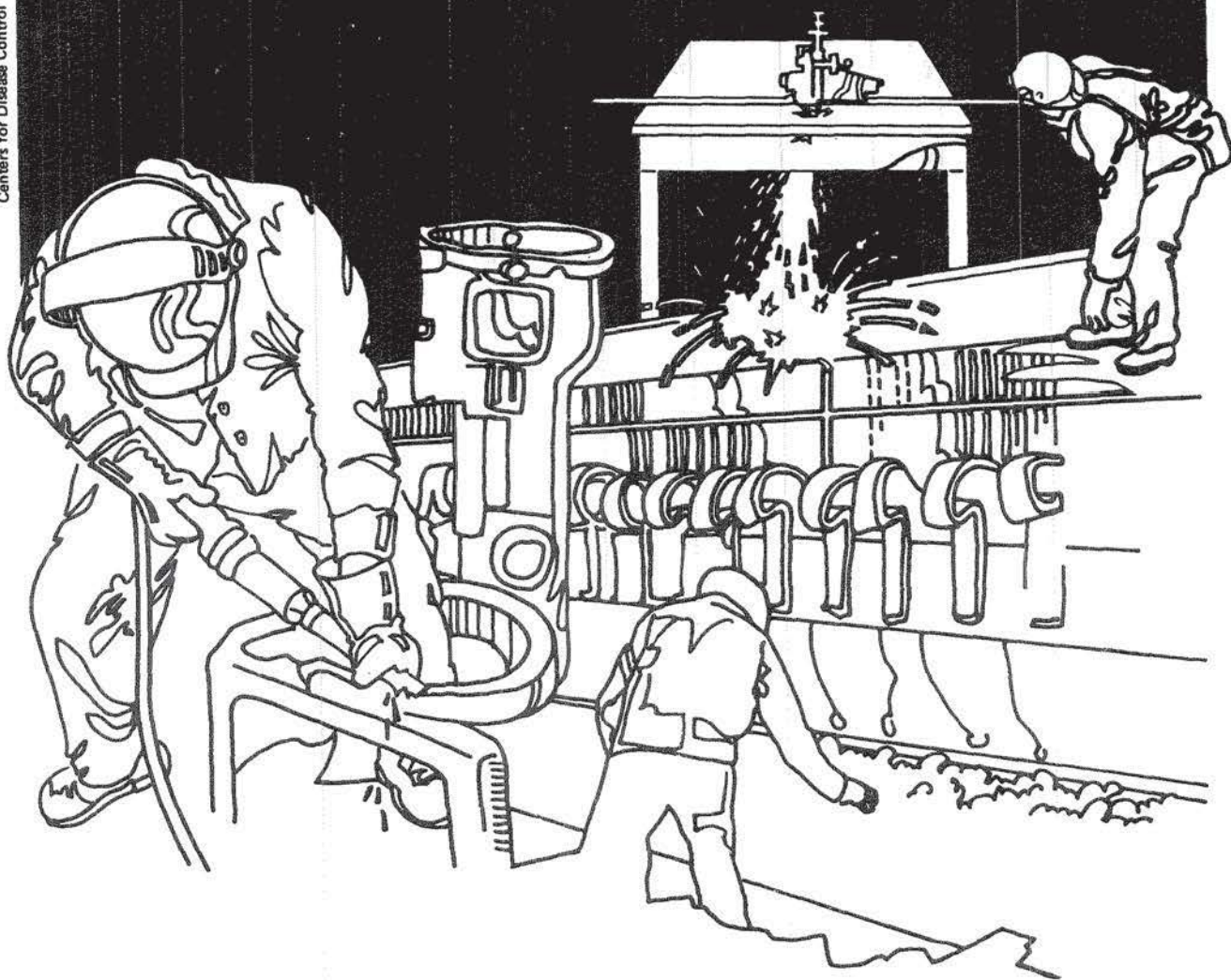


# NIOSH



## Health Hazard Evaluation Report

HETA 80-242-1106  
STERLING ORGANICS  
RENSSELAER, NEW YORK

## PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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



## I. SUMMARY

In August 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union - an authorized representative of employees at Sterling Organics, Rensselaer, NY - to evaluate an apparent dermatitis among workers engaged in the production of para-nitrobenzyl bromide (PNBB). Approximately two-thirds of 50 employees who had been exposed since production began in July 1980 had developed rashes. The request also concerned possible long-term health effects of exposure.

