

HETA 88-348-2081
NOVEMBER 1990
A.E. STALEY MANUFACTURING COMPANY
DECATUR, ILLINOIS

NIOSH INVESTIGATORS
Jane McCammon, M.S., C.I.H.
David Orgel, M.D.
Bruce Hills, M.S., C.I.H.

I. SUMMARY

In August, 1989, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Allied Industrial Workers of America International Union, Local 837 to evaluate potential hazards from exposures to emissions from the waste water treatment plant, as well as current and past exposures to asbestos at A.E. Staley Manufacturing Company. Other concerns included exposures to ethylene oxide, crystalline silica, grain dust, and other chemicals.

NIOSH investigators conducted a combined medical and environmental site visit on March 14-17, 1989. The asbestos screening program appeared to be in conformance with NIOSH guidelines and OSHA requirements. Seven (9%) of 76 employees in the company's asbestos monitoring program had category 1 interstitial opacities; one of these also had pleural plaque.

Sixty-six of the approximately 200 employees in the waste treatment area completed a health questionnaire. Twenty-one (32%) felt that they experienced some symptoms from the waste treatment plant emissions. Area air samples were collected in the waste treatment plant for sulfur dioxide, sulfates, sulfites, propyl mercaptan, ethyl mercaptan, hydrogen sulfide, aliphatic amines, and volatile organic compounds. None of these compounds were detected at levels that would be suspected to cause symptoms in exposed workers.

Area and personal breathing zone samples for propylene oxide were collected in the starch processing areas. On March 14, 1989, personal breathing zone sample results ranged from non-detectable (less than 0.15 ppm for a 28 liter air sample) to 630 parts per million (ppm) measured during a 45-minute sampling period. The OSHA permissible exposure limit (PEL) for propylene oxide is 20 ppm as an 8-hour time-weighted average (TWA). NIOSH considers propylene oxide to be a potential occupational carcinogen and exposure should be limited to the lowest feasible level. Area samples were as high as 2400 ppm during a 55-minute sampling period. The cause of these high propylene oxide levels was a glycerol seal failure on the reactor vessel. On March 15, 1989, area airborne concentrations of ethylene oxide ranged from non-detectable to 7.4 ppm during a 2-hour sampling period. No detectable ethylene oxide was found on personal samples collected on that day.

Area air sample results collected for vinyl acetate in the starch-vinyl acetate processing building ranged from 0.94 ppm on a tank to 20 ppm on a starch drying press. Personal breathing zone sample results from three operators ranged from non-detectable (less than 0.9 ppm for a 3 liter air sample) to 5.7 ppm for a period of 165 minutes. The OSHA PEL for vinyl acetate is 10 ppm as an 8-hour TWA, with a 15-minute ceiling of 20 ppm. The NIOSH recommended exposure limit (REL) for vinyl acetate is 4 ppm for a 15-minute ceiling.

A follow-up site visit on July 10-12, 1989, was conducted to monitor for ethylene oxide in the starch reactor room. Personal breathing zone samples ranged from 0.02 to 0.22 ppm. The OSHA PEL for ethylene oxide is 1 ppm as an 8-hour TWA, with a 15-minute ceiling of 5 ppm. NIOSH considers ethylene oxide to be a potential occupational carcinogen and exposures should be limited to the lowest feasible level. Area samples ranged from non-detectable (less than 0.003 ppm for a 42 liter air sample) to 3.1 ppm.

The company's asbestos screening program appears to follow NIOSH and OSHA recommendations and has found radiographic signs of early pneumoconiosis in a substantial number of workers. Sources of asbestos in the plant are currently being identified and removed by a firm trained in asbestos abatement. Monitoring in the waste water treatment and mechanics building failed to identify any substance that would explain the health problems experienced by the employees. Hazardous levels of propylene oxide were released into the starch reactor room on March 14, 1989, due to the failure of a reactor glycerol seal. Detectable levels of propylene oxide and ethylene oxide are also typically present in the reactor room. Engineering controls, improved employee work practices, and improvements in the respiratory protection program are needed to reduce employees' exposures to the lowest feasible levels.

