

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. HE 77-83-532

Norton Company
Plastics and Synthetics Division
Akron, Ohio

OCTOBER 1978

I. TOXICITY DETERMINATION

A health hazard evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) on August 2-3, 1977 in the Fabrication Department, Plastics and Synthetics Division, Norton Company, Akron, Ohio. All Fabrication Department employees working 1st and 2nd shifts were interviewed by NIOSH investigators. Many of the employees complained of headache, fatigue, and eye or sinus irritation. Cyclohexanone and acetic acid vapor concentrations were measured with direct reading instruments. The concentration levels measured and the results of the employee interviews were summarized in a report submitted to management and union representatives, September 2, 1977. Personal and general atmospheric samples were collected and analyzed to determine airborne concentrations of cyclohexanone, acetic acid, and Eastman 910® (Kodak Trade name for methyl 2-cyanoacrylate). Based on the results of the environmental investigation it has been determined that employee exposures to the substances evaluated at the time of this survey were within acceptable limits as established by the evaluation criteria. The potential for an occasional short duration overexposure to cyclohexanone does exist under certain conditions. It is possible that some of the symptoms reported by the employees interviewed may have been caused or aggravated by these short term exposures. Recommendations have been offered in this report for precautions that should be taken by employees, supervisors and managers for safe use, handling and storage of cyclohexanone. This report also contains recommended first aid treatment for skin accidentally bonded with Eastman 910®.

II. DISTRIBUTION AND AVAILABILITY

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 ninety (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, Ohio address.

Copies of this report have been sent to:

- a) Norton Company, Plastics and Synthetics Division, Akron, Ohio
- b) Authorized Representative of Employees
- c) United Rubber Workers International, Akron, Ohio
- d) U. S. Department of Labor - Region V
- e) NIOSH - Region V

For the purpose of informing the "approximately 37 affected employees", the employer will promptly "post" the Determination Report for a period of thirty (30) calendar days in a prominent place(s) near where the affected 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 any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees - United Rubber Workers, Local 731. The requestor had indicated that 15-18 women working in the Fabrication Department had complained of severe headache, chest and neck pains, eye and nasal irritation, breathing difficulties, nose bleeds, and a feeling of weakness or fatigue. The request alledged that four of the women had suffered chest pains and were subsequently hospitalized. The workers were concerned that the symptoms they had experienced were caused by their exposure to vapors released when working with cyclohexanone, Silastic 734® (Mfg. Dow-Corning), and Eastman 910 (Mfg. Eastman Kodak).

IV. HEALTH HAZARD EVALUATION

A. Description of Process - Conditions of Use

The Norton Company, Plastics and Synthetics Division manufacture PVC (Tygon®) tubing and other specialized tubings such as Fluran®, a fluoroelastomer, and Tygothane® a modified polyurethane material. The resins are mixed and blended with plasticizers and inhibitors. The mix is then milled, cooled and chopped into pellets which are then melted and extruded as plastic tubing of various lengths and sizes.

The Fabrication Department is responsible for the assembly, inspecting and packaging of tubing assemblies designed for use by the customer, a manufacturer of peristaltic pumps, which are commonly used by medical and clinical laboratories for performing blood tests.

The 40 x 50 ft. assembly room is closed off from other areas in the plant and is equipped with its own general dilution ventilation system. Approximately 20 women work assembly during the first shift and 6 work the second shift. The 8 hour shifts are continuous from 8:00 AM - 4:00 P.M. and 4:00 P.M. - midnight. The women are permitted to leave the assembly room during their two 10 minute breaks and during 15 minute lunch breaks.

The assembly work is done by hand on large tables. After the tubing had been cut to length (approximately 15") the fabricator lays out each piece of tubing side by side from one end of the table to the other. Lay-out requires approximately 30 minutes. Using tweezers, the fabricator then picks up a small plastic collar, dips the collar in an open pan of cyclohexanone, dabs the collar on a sponge and attaches the collar to the tube. Two collars are attached to each tube and approximately 1 hour is required to complete the assembly of all tubes on the table (about 25 dozen tubes). A fabricator completes roughly 1600-1800 tubes each shift. The tubes are then gathered in groups of 12, placed on trays and dried in ovens during the next shift. After inspection and quality control tests are completed the tube assemblies are packaged (1 dozen each) into vinyl plastic bags.