On September 30, 1980, NIOSH visited the facility to review the closed production process and collect wipe samples from surfaces within the production building. Prior to the NIOSH visit, the company had instituted new procedures for handling PNBB, including spraying potentially contaminated surfaces with a 2% ammonia aqueous solution. The company noted that the solution chemically changed PNBB into para-nitrobenzyl amine (PNBA).

The wipe samples were analyzed for PNBB, PNBA, and para-nitrobenzyl alcohol - an oxidation product of PNBB. One sample from an inner shower room contained para-nitrobenzyl alcohol. None of the other samples taken from surfaces near the closed system contained any of the compounds above the lower limit of detection of 0.6 micrograms per filter.

Since the company had instituted the new work practices, no employee had developed a rash. No employees had dermatitis on the day of the NIOSH visit. A review of medical records indicated that the rash was a contact dermatitis, probably due to both primary irritation and sensitization. No other health effects were reported.

NIOSH contacted former and current manufacturers of PNBB in the United States and England about long-term health effects. No chronic effects were reported. Since the NIOSH site visit, no significant cases of contact dermatitis have been reported by the employees at the facility.

The current engineering controls and work practices appear to be adequate to prevent the development of contact dermatitis. Because PNBB is a known intense primary irritant and sensitizer, direct exposure should continue to be avoided. As long the protective measures adequately prevent the development of immediate symptoms, they will also likely prevent the development of any potential long-term health effects.

Keywords: SIC 286 (Industrial Organic Chemicals); para-nitrobenzyl bromide, para-nitrobenzyl amine, contact dermatitis, respiratory irritation, mugagen.

## II. INTRODUCTION

In September 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union - an authorized representative of employees at Sterling Organics, Rensselaer, New York - to evaluate an apparent contact dermatitis among workers engaged in the production of para-nitrobenzyl bromide (PNBB). PNBB is a known primary irritant and skin sensitizer, requiring a closed production system. It is also weakly mutagenic(1). Since Sterling Organics began production in July 1980, approximately two-thirds of the regularly exposed employees had developed rashes. The request concerned appropriate control measures and asked for information about potential long-term health effects of exposure.

NIOSH visited the site on September 30, 1980. Wipe samples were collected from surfaces near the closed production system for analysis of PNBB, para-nitrobenzyl amine, and para-nitrobenzyl alcohol. Subsequently, NIOSH reviewed the medical records of affected employees. Current and former producers of PNBB were contacted to provide toxicity information concerning exposure to PNBB.

## III. BACKGROUND

Para-nitrobenzyl bromide (PNBB) -  $O_2NC_6H_4CH_2Br$  - is used as a reagent in a proprietary process in a room at this facility. Employees accessing this room wear a positive pressure, disposable plastic suit with an air supply line. Controlled access to the room takes place through a double-door shower and suit-removal room. After exiting, the employee takes a second regular shower.

Shortly after production began, employees reported developing severe skin itching and burning accompanied by redness and, sometimes, blisters. The dermatitis occurred mostly on the wrists and forearms, but could be located anywhere from the neck to the ankles. The medical department of the company examined the affected employees and recommended that they be removed from the



production area until the rashes resolved. The rash generally resolved within a week or two and the employee could then return to the area. Because of transfers and medical removals, approximately 50 employees worked in the area regularly between July and September, 1980. Two-thirds of these employees developed rashes while working in the area.

During the initial period of production, the closed system in the Kettle Room developed intermittent clogs and spills. Several cases of dermatitis were related to these episodes. Most of the other cases were ascribed to rips in the plastic protective suits or leakage through seams in the arms of the suits. Only in a few cases was a specific incident exposure not identified.

In August, employees requested an inspection by the Occupational Safety and Health Administration (OSHA). Representatives of OSHA visited the facility and administered questionnaires to approximately 40 employees. The results confirmed that most cases of dermatitis were associated with spills or with breakdowns in the personal protective equipment. No other health effects were identified. OSHA arranged for five affected employees to be seen by a dermatologist in early September 1980. The dermatologist concluded that the five employees had an "allergic eczematous contact dermatitis after working with the agent, PNBB."(2)

OSHA collected several wipe samples from surfaces in the Kettle Room and Finished Materials Ramp area for analysis for PNBB. It subsequently reported to NIOSH that some of the analyzed samples indicated the presence of small amounts of PNBB.

