for the mixtures range from 23 to 59 percent and are all within safe levels, well below the 100 percent limit which would mean that the 8-hour TWA for the mixture of vapors had been reached.

Laboratory analysis of the volatile emissions during the Making Room operations along with the detector tube sample results are reported in Table IV. There are primarily three operations in the Making Room which involve significant exposure to volatiles, as described in Section B(3): cleaning soles, cementing soles, and dyeing leather. Cleaning soles involves the use of Sole Cleaner #3015, cementing soles involves the use of an all-purpose cement, and the dyeing operation uses a leather dye.

The cementing sole task, which is locally exhausted, is alternated with the task of securing the sole to the boot on an automated press, so the charcoal tube records the exposure throughout both tasks. The charcoal tube analysis showed 17.9 ppm of toluene and 69.2 ppm of hexane, while no detectable ethyl acetate, acetone, or benzene was absorbed. These two exposures combine to give 87 percent of the permissible exposure for the mixture. The value of toluene was low, but the concentration of hexane was almost 70 percent of the criteria of 100 ppm. Simulated breathing zone samples with the detector tube for toluene and ethyl acetate gives concentrations of 70 ppm and 2000 ppm, respectively. These values are disturbing because the samples were obtained as close to the employee's head as possible to do without disturbing his work, but show markedly higher values for toluene (70 ppm) and ethyl acetate (2000 ppm) than the charcoal tube samples reveal. The charcoal tube analysis detected no ethyl acetate within the limits of the

analytical method. Some of the discrepancy may be explained by the fact that the worker spent part of his time while wearing the sampling pump and charcoal tube at the automated press where his exposure to volatiles would be greatly reduced. It is also possible in the case of the ethyl acetate detector tube, that other volatiles interfered and reacted with the adsorbing chemicals in the tube causing an increase in the detected value. This discrepancy between the two sampling techniques means one should evaluate the results from both with caution. A conservative evaluation would be to view the exposure recorded by the charcoal tubes as underestimating the actual exposure to the employee and to view the exposure recorded by the detector tubes as overestimating it. The overall conclusion one would draw is that the employee while cementing soles is likely to be at or even above the permissible exposure limit for the mixture of hydrocarbons.

The second row in Table IV reports the employee exposure during a typical morning while he is cleaning and cementing soles plus using the automated press. The charcoal tube analyses revealed a low concentration for toluene of 16.5 ppm, a moderately high exposure to hexane of 52.8 ppm, and a low concentration of acetone from the Sole Cleaner #3015 of 15.8 ppm. Within the limits of the detection methods, there was no ethyl acetate or benzene adsorbed. The laboratory also stated that it was not able to report a concentration for the petroleum naphtha volatilized from the Sole Cleaner #3015 because the mixture of solvents adsorbed on the charcoal was too complex to determine both the naphtha concentration and the concentrations of the other hydrocarbons requested. The value of 71 percent of permissible exposure does not reflect the naphtha concentration and significantly underestimates the hazard posed to the employee. There is also strong evidence that the acetone concentration is underestimated because the laboratory reported that the charcoal tube had become saturated with acetone and some was likely to have been lost during sampling. It is observed that during the cleaning sole operation (in the next row of Table IV), that there is a large discrepancy between the charcoal tube result and the detector tube result for acetone. The detector tube reports 1000 ppm of acetone while the charcoal tube analysis reports only 42.5 ppm. So it appears that not only is acetone adsorbing very poorly on the charcoal tube and that much is being lost, but also that the actual exposure is likely to be very high, quite close to the environmental standard. Given that the naphtha exposure is not recorded and that the acetone exposure is greatly underestimated by the charcoal tube analysis, it can be concluded that the obtained value of 71 percent of the permissible exposure for the mixture significantly underestimates the hazard posed to the employee during the combination of the two tasks. The actual percentage value is likely to be at or above the permissible exposure limit.

For the cleaning sole task alone, the breathing zone concentrations are given in the third row of Table IV. The results for toluene and hexane are similar to those reported in the other samples. No ethyl acetate was detected. There is a large discrepancy between the concentration of acetone reported by the charcoal tube analysis and that from the detector tube, as was noted earlier. The most important result noted, is that there is a concentration of benzene of 3.8 ppm, which is almost four times the NIOSH recommendation. The benzene is a contaminant in the Sole Cleaner #3015. Due to benzene's carcinogenic potential, the operating of cleaning soles should be modified on this basis alone.