KEYWORDS: SIC 2046 (wet corn milling), propylene oxide, ethylene oxide, starch, asbestos, sulfur dioxide, waste water treatment plant, mercaptans, vinyl acetate, silica.

II. INTRODUCTION

In August 1988, NIOSH received a request from the Allied Industrial Workers of America International Union, Local 837, to evaluate occupational exposures at A.E. Staley Company in Decatur, Illinois. The request covered the entire Decatur operation, with particular emphasis on suspected hazards from exposures to emissions from the waste water treatment plant, as well as health effects which might have resulted from past and current exposures to asbestos, crystalline silica, grain dust, ethylene oxide, and various other chemicals. An initial site visit and walk-through survey were conducted by NIOSH personnel on September 26, 1988. A combined medical and industrial hygiene survey was undertaken during March 14-17, 1989. A second industrial hygiene survey was conducted on July 10-12, 1989, to monitor employee exposures to ethylene oxide. On November 23, 1988; May 23, 1989; July 10, 1989; and on April 24, 1990, letters were sent to management and union representatives summarizing the NIOSH site visits and the progress of the evaluation.

III. BACKGROUND

Although this request covered suspected health hazards in the entire Staley Decatur facility, including past exposures, there were certain areas which seemed to be of more concern. The union was particularly worried about weaknesses that might exist in the medical monitoring program for asbestos-exposed individuals. The union felt that cases of asbestosis, lung cancer, and/or mesothelioma were either being missed in the company's monitoring program, or were not being reported. These concerns were based on cases of asbestosis diagnosed through medical tests conducted outside the company's auspices. In particular, one employee had died from a pleural mesothelioma, and approximately 15 other employees had recently been informed that they had asbestos-related disease after an independent screening sponsored by the union. These facts led the union to request assistance from NIOSH in evaluating the effectiveness of the company's asbestos medical monitoring program.

The union also emphasized problems experienced by mechanics working in a building adjacent to the waste water treatment plant. The mechanics had reported symptoms which they felt were related to exposures to substances from the waste water treatment process. Their symptoms included headaches, nausea, and nose bleeds. These symptoms seemed to occur when emissions from the waste water treatment plant drifted into the building, and particularly when the odor of the emissions was similar to that of onions. Concern about these symptoms was exacerbated by the fact that metal objects in the mechanics building turned black within a period of days when exposed to the air in the building. The company attempted to identify contaminants which become airborne from the waste water treatment plant to which the mechanics might be overexposed. Sampling was conducted by the company for hydrogen sulfide and mercaptans.

IV. PROCESS DESCRIPTION

The Decatur Staley plant covers 450 acres and contains approximately 150 buildings. There are over 900 persons employed in production at this plant, where each day, 160,000 bushels of corn are processed into starch and syrup products. Corn is brought to the plant by truck and rail, inspected for aflatoxin contamination, and stored in silos. It is delivered from the silos to the plant by belt-line. Steeped corn is coarsely ground to break loose the germ. Germ is removed from the slurry in cyclone separators. The germ fraction is processed for

corn oil. The kernel suspension contains starch, gluten, and fiber. The collected fiber is combined with gluten for feed use. The starch-gluten suspension is concentrated by centrifugation. The concentrated starch then passes through hydroclones to remove the last traces of protein. Starch suspension may then be marketed as unmodified corn starch, modified by chemical or physical means, or hydrolyzed to corn syrup.

Ethylene oxide, propylene oxide, and vinyl acetate are among the chemicals used to modify starch at this site. Starch modification is accomplished by a batch process in a building separated from the main plant. A starch slurry is pumped from the main plant to reaction vessels in the starch reaction building. Caustic is added to the starch as it is pumped to the reaction vessels. Oxygen is purged from the vessel head space with nitrogen prior to the addition of the specific reaction chemical. The batch is allowed to react for a specified time period, after which the reaction is stopped by the addition of an acid. The reacted starch is then pumped back to the main plant for further processing.