Through the summer, the company modified the production process to decrease the frequency of clogs and spills. In late August, the plastic suits with seams were replaced by polyvinyl chloride (PVC) suits, including double boots and gloves. In mid-September, the company introduced a 2% ammonia aqueous solution developed by its laboratory to react chemically with and destroy the PNBB. The solution is used to wash the surfaces of the 55 gallon drums before their transfer out of the Dryer Room. It is also applied to spills in the Kettle Room and is sprayed on the skin of employees who experience the initial burning associated with PNBB exposure. The solution had been in use for two weeks prior to the NIOSH visit.

#### IV. EVALUATION DESIGN AND METHODS

##### A. Environmental

Since the use of the ammonia solution had been implemented after the environmental sampling was done by OSHA, wipe samples were again taken by NIOSH to assess the presence of PNBB on building surfaces outside of the Dryer Room. Eight moistened wipe samples (Whatman 50 smear tabs) were taken from surfaces in the production area, exclusive of the Dryer Room. Each sample was taken from a 1 foot by 1 foot area.

After the samples had been collected, but before they had been analyzed, the company notified NIOSH that their laboratory had determined that the resulting substance of the PNBB/ammonia reaction was para-nitrobenzyl amine



(PNBA). Because of this information and delays in analyzing the samples (performed in May 1981), the samples were analyzed for the presence of PNBB, PNBA, and para-nitrobenzyl alcohol - an oxidation product of PNBB.

Each smear tab was extracted with methanol and injected onto a HPLC column (Vydac 201 TP Reverse Phase). The column effluent was monitored with an ultraviolet (UV) absorbance detector set at 254 nanometers. Since the samples were area wipe samples, the analysis only indicated the presence or absence of the three substances.

Because of potential systemic toxicity of para-nitrobenzyl amine (PNBA), the NIOSH chemical laboratories attempted to develop an alternate solution for washing skin that had been exposed to PNBB. It was reasoned that para-nitrobenzyl alcohol would be a preferred reaction product to PNBA because, as an alcohol, it would probably have less systemic toxicity and be less of an irritant than the amine. Solutions tested included 1) a saturated solution of sodium bicarbonate in water, 2) a saturated solution of sodium bicarbonate in isopropyl alcohol, and 3) a saturated solution of sodium bicarbonate in isopropyl alcohol with potassium iodide added. Each solution was mixed with a solution of PNBB in methanol. Aliquots of the resulting solution were taken at one-half hour intervals and analyzed for the presence of PNBB.

#### B. Medical

No employees had dermatitis on the day of the NIOSH site visit. No significant dermatitis has developed since employees began wearing the PVC suits and using the ammonia/water solution. NIOSH reviewed the medical records of affected employees and requested the records of the dermatologist who had seen the 5 affected employees for OSHA.

Since the request expressed concern about long-term health effects of PNBB exposure, NIOSH contacted other current and former producers of PNBB about known toxicity. PNBB has been manufactured for approximately 10 years in England. Thus NIOSH contacted the Employment Medical Advisory Service (EMAS) in England concerning the long-term toxicity of PNBB.

#### V. EVALUATION CRITERIA

No governmental environmental criteria currently exist for airborne concentrations of PNBB, PNBA, or para-nitrobenzyl alcohol.

Para-nitrobenzyl bromide has slight to moderate acute oral toxicity in laboratory animals. Its single dose toxicity causing a 50 percent mortality (LD<sub>50</sub>) is 1174 milligrams per kilogram of body weight (mg/kg) in rats and 228 mg/kg in mice(3). On the other hand, PNBB is highly toxic by inhalation with toxic respiratory effects (tracheal irritation) observed in rats exposed to an air concentration of 14 milligrams per cubic meter of air (mg/m<sup>3</sup>) (4). A no effect level was noted to be 2.0 mg/m<sup>3</sup>.

PNBB is a severe primary irritant of the skin and the eye of rabbits and will produce a marked skin sensitivity in guinea pigs(3,4). It is also a severe primary irritant and skin sensitizer in humans(5). Direct contact with PNBB should be avoided.