A charcoal tube sample was obtained on the combined operations of cleaning, cementing, and pressing soles, plus dyeing the leather. The results of the analysis for toluene, hexane, ethyl acetate, and acetone are lower than the values reported for the other samples. The laboratory did not determine the benzene concentration. The results for the volatiles peculiar to the leather dye itself (butyl acetate, isobutyl acetate, cellosolve, isopropyl alcohol, and xylene) are all negative within the limits of the method of analysis. From the basis of this charcoal tube sample it can be tentatively stated that the leather dyeing operation is reasonably safe, as performed at the ventilated bench.

The results in Table V indicate the breathing zone concentrations of the volatiles from rubber cement and Sole Cleaner #3015 in the Boot Department and the volatiles from the rubber cement during Bench Work. The charcoal tube analysis of the sample from the Bench Work showed 61 mg/M³ of petroleum naphtha, which is well below the standard and there was no isopropyl alcohol or acetone detected. The charcoal tube analysis of the samples from the Boot Department reported a high value of 302 mg/M³ for petroleum naphtha, which is well below the standard, and a high value of >77 ppm of acetone which is also safely below the criteria. No isopropyl alcohol was detected. All the acetone concentrations saturated the charcoal tube and the values reported are minimum levels. Even though the acetone concentrations are underestimated, it is unlikely that the true levels approach the OSHA standard. Since the "percent of Permissible Exposure for the Mixtures" all range between 3 and 23 percent, it can be said that the Bench Work and Boot Department exposures do not pose a hazard to the workers.

3. Results from the Good Year Stitching Operation

The bottle containing the thread lubricant was sampled with a detector tube for methanol. A trace was discovered. Upon performing a simulated breathing zone sample on the operator, with a detector tube, no methanol was detected. Further evaluation was discontinued, and the sewing operations in general are considered not to pose a health hazard to the workers.

4. Results from the Medical Interviews

The pertinent information from the 19 questionnaires collected is summarized below. 11 out of the 19 people reported some present or post health effect from working at L. L. Bean. Most of the problems were not serious in nature. The major symptom was upper respiratory tract or eye irritation from wool dust (5 people out of 19). One person reported minor skin irritation from handling wool. There was one complaint of minor eye irritation from leather dust. Three people noticed that they got occasional headaches at work. Two of them hypothesized that the cause was due to the noise level in the plant and one said that it was due to the solvent vapors from the Making Room. There was reported a case of minor skin dryness and sinus congestion from using solvents and latex cement.

The Making Room was a source of a number of symptoms, some of them neurological. Two employees observed occasional light-headedness when working with the solvents and cements in this area. One employee reported a range of symptoms when in the past he worked there, including sinus congestion, nausea, numbness and tingling, palpitation, and loss of sensation in the nose. It was also stated by a number of employees that very few individuals in the past could

tolerate working in the Making Room because of the organic vapors. This further substantiates the idea that the organic vapor concentrations at the Making Room operations are somewhat higher than the charcoal tube analysis revealed.

It should be noted that many workers in the area immediately surrounding the bench where the nylon and polypropylene cords were heat cut, stated they felt irritation and annoyance at the decomposition products resulting.

A review of the OSHA Form 102 showed no occupational health problems in the last two years.

5. Ventilation Results

A summary of the results from the evaluation of the local exhaust ventilation systems in use at the Finishing Line and Making Room are depicted in Table VI. It is observed that on the Finishing Line the buffing wheels, the brusher, and one of the heel scourers perform somewhat lower than the recommended minimum velocity of 500 fpm. Their performance, even though it is lower than the guideline, is not a condition that needs remedying. It was observed that the rotating motion of these devices effectively directed the generated dusts into the partially enclosing exhaust hoods. The low toxicity potential of the contaminant, synthetic rubber dust, along with the fact that the environmental sampling showed that very little dust (approximately 0.32 mg/M^3) escaped into the breathing zone of the operator, demonstrates that the system is functioning adequately for this purpose.