Tubing made from materials other than PVC is also assembled in the Fabrication Department, but in much smaller amounts. The tubing is assembled in much the same manner as PVC but the collars are attached to polyurethane tubing using Silastic 734 and to the Fluran tubing using Eastman 910. At the time of the survey only 3 women on 1st shift and one woman on 2nd shift were using Silastic. Daily assembly with Eastman 910 is not required but is scheduled in accordance with customer demand. When scheduled, only one fabricator, working the first shift is utilized to fill the demand. Tubing assembly with Eastman 910 is normally performed by the same fabricator.

Fresh air to the assembly room is provided through an intake from the roof through ceiling mounted diffusers. The system is designed to provide up to 10,000 cubic feet of fresh air per minute. The air was exhausted to the outside through 2 louvered, floor level, 4 ft. x 4 ft. wall openings at one end of the room. Four fans were mounted on the wall, opposite the louvered openings, to provide additional circulation of the workroom air. An effort had been made to capture and exhaust any vapors released from Eastman 910 by use of a special down draft table where the Fluran tubes are assembled.

B. Evaluation Design and Study Progress

1. Environmental Survey

On August 2nd and 3rd, 1977, an environmental survey was conducted by NIOSH Industrial Hygienists. Following the entrance interview the NIOSH investigators were given a walk through tour of the entire facility. Confidential employee interviews were conducted with all employees working 1st and 2nd shift in the Fabrication Department. The job classifications included assembly workers, cutters, pullers, inspectors and packers.

Cyclohexanone vapor levels in the assembly room were measured directly with an HNU PI 101 photoionization hydrocarbon detector.* The level of acetic acid released from Silastic 734 during curing was measured with direct reading gas detector tubes. Personal and area atmospheric vapor samples for cyclohexanone, acetic acid, and Eastman 910 (Kodak trade name for methyl 2-cyanoacrylate) were collected. Employee work procedures were closely monitored, photographs were taken, and the ventilation systems were checked with smoke tubes and an air velocity meter. Material Safety Data Sheets on cyclohexanone and Silastic 734 were provided by management. Annual environmental monitoring records for cyclohexanone conducted by the Norton Company were also provided to NIOSH investigators.

C. Environmental Evaluation Methods

In addition to the direct reading detector methods, samples were collected over longer work periods using the following methods.

Cyclohexanone was collected by drawing air samples through glass tubes containing vapor adsorbing activated charcoal. A known quantity of air was pulled through these tubes by means of battery powered air sampling pumps operating at approximately 200 cc of air per minute. An area sample was collected from a fixed location in the center of the assembly room and six personal samples were obtained by attaching air sampling equipment to assembly workers who were seated at different tables throughout the assembly area. The collected samples were later desorbed with carbon disulfide and analyzed quantitatively for cyclohexanone by gas chromatography using a flame ionization detector.

Two of the 3 fabricators using Silastic 734 were sampled in order to determine their exposure to acetic acid vapor. An air sample was also collected just above the table work surface. The samples were collected with charcoal tubes connected to air sampling pumps operating at flow rates of one liter per minute (LPM). The samples were analyzed by desorption with formic acid and the amount of acetic acid was measured with a gas

chromatograph and flame ionization detector. The analytical sensitivity of the method was reported by the laboratory to be 1.0 micro gram acetic acid per samples.(1)

Methyl 2 - cyanoacrylate vapors released from Eastman 910 were collected by bubbling the air sampled through a midget impinger containing 0.5 Normal sodium hydroxide. The collected methyl 2-cyanoacrylate polymer was degraded to quantitatively release formaldehyde which reacts with a chromatropic acid reagent and is then measured colometrically(2). One personal and one area sample were collected using air sampling pumps operating at 1 LPM.

A portable velometer was used to check the air flow of the dilution ventilation. Air flow was measured at several air supply ceiling diffusers and at the outside of the louvered exhaust ports.