PNBB was shown in in vitro testing to be a weak mutagen not requiring metabolic activation(1). It tested positively only in the Salmonella typhimurium TA100 tester strain of bacteria. It should be noted that chemicals that cause cancer are likely to cause mutation. Using Salmonella typhimurium tester strains, McCann and Ames found that 90% of the carcinogens tested were mutagenic, and 87% of the "noncarcinogens" were nonmutagens(6). On the other hand, not all mutagens cause cancer. In general, the potency of a chemical to cause mutations correlates with its tendency to cause cancer(6). Thus weak mutagens, such as PNBB, are least likely to be carcinogenic. No experimental animal tests have been conducted to evaluate the carcinogenic potential of PNBB. Until more information becomes available, it would be prudent to minimize exposure.

The toxicity of para-nitrobenzyl amine (PNBA) has not been widely evaluated. One study indicates that it is moderately toxic by intravenous injection in mice(7). The LD<sub>50</sub> was 100 mg/kg. No human toxicity has been reported. No positive toxicity information has been reported on para-nitrobenzyl alcohol.

## VI. RESULTS AND DISCUSSION

### A. Environmental

Eight moistened wipe samples taken from surfaces in the building were analyzed for the presence of PNBB, PNBA, and para-nitrobenzyl alcohol. The sampling locations are indicated in Figure 1. One sample taken from the inner shower room leading to the Dryer Room indicated the presence of para-nitrobenzyl alcohol. No other samples were found to have any of the compounds above the lower limit of detection of 0.6 micrograms per filter. Thus there is no evidence of PNBB contamination of surfaces in areas of the building where workers wear regular work clothes, without special protective clothing.

Because of the limited literature indicating a moderate systemic toxicity of PNBA, the NIOSH laboratories investigated alternate procedures for washing skin that had been exposed to PNBB. Three alternate solutions were tested as described above. The PNBB precipitated from the sodium bicarbonate/water solution. For both the sodium bicarbonate in isopropyl alcohol solution and the sodium bicarbonate/potassium iodide in isopropyl alcohol solution, more than 90% of the PNBB remained in solution after 2 hours of testing. Thus none of the three solutions proved to be an acceptable alternate to the 2% ammonia in water solution that is currently being used.

### B. Medical

A review of the medical records confirmed that most cases seemed to be associated with leaks of PNBB in the Kettle Room, tears in and leakage through the seams of the initial plastic protective suits, and residual PNBB on the surfaces of the 55 gallon drums after their removal from the Dryer Room. The rashes were mostly located on the wrists, forearms, and necks, but appeared on all parts of the body. The rashes resolved within one to two weeks after removal from exposure. Not all persons who returned to the production facility developed recurrent rashes. The documentation is not



adequate to assess to what extent sensitization had occurred among the affected employees. The dermatologist who examined the 5 affected employees for OSHA concluded that PNBB causes an allergic contact dermatitis.

The Employment Medical Advisory Service (EMAS) of England - a governmental agency with responsibilities similar to those of NIOSH - reported that a branch of Sterling Organics in England has manufactured PNBB for 8 years. A representative of EMAS visited the facility in England and reviewed their medical experience. EMAS concluded that PNBB is an "intense contact dermatitic agent and a contact skin sensitizer." (5) They found no evidence to suggest that the chemical is "either faeto-toxic(sic) or a human carcinogen."

### C. Discussion

Since the NIOSH visit, the company has instituted two new procedures to further reduce potential exposure to PNBB. The sanitation procedures have been revised to outline the cleaning methods to be performed in each area of the production facility, to specify a frequency for cleaning, and to require that cleaning be documented. The amount of drum-handling has been reduced by preparing and labeling the drums at the production area and then transporting them to the warehouse where they are loaded directly onto trailers. Potential exposure to warehouse workers has been eliminated.

Environmental sampling at the time of the NIOSH visit indicates that there is no substantial contamination of PNBB outside the closed production system. Employees working within the Dryer Room are required to wear a positive pressure PVC suit with an air supply line. Since begining to wear the PVC suits, no employees have reported significant new cases of dermatitis. NIOSH concludes that the combination of using the closed production system and wearing the PVC protective suits provides adequate environmental protection.

The use of the 2% ammonia in water solution also appears to have decreased the incidence of dermatitis among inadvertently exposed employees. The solution is reported to change PNBB into PNBA. PNBA has not been evaluated in humans, and thus, its toxicity remains unknown. In one animal study it was shown to have moderate systemic toxicity(7). Because of this report, NIOSH attempted to develop an alternate solution for washing skin contaminated with PNBB. No solution successful at neutralizing PNBB was developed. Considering the limited positive toxicity information available on PNBA, NIOSH believes it is reasonable to continue using the ammonia/water solution until an alternate solution is developed.