The exhaust hoods on the Making Room benches are observed to meet the performance standards needed to capture the vapors of the toxicity of those that are generated from the surface of the work bench. With the use of smoke tubes, it was observed though that the vapors that would escape from the boots on the drying rack would hover over the rack and also stay in the vicinity of the worker's head while cementing. Only a portion of them would be captured by the ventilation system, and these would pass right through the employee's breathing zone on route to the exhaust hood. These drying rack vapors account for almost all the solvent exposure recorded by the charcoal tubes and detector tubes. Modification so the vapors from the drying rack are exhausted should be considered.

6. Conclusion

a. From the results of the environmental sampling and to the best toxicological information to date, it can be concluded that the Leather Cutting, Leather Skiving, Finishing Line, Bench Work, Leather Dyeing, and Good Year Stitching operations, plus the work performed in the Intersole Department, Rebuilt Department, Boot Department, and the Packing Room do not pose any serious health hazards to the employees involved.

b. Sole Cleaner #3015, as used in the Making Room to clean soles prior to bonding to the boots, poses a health hazard to the employee(s) involved, in the form of benzene exposure which has the potential to cause leukemia and damage the blood forming tissue of the body.

c) Analysis by charcoal tubes showed that the exposure at the cementing sole operation in the Making Room to be just below the environmental criteria for a mixture of toluene and hexane vapors. Results from detector tubes reported above standard concentrations of ethyl acetate and close to standard concentrations of toluene. These results lead one to believe that the overall permissible exposure for the mixture would be in excess of the standards. Observations of the exhaust ventilation with a smoke tube showed that vapors from the drying rack tend to remain in the vicinity of the worker's head and are only partially exhausted. The combination of contradictory environmental data and evidence of ineffective ventilation is sufficient to warrant modifications so that the drying rack emissions are exhausted, lowering the worker's exposure to the vapors.

d. Because of the toxicity of the thermal decomposition products of nylon and polypropylene and the irritation commented on by some employees, it is felt proper to make some minor modifications of the heat cutting operation to be discussed in the next section of this report.

F. Recommendations

1. Sole Cleaning in the Making Room

It is recommended that this operation be moved to the locally exhausted bench on the opposite side of the cementing sole bench. Since the leather dyeing operation which normally takes place at this bench is usually performed by the same employee who does the sole cleaning, it is not anticipated that the two operations will be vying for the same bench simultaneously. The installation of another hooded bench which would be locally exhausted to the outside is also a satisfactory solution.

It is also recommended that another sole cleaner be purchased and used instead of Sole Cleaner #3015. The manufacturer of the new sole cleaner to be purchased should be contacted ahead of time, to obtain proof that his product is not contaminated with benzene. To ensure the health of the workers, it is still recommended that the new product be used under ventilation.

2. Cementing Soles in the Making Room

The vapors from the drying rack need to be exhausted away from the employee. This can be accomplished either by installation of a locally exhausted canopy hood over the drying rack or alternatively by moving the drying rack to a position directly in front of the present exhaust hood/bench. The working surface of the bench would have to be widened to accommodate the employee and the all-purpose cement pot, which would be off to the side but still close enough to be exhausted. A baffle of plywood or other material should be added to the aisle side of the work bench, extending the entire length of the drying rack, so the vapors will be captured more effectively. A new baffle would also have to be added on the other side of the hood to replace the one removed during the widening of the work bench. The use of a smaller and more compact drying rack would reduce the amount of extension needed on the work bench, and also the exhaust ventilation would be more efficient in that less of a volume of space would have to be exhausted. These alterations should provide for effective capture of the vapors without drawing them past the breathing zone of the employee.

3. Heat Cutting Nylon and Polypropylene Cord

This operation should be locally exhausted to the outside. Movement of the operation to a bench by a window and installation of a small unit exhausting to the outside would be sufficient. Use of flammable solvents in the area of the heat cutting should be prevented.

4. Minimizing Contact with Solvents

As noted in the Toxicology Section, the solvents and adhesives used at L. L. Bean, have the ability to dehydrate the skin and cause dermatitis upon prolonged contact. Rubber, impervious gloves should be worn by personnel who have skin contact with these chemicals.