D. Evaluation Criteria

In order that workers and supervisors might better understand the hazardous properties and toxicity of the substances evaluated during this survey, the following information is provided:

Cyclohexanone - This substance is a colorless to pale yellow liquid with a mild peppermint odor. It is often used as a solvent in paint removers, for printing inks and in the plastics industry. Although cyclohexanone can affect the central nervous system causing narcosis and death at high concentrations, such concentrations are not likely to occur during industrial applications unless it is handled at elevated temperatures. Cyclohexanone has strong warning properties at low concentrations. Hazardous concentrations which could cause systemic injury are not likely to be tolerated due to objectionable eye, nose and throat irritation at levels above 75 parts per million (PPM). Exposures to low concentrations of any solvent which can depress the central nervous system may lead to headache.

The current Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for cyclohexanone is 50 PPM based on an 8 hour time weighted average (TWA). This level is also the current permissible exposure limit enforced by the Occupational Safety and Health Administration (OSHA). Some unaccustomed workers may experience irritation at concentration above 25 PPM.(4) The NIOSH recommended environmental limit for cyclohexanone is 25 PPM as a TWA concentration for up to a 10 hour work shift in a 40 hour work week.(6)

Acetic acid (Released from Silastic 734 during curing) - Acetic acid vapors may produce irritation of the eyes, nose, throat, and lungs. Inhalation of vapors at high concentrations may cause serious damage to the respiratory tract. Chronic exposure to vapors may result in pharyngitis (sore throat) and acute bronchitis. The OSHA standard for acetic acid is 10 PPM.(5) The ACGIH also recommends a TLV of 10 PPM acetic acid to prevent undue irritation.(3)

Methyl 2-cyanoacrylate (Eastman 910) - This strong, fast-setting adhesive material has been reported not to cause serious adverse reactions. A study of simulated work bench exposure to methyl 2-cyanoacrylate vapors determined the odor threshold to be 1 - 3 PPM with nasal irritation reported at approximately 3 PPM and eye irritation at 5 PPM. The ACGIH TLV is 2 PPM which was established to prevent irritation.(3)

E. Evaluation Results and Discussion

The results of the employee interviews are presented in Table 1. Headache, fatigue, eye and sinus irritation were the symptoms most frequently reported.

The environmental monitoring and sampling results for cyclohexanone are presented in Table 2 and 3. The amounts of cyclohexanone vapor detected in the assembly room were acceptable based on an evaluation criteria of 25 PPM. The atmospheric sampling data listed on Table 3 is considered to be representative of the actual time weighted average cyclohexanone exposures for the assembly room fabricators. The direct reading measurements (Table 2) represent the instantaneous cyclohexanone vapor concentrations at the actual time the measurements were taken. A transient exposure to cyclohexanone, above 50PPM, was detected in the breathing zone above table 16 at 10:30 a.m. Full shift sampling for determination of time weighed average exposures include periods of non-exposure such as breaks and lunch periods. The direct measurements were taken in the employees breathing zones when the employees were using cyclohexanone.

All samples collected and analyzed for acetic acid and for methyl 2-cyanoacrylate were below NIOSH detection limits of 1.0 microgram acetic acid per charcoal tube and 1.7 micrograms methyl 2-cyanoacrylate per ml of impinger collection solution (0.5N sodium hydroxide). Based on a 395 liter sample these limits would permit detection of acetic acid at concentration greater than .001 PPM and of methyl 2-cyanoacrylate at concentrations greater than .005 PPM. Sampling data for acetic acid and methyl 2-cyanoacrylate is presented in Table 4.

Because arsenic is sometimes used with silastic compounds as an anti-mildew agent bulk samples of Silastic 734 were analyzed for arsenic content. Results from the analysis indicate that this sample of Silastic 734 did not contain arsenic. Sensitivity of the analytical method was reported by the laboratory to be 0.02% arsenic by weight of sample.