Discussions with manufacturers of PNBB in the United States and England revealed that there are no known long-term health effects associated with PNBB exposure after approximately 10 year of experience. It should be noted that certain conditions, such as cancer, can develop with a latency substantially longer than 10 years. Thus the known human experience does not rule out the possibility that health effects could develop in the future. On the other hand, PNBB is an intense primary irritant and sensitizer. Minimal contact results in severe dermatitis or respiratory irritation. It can be assumed that protective measures which prevent the development of dermatitis and respiratory irritation are adequate to prevent the development of other potential health effects.



## VII. CONCLUSIONS

The current engineering controls and work practices appear to be adequate to prevent the development of contact dermatitis and respiratory irritation. Because PNBB is an intense primary irritant and sensitizer, direct exposure should continue to be avoided. As long as these protective measures adequately prevent the development of immediate symptoms, they will also likely prevent the development of any potential long-term health effects.

## VIII. AUTHORSHIP AND ACKNOWLEDGEMENT

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

For the purpose of informing the "affected employees", the employer should post this report for at least 30 days in a prominent place(s) near where the employees work.

Copies of this report will be available from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio, 45226, for 90 days. Thereafter, copies will be available from the National Technical Information Service (NTIS), Springfield, Virginia. Information concerning its availability through NTIS can be obtained from the NIOSH publication office at the above Cincinnati address.

Copies of this report have been sent to:

Sterling Organics, Rensselaer, New York  
International Chemical Workers Union, Akron, Ohio  
New York State Department of Health  
Occupational Safety and Health Administration, Region II



Past conditions cannot be duplicated; however, events may be reconstructed. The sources of the vapors were likely multiple. Employees occupied the sixth floor office while construction was continuing. Ethyl acrylate, a respiratory irritant with a strong acrid odor, was contained in caulking applied to the window frames in early June. Its vapors likely affected many persons for several days. Additionally, organic solvents were present in the construction materials and varnish applied during working hours. Small amounts of vapors could also have been generated in the art studio. Finally, under certain wind conditions, vapors from the exhaust stack of the hat manufacturer could have drifted into the intake of the air moving system, which is located approximately 10 feet below the exhaust stack on the north side of the building. Once a vapor enters a modern office, which typically recirculates 80% to 90% of the air, it tends to remain in the system for some time.

While it is unlikely that any one substance accumulated to toxic levels, it is possible that the mixture of vapors could have interacted to have caused a physiologic response. Clearly, several persons experienced a common pattern of symptoms beginning in early June. Furthermore, as these employees continued to develop symptoms in the face of multiple odors, a new office situation, and continuing construction, other employees began to experience multiple symptoms of ill-health. These later symptoms likely represent manifestations of stress experienced by the employees due to the disrupted office environment. During interviews many employees reported anxiety, frustration, and stress over the conditions in the new office. The evolution over time into a non-specific pattern of symptoms indicates that a toxic exposure was probably not solely responsible for all of the observed health effects.

While airborne concentrations of vapors are substantially below toxic levels and the building is safe for occupancy, odors can still be detected. These odors and "stale air" could be unpleasant to some employees and, possibly, be associated with further stress-related symptoms. Therefore, recommendations are made to further reduce these odors.

## VII. Recommendations

1. The Art Studio (room 615) should be equipped with a separate exhaust to remove vapors from the studio and not recirculate them to the rest of the office.
2. The exhaust stack from the hat manufacturer should be extended a minimum of 10 feet to avoid recirculation of vapors.
3. The current ratio of 1/3 fresh air, 2/3 recirculated air should be maintained as feasible.
4. Future office refitting by New York University should be completed and the spaces aired out before occupancy by office employees.



5. An office health committee should be established to review complaints relating to health problems or discomfort. The committee should have representatives from the administration, employees, and building management.