V. REFERENCES

1. McConnell, WJ, JW Fehnel, and JJ Ferry, (1942), "Potential Health Hazards of the Leather Industry." J. Ind. Hyg. and Tox., 24: 93-108.
2. Personal Communication with Paul Alvarado, NIOSH Regional Program Consultant, Region I, Memorandum of Oct. 28, 1976 in Official HESB File No. 76-46.
3. National Institute of Occupational Safety and Health, (1976) Preliminary Draft of NIOSH Manual of Sampling Data Sheets, Measurements Research Branch, Cincinnati, Ohio 45202.
4. Chrostek, WJ, and C Meyer, Health Hazard Evaluation Report No. 76-9-345, NIOSH (1976).
5. Walsh, ED, (1953), "Chromate Hazards in Industry," J.A.M.A., 153:1305-1308.
6. Acheson, ED, RH Cowdell, and B Jolles (1970), "Nasal Cancer in the Northamptonshire Boot and Shoe Industry," British Medical Journal, 1:385-393.
7. Acheson, ED, RH Cowdell, and E Rang, (1972), "Adenocarcinoma of the Nasal Cavity and Sinuses in England and Wales," J. Ind. Med., 29:21-30.
8. NIOSH, (1975), Criteria for a Recommended Standard...Occupational Exposure to Chromium (VI), HEW Publication No. (NIOSH) 76-129.
9. Unger L, and MC Harris, (1974), "Stepping Stones in Allergy," Annals of Allergy, 33:228-248.
10. Autian, J, "Toxicology of Plastics," in Toxicology, The Basic Science of Poisons, LJ Casarett and J Doull (Editors), Macmillan Publishing Co., Inc., New York, New York, 1975.
11. NIOSH, (1974), Criteria for a Recommended Standard...Occupational Exposure to Ammonia, HEW Publication No. (NIOSH) 74-136.

12. NIOSH, (1976), Update Criteria and Recommendations for a Revised Benzene Standard, Memorandum Circulated August 1976.
13. American Conference of Governmental Industrial Hygienists, (1971), Documentation of the Threshold Limit Values, 3rd Ed., ACGIH, Cincinnati, Ohio.
14. Abdel-Rahman, MS, LB Hetland, and D Couri, (1976), "Toxicity and Metabolism of Methyl N-butyl Ketone," Am. Ind. Hyg. Assoc. J., 37(2):95-102.
15. Carpenter, CP, ER Kinkead, DL Geary, LJ Sullivan, and JM King, (1975), "Petroleum Hydrocarbon Toxicity Studies. III Animal and Human Response to Vapors of Stoddard Solvent," Toxicology and Applied Pharmacology, 32:282-297.
16. NIOSH, (1976), Criteria for a Recommended Standard...Occupational Exposure to Isopropyl Alcohol, HEW Publication No. (NIOSH) 76-142.
17. Code of Federal Regulations, July 1, 1975 (29 CFR 1910.1000).
18. NIOSH, (1973), Criteria for a Recommended Standard...Occupational Exposure to Toluene, NIOSH, Cincinnati, Ohio, Publication #SSM 73-11023.
19. NIOSH, (1975), Criteria for a Recommended Standard...Occupational Exposure to Xylene, HEW Publication No. (NIOSH) 75-158.
20. Iglauar N, and FF Bentley, (1974), "Pyrolysis GLC for the Rapid Identification of Organic Polymers," Journal for Chromatographic Science, 12:23-33.
21. Price J, Health Hazard Evaluation Report, No. RHE 76-60. (Not yet published), NIOSH (1977).
22. ACGIH, (1974), Industrial Ventilation - A Manual of Recommended Practice, 13th Ed., Committee on Industrial Ventilation, P.O. Box 453, Lansing, Michigan, p. 4.5.

VI. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By:

Jack Gill
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluation and
Technical Assistance Branch
Cincinnati, Ohio

Originating Office:

Jerome P. Flesch,
Acting Chief,
Hazard Evaluation and
Technical Assistance Branch
Cincinnati, Ohio

Acknowledgments

Initial Survey:

Paul Alvarado
Regional Program Consultant
Region I, NIOSH
Boston, Massachusetts

Laboratory Analysis:

Utah Biomedical Test Laboratory
Salt Lake City, Utah

Medical Review of Questionnaires:

Channing Meyer, M.D.
Chief, Medical Section
Hazard Evaluation and Technical
Assistance Branch
Cincinnati, Ohio

TABLE I

Breathing Zone Concentrations of Total Particulates in
the Cutting Department and Finishing LineL.L. Bean, Inc.
Freeport, Maine

November 4 & 5, 1976

<u>Job Classification</u>	<u>Sample Period</u>	<u>Total Particulate* (mg/M³)^a</u>	
		<u>Leather and Wool Dust</u>	<u>Synthetic Rubber Dust</u>
Leather Cutter for the Soles of the Camp Boot	8:37 - 15:30	0.54	-
Operator of the Finishing Line	8:13 - 16:17	-	.32
Environmental Criteria		-	10

mg/M³ - Approximate milligrams of particulate per cubic meter of air sampled.