V. METHODS

A. Environmental

From March 14-17, 1989, area air samples were collected at various sites in the waste water treatment plant to determine the presence and concentration of sulfur dioxide, sulfates, sulfites, aliphatic amines, mercaptans, hydrogen sulfide, and volatile organic compounds. The same array of area air samples was collected in the mechanics' building. Personal breathing zone samples for airborne hydrogen sulfide were also collected here. Personal breathing zone and area samples for airborne propylene oxide were collected in the starch reaction area, the pump house, and flash drying area. Due to the nature of exposures, most of the charcoal tube samples for propylene oxide were also analyzed for ethylene oxide. Air samples were also collected for vinyl acetate in the starch reaction area, the pump house, the pressing operation, and the waste water treatment plant.

Bulk samples of corn dust were collected from elevator A and dust collector D for analysis of pesticide and silica content. A bulk sample of ash from the Cogen building was provided by the union. This ash is the waste product of burning high-sulfur coal which is treated with lime. It was analyzed for silica, sulfates, sulfites, metals, calcium oxide, and calcium hydroxide.

The limits of detection (LOD) and limits of quantitation (LOQ) for each analytical method used are listed in Table 1.

Sulfur dioxide, sulfates, and sulfites: Each area air sample for these compounds was collected on two filters connected in sequence (a potassium hydroxide-treated cellulose filter preceded by 0.8 micrometer cellulose ester membrane filter) at a flow rate of 1.5 liters per minute (lpm). Sulfur dioxide is collected on the treated filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and quantitated as total particulate sulfate and sulfite. The samples were analyzed by ion chromatography.

Direct-reading measurements of sulfur dioxide were also obtained using Drager detector tubes with a range of 0.5 to 25 ppm.

Aliphatic amines: Area samples for airborne aliphatic amines were collected on 150/75 mg silica gel tubes at a flow rate of 0.2 lpm. The samples were analyzed by gas chromatography mass spectroscopy (GC/MS) according to NIOSH P&CAM 221 (1).

Mercaptans: Glass fiber filters treated with mercuric acetate were used to collect area samples to detect the presence of simple mercaptans. The flow rate was 1 lpm. The analytical method for these compounds is presently under development. The results obtained by the analysis are qualitative in nature, although quantification of ethyl and propyl mercaptan was attempted to estimate the order of magnitude of mercaptan presence. Prior to analysis, the filters were desorbed with a mixture of 1,2-dichloroethane and 25% hydrochloric acid. The 1,2-dichloroethane was separated and analyzed by gas chromatography using a flame photometric detector with a sulfur filter.

Hydrogen sulfide: Direct-reading area and personal breathing zone exposure concentrations of hydrogen sulfide were obtained using Drager long-duration detector tubes with a range of 0.5 to 60 ppm. In addition, direct-reading area measurements were obtained using an Ecolyzer 6000 monitor with a range of 0-250 ppm.

Volatile organic compounds: Area samples were collected on 100/50 mg charcoal tubes at a flow rate of 0.2 lpm for analysis by GC/MS to identify specific volatile organic compounds. Samples were desorbed with carbon disulfide and screened by gas chromatography using a flame ionization detector. Selected samples were further analyzed by GC/MS.

Propylene oxide and ethylene oxide: On March 14-16, 1989, samples were collected on charcoal tubes at a flow rate of 0.1 lpm for analysis of propylene oxide and ethylene oxide. Samples were analyzed by gas chromatography and flame ionization detection according to NIOSH Method 1612 (1).

Ethylene oxide: On July 10-11, 1989, personal breathing zone and area samples for ethylene oxide were collected in the starch reaction building. Samples were collected on hydrogen bromide-coated 100/50 mg petroleum charcoal tubes at a flow rate of 0.1 lpm, then analyzed by gas chromatography and electron capture detection according to NIOSH Method 1614 (1). The process involving propylene oxide had been suspended, so monitoring for this compound was not performed.

Vinyl acetate: Area samples for vinyl acetate were collected on Amborsorb XE347 140/70 mg tubes at a flow rate of 0.1 lpm. The samples were analyzed by gas chromatography with a flame ionization detector according to OSHA Analytical Method No. 51 (2).