#### VIII. AUTHORSHIP AND ACKNOWLEDGEMENT

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Copies of this report have been sent to:

New York University, Public Affairs Department  
U.S. Department of Labor, Region II  
New York State Department of Health, Division of Occupational Safety and Health  
NIOSH, Public Health Service, Region II



Table I

Health Effects of Suspected Vapors

<u>Substance</u>	<u>Odor</u>	<u>Health Effects</u>
Ethyl Acrylate (2)	Sharp Acrid	Irritation of eyes, respiratory tract, and skin. Burning and tearing of eyes.
Formaldehyde (2,4)	Sharp, Bitter Acrid	Irritation of eyes and respiratory tract. Suspected carcinogen. Tingling of eyes, nose, and posterior pharynx at 2-3 ppm (3-4.5 mg/m <sup>3</sup> ). Tearing of eyes at 4-5 ppm.
Hexane (2,5)	Gasoline-like	Mild upper respiratory irritant and central nervous system depressant; chronic exposure causes peripheral neuropathy. Dizziness greater than 1000 ppm (3600 mg/m <sup>3</sup> ). Slight nausea, headache and irritation on eyes and throat at 1500 ppm (5400 mg/m <sup>3</sup> ).
Toluene (6)	Sweet, pungent	Mild fatigue, weakness, confusion, lacrimation and mild paresthesias of the skin at 200 ppm (750 mg/m <sup>3</sup> ). Euphoria, headache, and dizziness at 600 ppm.
1,1,1- Trichloroethane (7)	Chloroform-like	Irritation of eyes, light headedness, and incoordination at 1000 ppm (5485 mg/m <sup>3</sup> ) for 20 minutes.

Table 2

Environmental Sampling for Organics on 9/4/80

<u>Sample Location</u>	<u>Sample Volume (liters)</u>	<u>Analysis <sup>①</sup> (mg/m<sup>3</sup>)</u>	
		<u>Toluene</u>	<u>Others</u>
Room 605 (Exterior, SE corner)	270	0.15	N.D. <sup>②</sup>
Room 615 (Art Studio, NE corner)	534	0.13	N.D.
Room 623 (Exterior, NW corner)	411	0.11	N.D.
Room 602 (Interior, SE)	218	0.18	N.D.
Room 624 (Interior, W end)	365	0.08	N.D.
Open Office (NE area)	382	0.11	N.D.
Open Office (SW area)	526	0.11	N.D.

1. Analysis by gas chromatography for identification of organics.

2. None detected.



Table 3

Environmental Sampling for Organics on 9/10/80

<u>Sample Location</u>	<u>Sample Volume (liters)</u>	<u>Analysis<sup>1</sup> (mg/m<sup>3</sup>)</u>	
		<u>Toluene</u>	<u>Others</u>
Room 605 (Exterior, SE corner)	452	0.13	N.D. <sup>2</sup>
Room 615 (Art Studio, NE corner)	618	0.13	N.D.
Room 619 (Exterior, N wall)	537	0.15	N.D.
Room 624 (Interior, W end)	662	0.17	N.D.
Open Office (NE area)	690	0.16	N.D.
Open Office (SW area)	670	0.15	N.D.
Open Office (SW area)	674	trace	N.D.
Exhaust Stack			

1. Analysis by gas chromatography for identification of organics.

2. None detected

Table 4

Environmental Sampling for Organics on 9/22/80

<u>Sample Location</u>	<u>Sample Volume (liters)</u>	Analysis <sup>1</sup> (mg/m <sup>3</sup> )			
		<u>Toluene</u>	<u>C<sub>6</sub>-C<sub>7</sub></u>	<u>Hexane</u>	<u>1,1,1 trichloro- ethane</u>
Room 615 - Center (Art Studio)	286	0.07	trace	n.d. <sup>2</sup>	n.d.
Room 615 - Window (Art Studio)	288	0.04	trace	n.d.	n.d.
Room 615 - East wall (Art Studio)	252	0.08	trace	n.d.	n.d.
Exhaust Stack	248	2.50	6.6	1.57	3.47
Temporary Art Studio <sup>3</sup> - South Hall	474	0.15	7.8	3.86	12.53
Temporary Art Studio - Middle	484	0.12	6.7	3.00	8.06
Temporary Art Studio - N.W. corner	488	0.06	2.9	0.12	3.48