* - One blank was found to have .05 mg of particulate, five times the lower limit of detection.

TABLE II

Breathing Zone Concentrations of Total Chromium
in the Cutting Department and Leather Skiving OperationsL.L. Bean, Inc.
Freeport, Maine

November 4 & 5, 1976

<u>Job Classification</u>	<u>Sample Period</u>	<u>Total Chromium* (mg/M³)^a</u>
Leather Cutter - for the soles of the Camp Boot	8:30 - 16:55	0.003
Leather Cutter	8:58 - 16:18	0.001
Leather Cutter	8:25 - 15:06	0.001
Leather Skiver on Fortuna Leather Splitter Machine	8:36 - 16:12	0.001
Leather Skiver on United Shoe Machine # 46	14:15 - 16:40	0.0007
Environmental Criteria		0.5

^amg/M³ - Approximate milligrams of chromium per cubic meter of air sampled.

* - One blank was found to have .0002 mg of chromium, which is the lower limit of detection for the analytical method.

TABLE III
Breathing Zone Exposures to Latex Cement in the Intersole Department, Rebuilt Department
Bench Work, and Packing Room and to Leather Stretcher in the Rebuilt Department

L.L. Bean, Inc.
Freeport, Maine

November 4 & 5, 1976

Sample Location	Sample Period	Type of Sample	Ammonia+ (ppm) ^a	Concentrations of Contaminants			Acetone (ppm)	Isopropyl Alcohol (ppm)	% of Permissible Exposure for the Mixture*
				Toluene (ppm)	Benzene (ppm)	Naptha++ (mg/M ³) ^b			
Intersole Dept.	13:36 - 14:29	Impinger	.05	-	-	-	-	-	
	11:00 - 12:28	Impinger	ND**	-	-	-	-	-	
	-	Detector Tube***	3	Trace	ND	-	-	-	
	9:35 - 12:34	Charcoal Tube	-	4.2	ND****	370	-	-	23%
Bench Work	8:00 - 9:23	Impinger	ND	-	-	-	-	-	
	-	Detector Tube	Trace	Trace	-	-	-	-	
Packing Room	9:06 - 12:06	Impinger	ND	-	-	-	-	-	
	-	Detector Tube	Trace	Trace	-	-	-	-	
	13:53 - 16:26	Charcoal Tube	-	10.1	ND	972	-	-	59%
Rebuilt Dept.	14:00 - 16:25	Charcoal Tube	-	14.1	-	784	ND	12.2	56%
	-	Detector Tube	-	ND	-	-	-	-	
Environmental Criteria			50	100	1	2000	1000	400	

^appm - parts of contaminat per million parts of air sampled

^bmg/M³ - approximate milligrams of naptha per cubic meter of air sampled

* - one blind blank ammonia sample was found to have 18 mg of ammonia per ml of impinger solution, 90 times the lower limit of detection

++ - one blind blank charcoal tube sample was found to have .07 mg Naptha, seven times the lower limit of detection

* - % of Permissible Exposure for the mixture is calculated according to the formulas in Section D (2) of this report from the results of charcoal tube samples. Ammonia concentrations are not used in calculating the Em because ammonia is not additive in effect with the narcotic properties of hydrocarbons.