F. Recommendations

1. The dilution ventilation system in the fabrication room was supplying a sufficient volume of fresh air to maintain cyclohexanone concentration below acceptable levels under normal conditions. The system should be redesigned during the summer months to boost ventilation capacity when elevated temperatures result in a greater vaporization of cyclohexanone. It is recommended that cyclohexanone levels be monitored subsequent to any changes made to the ventilation system and when reconfigurations are required for the winter heating season.
2. Clean rags should be used to mop up cyclohexanone spills immediately. Saturated rags should be placed in closed containers. Rags left on the floor under storage cans to soak up spills are a potential source of high vapor levels when these rags become saturated with cyclohexanone.
3. High exposures to cyclohexanone can occur when transferring the liquid from one container to another. Such operations should be performed in well ventilated areas and good work practices should be performed to prevent spills.
4. Employees should report to their supervisors immediately if they experience symptoms of nausea, drowsiness, sore throat, headache or eye irritation. The supervisor should immediately investigate the employee's work station to determine if environmental conditions or poor work practices might have caused these complaints.
5. A smoke tube check at the down draft table indicated that the system was not very effective in capturing vapors released when using Eastman 910. There was considerable cross draft interference; and air from a wall fan was deflecting off a wall above the table causing an air movement from the down draft vent holes toward the employee's breathing zone. Side shields, exhaust hood deflectors, and a larger exhaust fan would probably correct the down draft table exhaust system deficiencies.
6. When using cyanoacrylate adhesive the possibility of accidental skin bonding does exist. Accidental skin bonding does not require surgery for separating the bonded skin. The

following first aid treatments have been recommended by the Loctite Corporation, Newington, Connecticut. Supervisors should be knowledgeable of the proper handling of accidental skin bonds to prevent potential injury.

Skin bonds: Do not try to pull the bonded surfaces apart with a direct opposing action. Immerse the surfaces in warm, soapy water. Peel or roll the surfaces apart by using a blunt edge such as a spoon handle. Wash adhesive off the skin with soap and water.

Eyelid to eyelid or eyeball bonds: Do not try to open the eyes by manipulation. If eyelids are stuck together or bonded to the eyeball, wash thoroughly with warm water and apply a gauze patch. The eye will open without further action, typically in 1 to 4 days.

Adhesive on the eyeball: Cyanoacrylate introduced into the eyes will attach itself to the eye protein and will dissociate from it within a matter of hours, even if gross contamination has occurred. During the period of contamination before clearance takes place, weeping will occur and double vision may be experienced.

Mouth: If lips are accidentally stuck together, apply a stream of warm water to the lips and encourage maximum wetting and pressure from saliva inside the mouth. Peel or roll lips apart gently; do not try to pull the lips with a direct opposing action.

It is almost impossible to swallow cyanoacrylate. The adhesive solidifies and adheres to the mouth. Saliva will lift the adhesive in one-half to two days. If a lump forms in the mouth, position the patient to prevent ingestion of the lump when it detaches.

Burns: Cyanoacrylates give off heat on solidification. In rare cases, a large drop may cause a burn. Burns should be treated normally after the lump of cyanoacrylate is released from the tissue as described above.

V. REFERENCES

1. P&CA Method No. 127, NIOSH Manual of Analytical Methods, HEW Publication No. (NIOSH) 77-157A, Vol. 1.
2. P&CA Method No. 125, NIOSH Manual of Analytical Methods, HEW Publication No. (NIOSH) 77-157A, Vol. 1.
3. Documentation of Threshold Limit Values, American Conference of Governmental Hygienists (ACGIH), 3rd Edition, 1971

4. Patty, F.A., Industrial Hygiene and Toxicology, Second Revised Edition, Vol 11., Interscience Publishers, New York, 1967
5. Occupational Diseases, A Guide to Their Recognition, Revised Edition, DHEW(NIOSH) Publication No. 77-181(June 1977).
6. NIOSH Memorandum to the Assistant Secretary for Occupational Safety and Health, U.S. Dept. of Labor, Subject: Criteria for for a Recommended Standard... Occupational Exposure to Ketones, June 30, 1978