Ash: A portion of the bulk sample of ash from the Cogen building was digested and analyzed for trace metals content by inductively-coupled argon plasma, atomic emission spectroscopy. A separate portion of the ash sample was analyzed qualitatively for minerals such as silica, lime, anhydrite, hematite/magnetite and portlandite by X-ray powder diffraction (XRD).

Corn Dust: Portions of the two bulk samples of corn dust were sonicated in toluene

and analyzed for organochlorine pesticides by a gas chromatograph equipped with an electron capture detector. The samples were analyzed for organophosphate pesticides by a gas chromatograph equipped with a flame photometric detector. Separate portions of the corn dust samples were analyzed for silica (quartz and cristobalite) using X-ray diffraction according to NIOSH Method 7500 (1).

B. Medical

1. Asbestos Screening Program

To address the concerns about the company's asbestos screening program, the program was reviewed for compliance with NIOSH and OSHA guidelines. These guidelines are enumerated in the NIOSH publication, Occupational Respiratory Diseases (12), and the OSHA standard for occupational exposure to asbestos in general industry and construction (29 CFR Parts 1910 and 1926).

2. Evaluation of Health Complaints from the Waste Treatment Fumes

The initial request, supported by information obtained during the initial site visit, directed our follow-up evaluation toward the health effects caused by the airborne mist from the waste treatment plant. This was for two reasons: 1) maintenance personnel in building 54 complained that these mists were discoloring metals and causing headaches, upper respiratory and eye irritation, fatigue, and malaise, and the complaints in other personnel could be traced to similar, although less frequent, exposures to the same mists, and 2) exposures in other parts of the plant were apparently well controlled with appropriate engineering and work practices. We, therefore, planned a questionnaire survey of health complaints among employees in the waste treatment area.

VI. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled to the level set by the evaluation criterion. These combined effects are not often considered in the establishment of evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are the following:

1) NIOSH Recommended Exposure Limits (RELs) (3), 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs) (4), and 3) the U.S. Department of Labor (OSHA) Permissible Exposure Limits (PELs) (5). Often, the NIOSH recommendations and the ACGIH TLVs are lower than the corresponding OSHA PELs. The OSHA PELs may also be required to take into account the feasibility of controlling exposures in various industries where the agents are used. The NIOSH RELs, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits (STELs) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

Propylene Oxide

Skin contact with liquid propylene oxide can cause contact dermatitis. Exposure to propylene oxide vapor can cause irritation of the eyes, nose, throat, and lungs. In one report, humans exposed to propylene oxide vapor received corneal burns (6). Exposure to propylene oxide can also result in a reduced capacity to repair DNA synthesis following the in vitro induction for DNA damage to their blood lymphocytes (7). Unscheduled DNA synthesis is a step in the enzymatic repair of DNA damage. Studies on the carcinogenic effect of propylene oxide in laboratory animals performed by the National Toxicology Program and by other researchers have concluded that there is evidence that propylene oxide is an animal carcinogen (8). Based on this research, NIOSH therefore recommends that propylene oxide be considered a potential occupational carcinogen in conformance with the OSHA Cancer Policy. The excess cancer risk for workers exposed to propylene oxide has not yet been established, but the probability of developing cancer should be decreased by minimizing exposure. As a matter of prudent public health policy, employers should assess the conditions under which workers may be exposed to propylene oxide and take reasonable precautions (such as appropriate engineering and work practices controls) to reduce exposures to the lowest feasible concentrations (9).

OSHA has established an 8-hour TWA PEL of 20 ppm for propylene oxide to protect workers against the risk of primary irritation and central nervous system depression (5). However, during the OSHA rule-making process, NIOSH disagreed with the proposed permissible exposure limit, recommending that propylene oxide be designated as a potential occupational carcinogen (10).

The ACGIH TLV for propylene oxide is 20 ppm as an 8-hour TWA (4). The TLV is based on the acute toxicity of propylene oxide and its "lesser toxicity in relation to ethylene oxide".