1. Analysis by gas chromatography for identification of organics.

2. None detected

3. Located on 7th floor of 4 Washington Place, New York City.

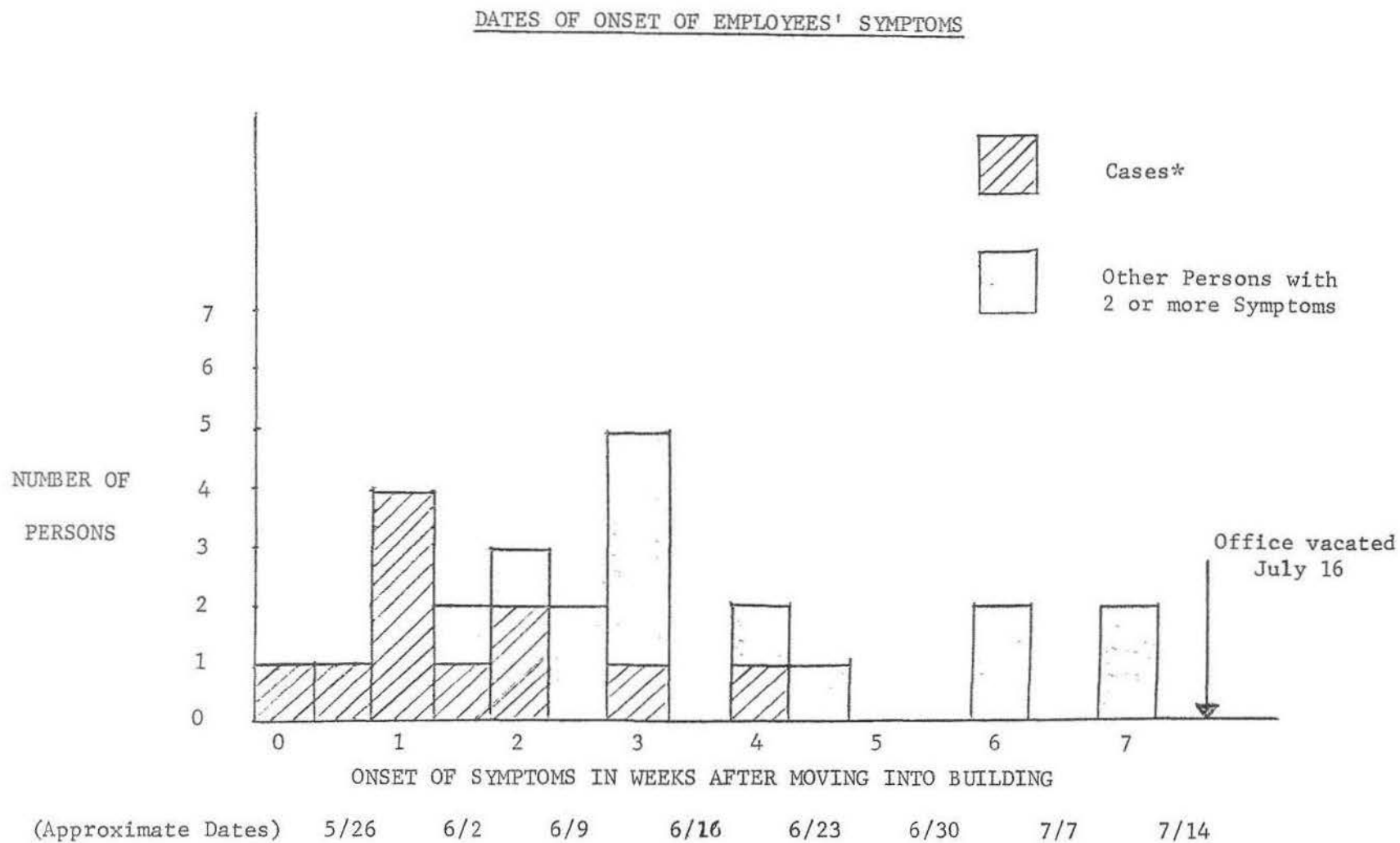


Table 5

Prevalence of Symptoms During Summer 1980  
Among Employees of the Public Affairs Department  
(Percent experiencing symptoms)

<u>Symptoms</u>	<u>Total</u> (N=36)	<u>Female</u> (N=23)	<u>Male</u> (N=13)
Fatigue	58	70	38
Headache	50	52	33
Burning Eyes	42	48	31
Dizziness	39	43	31
Nausea	39	57	8
Dry or Sore Throat	33	35	31
Chest Tightness	33	39	23
Tearing Eyes	22	26	15
Short of Breath	19	22	15
Sensitivating to Light	17	17	15
Rash	17	13	23
Cough	14	18	8
Stuffy Nose	8	13	0
Wheezing	8	9	8
Vertigo	3	0	8
Cigarette Smoking	36	43	23

Figure 1



\* Cases defined as experiencing 4 of 5 symptoms: fatigue, headache, dizziness, burning eyes, or dry or sore throat.



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