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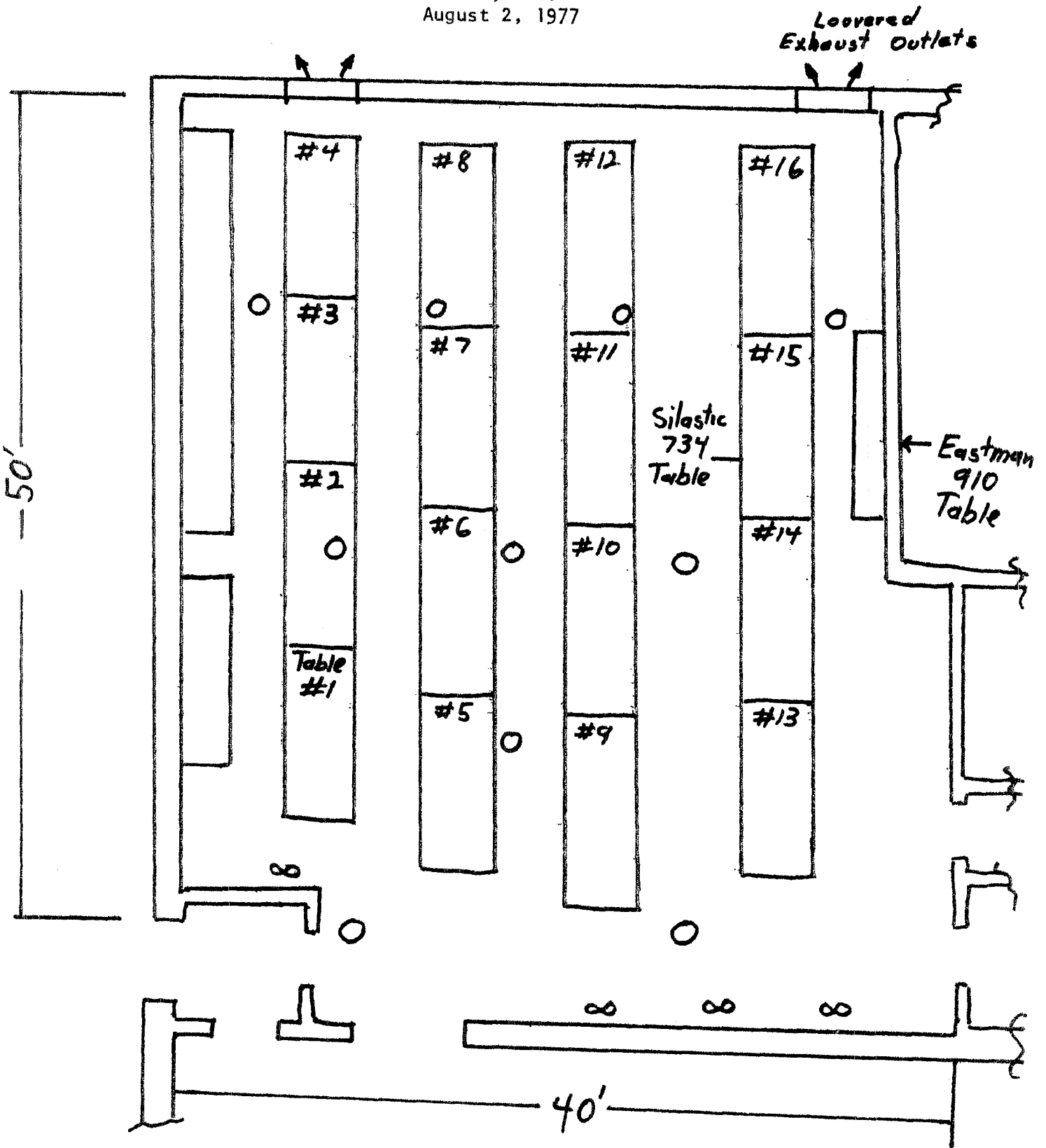
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FIGURE 1
Fabrication Department
Norton Company
Akron, Ohio
August 2, 1977



O = Ceiling Air Supply



TABLE 1
SUMMARY OF RESULTS
FROM EMPLOYEE INTERVIEWS
AUGUST 2, 1977
NORTON COMPANY

Symptoms recorded on this summary are those which employees believed were caused by their work exposure. Many employees reported more than one symptoms.

First Shift (23 Employees Interviewed)
Second Shift (10 Employees Interviewed)

Symptom Reported	First Shift			Second Shift		
	Current	Past	% of Total Shift	Current	Past	% of Total Shift
Headache	7	5	52	0	1	10
Fatigue	7	3	43.5	0	3	30
Bad Taste	1	1	8.7	1	0	10
Nausea	1	1	8.7	2	0	20
Intermittent Vomiting	1	0	4.4	0	0	0
Nose Bleeds	2	0	8.7	0	1	10
Dizzy Spells	2	1	13	1	0	10
Breathing Difficulties	2	0	8.7	0	1	10
Running Nose	1	1	8.7	1	1	20
Dry Mouth and Throat	1	1	8.7	0	1	10
Sinus Irritation	4	1	21.7	0	1	10
Eye Irritation	5	0	21.7	0	1	10
Chest Congestion	0	1	4.4	1	1	20
Sinus Congestion	1	0	4.4	0	0	0
Watering Eyes-Vision Clouded*	1	0	4.4	0	0	0
No Complaint		4	17.4		4	40

* This complaint has been associated with exposure to Eastman 910 (Methyl-2-Cyanoacrylate).