Ethylene Oxide

NIOSH recommends that a worker's exposure be limited to 5 ppm ethylene oxide for no more than 10 minutes per workday, and that the worker's 8-hour TWA exposure be limited to less than 0.1 ppm (11). This NIOSH REL is based on the conclusion that ethylene oxide is mutagenic and carcinogenic in animals and is also capable of causing adverse reproductive effects. NIOSH has also concluded that ethylene oxide causes chromosomal damage in humans and has the potential for causing cancer and adverse reproductive effects in humans

(11).

The OSHA PEL and the ACGIH TLV for ethylene oxide is 1 ppm measured as an 8-hour TWA. No worker may be exposed to an airborne concentration that exceeds 5 ppm as averaged over a sampling period of 15 minutes (4,5).

Evaluation criteria for propylene oxide, ethylene oxide, vinyl acetate, sulfur dioxide, and sulfuric acid are listed in Table 2.

VII. RESULTS

A. Environmental

1. Starch Production

Propylene oxide - On March 14, 1989, area samples for propylene oxide in the starch reaction area (Building 116) ranged from non-detectable (less than 0.11 ppm for a 37 liter air sample) to over 2,400 ppm. When airborne concentrations were high, the sampling media became overloaded and breakthrough occurred. (If greater than 30% of the reported amount of contaminant is found on the backup portion of the tube, breakthrough has occurred.) Therefore, actual concentrations measured during the periods of high exposure were at least 30% greater than the reported value. The highest concentrations were found in the reaction tank area during the time when propylene oxide was delivered to the reaction vessels. The concentration of propylene oxide in the laboratory averaged 9 ppm, over a six and a half hour sampling period.

Personal breathing zone samples for characterization of propylene oxide exposures occurring on March 14, 1989, in the starch reaction area ranged from non-detectable (less than 0.15 ppm for a 28 liter air sample) to 630 ppm, during a sampling period of 45 minutes (Tables 3,4). The highest value reflects the exposure of one of the mechanics in the reactor room until the propylene oxide vapor became too strong for him to continue working. Although most of his work shift was spent outside of Building 116, his 8-hour TWA exposure to propylene oxide was 71 ppm. The operator in the reaction area experienced the second highest exposure of 140 ppm during a 60 minute sampling period. Most of his workshift was spent in the control room where exposure to propylene oxide was low, resulting in an 8-hour TWA exposure of 25 ppm. Both employees had exposures in excess of OSHA's PEL for propylene oxide (20 ppm as an 8-hour TWA). NIOSH has stated that propylene oxide should be regarded as a potential occupational carcinogen and exposures reduced to the lowest feasible level. On this basis, propylene oxide exposures measured during this survey are well above acceptable concentrations.

On March 15, 1989, area samples collected in the starch reaction area and adjacent laboratory contained no detectable (less than 0.11 ppm) propylene oxide. Personal breathing zone samples collected on that day ranged from non-detectable (less than 0.38 ppm for a 11 liter air sample) to 1.3 ppm (Table 5). No propylene oxide was added to the vats, but starch batches were being mixed from the previous day.

On March 16, 1989, area samples for propylene oxide collected in the starch reaction tank area and adjacent laboratory ranged from non-detectable (less than

0.38 ppm for a 11 liter air sample) to 140 ppm (Tables 6,7). Personal breathing zone samples for propylene oxide collected in those areas on that day revealed exposures ranging from non-detectable (less than 0.47 ppm for a 9 liter air sample) to 4 ppm, during a 2.5 hour sampling period (Tables 6,7). These data were of particular interest because propylene oxide was delivered to the vessels at half the rate used on March 14th. The data supports the company's contention that delivery of propylene oxide at a slower rate results in a lowering of airborne concentrations, but also shows that the potential for significant exposures continues to exist.

No propylene oxide was detected in samples collected in Building 16 (pump house, Table 8) or Building 26 (flash drying, Table 9). This may have been due, in part, to the fact that the propylated starch batch was held in the reaction area for an extended period, resulting in a complete reaction between the propylene oxide and the starch.