**ND - None Detected where the lower limit of detection of ammonia in an impinger is .2 ug/ml

*** - Detector tube measurements are all simulated breathing zone samples

**** ND - None Detected where the lower limit of detection with a charcoal tube is .01 mg/sample.

TABLE IV
Breathing Zone Concentrations of Volatiles from All-Purpose Cement, Sole Cleaner #3015, and Leather Dye in the Making Room

L.L. Bean, Inc.
Freeport, Maine

November 4 & 5, 1976

Job Classification	Sample Period	Type of Sample	Concentrations in Parts of Contaminants Per Million Parts of Air Sampled (ppm)										% of Permissible Exposure for the Mixture	
			Toluene	Hexane	Ethyl Acetate	Acetone	Benzene	Butyl Acetate	Isobutyl Acetate	Cellogolve	Isopropyl Alcohol	Xylene		
Cementing Soles	14:02 - 16:14	Charcoal Tube Detector Tube ^a	17.9 70	69.2 -	ND* 2000	ND -	ND -	- -	- -	- -	- -	- -	- -	87%
Cleaning and Cementing Soles	8:52 - 12:21	Charcoal Tube	16.5	52.8	ND	>15.8**	ND	-	-	-	-	-	-	71%
Cleaning Soles	14:00 - 15:30	Charcoal Tube Detector Tube	14.1 -	61.4 -	ND -	42.5 1000	3.8 -	- -	- -	ND -	ND -	ND -	ND -	380%***
Cleaning and Cementing Soles Plus Dyeing Leather	9:25 - 12:30	Charcoal Tube	9.9	43.0	ND	6.7	-	ND	-	ND	ND	ND	ND	54%
Environmental Criteria			100	100	400	1000	1	150		150	Nona	400	100	

^a - Detector tube measurements are all simulated breathing zone samples

^b - % of Permissible Exposure for the Mixture is calculated according to the formulas in Section D(2) of this report from the results of charcoal tube samples only

*ND - None detected where the lower limit of detection with a charcoal tube is .01 mg/sample

** - Acetone sample indicates a minimum concentration. Evidence that the charcoal tube was saturated with acetone.

*** - The percentage of permissible exposure is based only on the basis of benzene in this sample because, the other hydrocarbons do not have a destructive effect on the blood forming systems.

TABLE V

Breathing Zone Concentrations of Volatiles from Rubber Cement and Sole Cleaner #3015 in the Boot Department and Volatiles from the Rubber Cement During Bench Work

L.L. Bean, Inc.
Freeport, Maine

November 4 & 5, 1976

Analysis of Charcoal Tubes: Time Weighted Average Concentrations

<u>Job Classification</u>	<u>Sample Period</u>	<u>Isopropyl Alcohol (ppm)^a</u>	<u>Petroleum Naptha (mg/M³)^b</u>	<u>Acetone (ppm)</u>	<u>% of the Permissible Exposure for the Mixture^c</u>
Bench Work	11:28 - 12:25	ND*	61	ND	3%
Boot Dept./Cementing	13:42 - 16:20	ND	302	>77**	23%
Boot Dept./Cementing	8:57 - 12:20	ND	184	>25**	12%
Boot Dept./Boot Laying	14:10 - 16:20	ND	159	> 6**	8%
Environmental Criteria		400	2000	1000	

^a ppm - parts of contaminant per million parts of air sampled.

^b mg/M³ - approximate milligrams of contaminant per cubic meter of air sampled.

^c - % of Permissible Exposure for the Mixture is calculated according to the formulas in Section D(2) of this report.

*ND - None detected where the lower limit of detection with a charcoal tube analysis is .01 mg/sample.

**> - Acetone sample indicates a minimum concentration. Evidence that the charcoal tube was saturated with acetone.

TABLE VI

Capture Velocities of Local Exhaust Ventilation System on the Finishing Line and in the Making Room

L.L. Bean, Inc.
Freeport, Maine

November 5, 1976

<u>Location of Exhaust System/Description</u>	<u>Capture Velocity (fpm)*</u>	
Finishing Line: Buffing Wheels, average measurement of the exhaust on the three wheels	210	NOTE: Finishing Line measurements were conducted with the blast gates to the other hoods on the line closed.
Finishing Line: Edge Trimmer	1300	
Finishing Line: Heel Scourer	1000	
Finishing Line: Heel Scourer and Brusher		
Heel Scourer	300	
Brusher	400	
<u>Performance Criteria for the Above²²</u>	<u>Minimum of 500</u>	
Making Room: Cementing Bench (other side closed)**	120	
Cementing Bench (other side open)	100	
Making Room: Dyeing Bench (other side closed)	120	
Dyeing Bench (other side open)	100	
Performance Criteria for the Making Room ²²	100	

*fpm - linear feet of air movement per minute (measured by a Sierra Air Velocity Meter).

** - Refers to the fact that in the Making Room, the hoods are located back to back, both connected to the same exhaust duct.