TABLE 2
 PERSONAL BREATHING ZONE
 CYCLOHEXANONE LEVELS MEASURED
 WITH
 DIRECT READING INSTRUMENT
 ON AUGUST 3, 1977

<u>Time (Apx.)</u>	<u>Location</u>	<u>Instantaneous Concentration in PPM</u>
10:30 A.M.	Table 16	50-100
10:30 A.M.	Table 9	10-20
10:30 A.M.	Table 12	10-15
10:30 A.M.	Table 4	10
10:30 A.M.	Table 1	10-12
10:30 A.M.	Table 1	10-15
11:53 A.M.	Table 6	15-20
11:53 A.M.	Table 8	5-8
11:53 A.M.	Table 4	5
11:53 A.M.	Table 2	5
11:53 A.M.	Table 5	5
11:53 A.M.	Table 2	10
2:00 P.M.	Table 16	4
2:00 P.M.	Table 11	5
2:00 P.M.	Table 9	5
2:00 P.M.	Table 9	5
2:00 P.M.	Table 6	6
2:00 P.M.	Table 7	20
2:00 P.M.	Table 3	10
2:00 P.M.	Table 1	15

NOTE:

Current recommended Threshold Limit Value for cyclohexanone is 50 PPM time weight average (TWA) measured over an 8-hour period or 50 PPM Short Term Exposure Limit (15-minute exposure). NIOSH recommends a 25 PPM TWA limit measured over a 10-hour period.

See Figure 1 for work table location.

TABLE 3
 RESULTS OF ATMOSPHERIC SAMPLING FOR
 CYCLOHEXANONE
 NORTON COMPANY
 FABRICATION DEPARTMENT
 AUGUST 2, 1977

<u>Sample Number/Type</u>	<u>Job/Location</u>	<u>Sampled Volume (Liters)</u>	<u>Sample Duration</u>	<u>Time Weighted Average Concentration (PPM)</u>	
C1	Personal	Fabricator/Table 2	78	0807-1530	3
C2	Personal	Fabricator/Table 6	86	0810-1530	4
C3	Personal	Fabricator/Table 11	81	0819-1530	3
C4	Personal	Fabricator/Table 16	90	0822-1530	4
C5	Personal	Fabricator/Table 10	85	0824-1530	3
C6	Area	Sample Lost	(Broken Charcoal Tube)		
C7	Area	Fabricator/Table 4	81	0832-1530	2
C9	Blank	---	---	---	---

PPM = Parts of Cyclohexanone Vapor per Million Parts of Air.
 Note: See Figure 1 for table location.

Detection limit = 0.02 mg cyclohexanone per charcoal tube.

TABLE 4
NORTON COMPANY
FABRICATION DEPARTMENT
AUGUST 2, 1977

RESULTS OF ATMOSPHERIC SAMPLING
FOR
ACETIC ACID

<u>Sample/Type</u>	<u>Job/Location</u>	<u>Sampled Volume (liters)</u>	<u>Sample Duration</u>	<u>Concentration</u>
A1 Area	South End Table 15	422.3	0847-1551	ND
A2 Personal	Fabricator Table 15	397.1	0850-1534	ND
A3 Personal	Fabricator Table 15	405.0	0852-1533	ND
A4 Blank	---	---	---	---

ND = Not Detected

Limit of Detection = 1 microgram acetic acid per charcoal tube.

RESULTS OF ATMOSPHERIC SAMPLING
FOR
METHYL 2 - Cyano Acrylate

<u>Sample/Type</u>	<u>Job/Location</u>	<u>Sampled Volume (liters)</u>	<u>Sample Duration</u>	<u>Concentration</u>
E1 Area	Left Side Eastman Table	393	0904-1337	ND
E2 Personal	Fabricator Eastman Table	391	0908-1335	ND

ND = Not Detected

Limit of Detection = 1.7 microgram Methyl 2-cyanoacrylate
per milliliters of collecting solution

Note: See Figure 1 for work table location