Ethylene oxide - All of the charcoal tube samples for propylene oxide were also analyzed for ethylene oxide, with the understanding that this collection method, upon analysis, would underestimate the true concentrations since ethylene oxide does not readily bind to activated charcoal. The correct sampling medium for ethylene oxide is charcoal coated with hydrogen bromide. The analytical data indicated significant amounts of breakthrough on all samples where ethylene oxide was detected. These results, therefore, must be viewed as conservative estimates of actual airborne concentrations.

Area sample concentrations of ethylene oxide measured in the starch reaction area on March 14, 1989, ranged from non-detectable (less than 0.15 ppm for a 28 liter air sample) to 33 ppm over a four-hour period (Tables 3,4). Personal breathing zone sample concentrations measured on that day ranged from non-detectable (less than 0.15 ppm) to 12 ppm during a 45-minute period (Table 3). A mechanic was exposed to the highest time-weighted average, which was 1.4 ppm, during a sampling period of slightly over 6 hours. Exposures in excess of all evaluation criteria listed in Table 1 were measured.

Area concentrations of ethylene oxide measured on March 15, 1989, ranged from non-detectable (less than 0.62 ppm for an 8 liter air sample) to 7.4 ppm during a two-hour sampling period (Table 5). Ethylene oxide was not detected on personal samples collected on that day.

Area concentrations of ethylene oxide measured on March 16, 1989, ranged from non-detectable (less than 0.62 ppm for an 8 liter air sample) to 0.67 ppm. Ethylene oxide was not detected on personal breathing zone samples collected on that day (Table 7). Ethylene oxide was not detected in any area other than the starch reaction area.

Vinyl Acetate - Area samples collected in the starch-vinyl acetate processing building ranged from 0.94 ppm on a tank to 20 ppm on a starch drying press (Table 10). Personal breathing zone sample results for three operators ranged from non-detectable (less than 0.92 ppm for a 3 liter air sample) to 5.7 ppm over a period of 165 minutes.

Monitoring for ethylene oxide in Building 116 was repeated on July 10-11, 1989. Personal breathing zone samples for the operators ranged from 0.02 to 0.22 ppm

(Tables 11, 13, 14, 16, 17). Area samples collected adjacent to reactor tank 1 ranged from non-detectable (less than 0.003 ppm for a 42 liter air sample) to 3.1 ppm (Tables 11-17).

2. Waste Water Treatment and Mechanics Building

Sulfur dioxide, sulfates, and sulfites - sulfur dioxide was not detected on any treated filters or detector tubes. Concentrations of sulfates on filter samples ranged from 7.2 to 38 micrograms per cubic meter of air. Concentrations of sulfites samples ranged from 4.3 to 7.2 micrograms per cubic meter of air. The results for particulate sulfate represent the presence of total sulfate, in both ionic and molecular forms including sulfuric acid and sulfate salts. Since no other sulfates present are more irritating than sulfuric acid, a comparison of these results to the evaluation criterion for sulfuric acid is appropriate as the most conservative approach. Using this approach, the sulfate data are well below the evaluation criterion.

The presence of sulfite on the untreated filter indicates that sulfur dioxide gas reacted with something in the air or on the filter to form a solid which cannot pass through the filter. As such, the sulfite data should be multiplied by a conversion factor (0.8) to correct for differences in molecular weights and compared with evaluation criteria for sulfur dioxide. If this is done, the results are still well below the evaluation criteria for sulfur dioxide.

Mercaptans - Propyl mercaptan was detected on all but three of the 19 filter samples analyzed. Ethyl mercaptan was detected on four samples. Although propyl mercaptan was found more consistently, ethyl mercaptan was found in quantities higher, by an order of magnitude. No other sulfur-containing compounds were detected on the mercuric acetate-treated filters.

Hydrogen sulfide (H₂S) - H₂S was not detected with either sampling method used.
Aliphatic amines - Aliphatic amines were not detected on any samples.

Volatile organic compounds - Samples analyzed by GC/MS revealed low levels of several aliphatic hydrocarbons in the C9 to C11 range (nonane, decane, undecane), toluene, xylene, and traces of 1,1,1-trichlorethane.

Other areas

No silica (quartz or cristobalite) or pesticides were found in either bulk sample of corn dust collected from elevator A or dust collector D.

The bulk sample of ash from the Cogen building was composed of 9.2% silica (quartz), and contained 1,400 micrograms of sulfate per gram of ash. The qualitative X-ray diffraction analysis of the ash sample indicated the presence of lime, quartz, anhydrite (CaSO₄), and hematite/magnetite (Fe₂O₃). The following metals were detected in the ash sample: calcium (26.1%), iron (5.0%), aluminum (3.27%), magnesium (0.58%), sodium (0.41%), titanium (0.19%), phosphorus (0.07%), manganese (0.06%), strontium (0.05%), barium (0.02%), and zinc (0.01%). Based upon these analytical results, exposures of most concern related to the ash would be total and/or respirable dust and silica exposures. No clear source of the irritation symptoms reported by the workers in this operation was evident from this evaluation.

B. Medical

1. Asbestos Screening Program

The asbestos screening program began in 1987. The program is administered by the Staley medical department. One physician completed all of the physical examinations and interpretations of laboratory data during this period.

All pulmonary function tests are conducted by a technician who completed a NIOSH approved course in screening spirometry and are supposed to be done once a year. A Vitalograph II pulmonary function machine with package software was purchased in 1986. The machine is calibrated daily with a calibration program using temperature and barometric pressure and a 3 liter calibration syringe. The machine has a 12 second readout of volume versus time, with a maximum 7.5 liter volume. The time display is 2 centimeters per second, and the volume display is 10 mm per liter. All of these meet or exceed American Thoracic Society specifications (13).

Pulmonary function tests are done with nose clips, and at least three satisfactory tracings are obtained during each test. The software on the machine takes the best of the three readings to calculate its results.

Results are reported graphically and are adjusted for norms based on height, weight, and sex. A ratio of FEV1/FVC is used for interpretation to reduce variability.

A posterior/anterior chest x-ray is used. This is read by one of two B readers employed on a contract basis. A baseline chest x-ray is to be obtained, with follow-up chest x-rays based on the OSHA standard. Results are reported using the NIOSH recommended form.

A yearly physical examination and questionnaire is based on the OSHA standard. This includes a more complete baseline examination upon entry to the program.

Seventy-six medical files from the asbestos screening program were reviewed, including those of 6 workers who reportedly had asbestosis. The files were first reviewed for frequency of physical examinations, questionnaire, pulmonary function test, and chest x-rays. All employees had at least one pulmonary function test, two employees (3%) did not have a documented physical examination, 1 (1%) did not have a questionnaire, and 1 did not have a baseline chest x-ray. All employees had at least one pulmonary function test. Four (5%) employees had 2 or more years between follow-up physical examinations, 9 (12%) had 2 or more years between follow-up questionnaires, and 5 (7%) had 2 or more years between PFTs. Thus, the asbestos screening program was successful in obtaining baseline testing on most of its employees, but regular follow-up monitoring has not been as successful.

We also reviewed the medical files for abnormalities. Eighteen (24%) of the participants had a chest x-ray with interstitial opacities. One of the 7 chest x-rays with profusion 1/0 or 1/1 had circumscribed pleural thickening (plaque), and 3 of the 11 with profusion 0/1 had diffuse pleural thickening. Six employees (8%) had an abnormal respiratory physical examination; 3 (4%) had respiratory complaints on the initial questionnaire. Six (8%) had a restrictive pulmonary function pattern,

and 27 (35%) had an obstructive pattern. Of the 18 employees with interstitial opacities on chest x-ray, 3 had a restrictive pulmonary function pattern; none of the 4 with pleural thickening had a restrictive pattern. None of the 18 had an abnormal physical examination or respiratory complaints on the questionnaire. None of the 6 employees with alleged asbestosis was in this group.

2. Questionnaire survey

Sixty-six (33%) of the approximately 200 employees in the waste treatment area completed the questionnaire (Tables 18-20). All were men; they had a mean duration of employment at Staley of 22 years (range 10-38 years). Twenty-one employees (32%) felt they experienced some symptoms from the waste treatment plant emissions. However, the proportion of those reporting symptoms from work throughout the plant was greater than that reported for the waste treatment area alone.

Employees were asked to name the areas causing the most health complaints. The most frequently named was the bleach laboratory, by 10 employees. All other places were mentioned by only 1 or 2. These included: BSS area, filter aid area, gap area, tunnel, packing room, clarifier room, reactor areas, sludge room, acid area (5th floor), wet milling, basins, and "all areas, many jobs, many areas."

VIII. DISCUSSION

During the first day of industrial hygiene sampling, NIOSH investigators were forced to evacuate the starch reaction area when the odor of propylene oxide became strongly evident as the compound was being pumped into a reaction tank. The outdoor alarm system, which is triggered by concentrations of 2,000 ppm of propylene oxide, sounded during this incident. A respirator was requested for reentry into the area. The Scott air pack was found to be missing from the storage container, and no other respirators were immediately available. When a respirator was located and donned by the NIOSH investigator, breakthrough or leakage occurred within a few minutes of exposure in the area. Operators continued to enter the area with no personal protection. Employees stated that based on the strong odor, the release of propylene oxide into the reactor room was the "worst occurrence of a propylene oxide leak in a long time." However, an odor of propylene oxide is frequently noticed by employees during the propylation of a starch batch.

An investigation of the incident revealed that several work practices designed to reduce exposure to reaction compounds throughout the starch stream were not being followed in the starch processing area. For example, reactor tank seals appeared to be malfunctioning. A contributing factor was the rate at which propylene oxide was delivered to the reactor tanks. The delivery rate typically used before this evaluation (and accidentally on the day of the incident described), blows the glycerol seal at the top of the reactor. The replacement of the glycerol was reported to be sporadic.

There was evidence that two production practices which had been developed to reduce the potential for downstream exposure to ethylene oxide and propylene oxide were also not being followed. The first practice is to routinely test the headspace of the reactor tanks containing ethylated starch batches for residual ethylene oxide prior to forwarding the starch from the reaction phase to the next process step. Monitoring equipment for headspace analysis was in place but not in use. According to the company if ethylated starch batches are allowed to react until headspace residual ethylene oxide was below a certain value, downstream exposures to the compound were eliminated. Operators were unsure of the

proper way to operate the monitoring equipment, and unclear about the proper reading that should be obtained prior to pumping the batch to the next step in the process. In addition, questioning of operators and other technical personnel revealed that demand for product often resulted in propylated and ethylated batches being pumped from the area prior to the prescribed holding time which had been established to allow for complete reaction. Operators in other parts of the starch stream process commented on being able to smell ethylene oxide and propylene oxide in the batches of starch pumped to them from the reaction area, which indicated that the potential for exposures to both compounds exists throughout the starch stream.

No specific air contaminant was found which would explain the symptoms being experienced by workers exposed to emissions from the waste treatment plant. It is important to note, however, that these emissions vary from day to day, and that on the day of the industrial hygiene survey, the emissions did not have the odor of onions or garlic as they reportedly do on days when workers reported experiencing symptoms of irritation. Further, the emissions did not have the intense sulfur smell that was present during the initial walk-through survey.

IX. CONCLUSION

Employees in the speciality starch reaction building (Building 16) were exposed to hazardous levels of propylene oxide in March, 1989. Monitoring in March and July, 1989, demonstrated that employees are also exposed to ethylene oxide. The results of the ethylene oxide monitoring in July, 1989, showed that the controls put into effect since March, 1989, to reduce emissions were effective in reducing ethylene oxide air concentrations. However, both substances are potential human carcinogens; therefore, employee exposures should be reduced to the lowest feasible concentrations.

X. RECOMMENDATIONS

A. Environmental

1. Excessive exposures to propylene oxide and ethylene oxide were measured in the starch reaction area during March 1989. As discussed during the closing conference on March 17, 1989, and in the letter of May 23, 1989, immediate steps should be taken to implement engineering controls to reduce exposures to reaction chemicals in the starch reaction area.
2. The use of respirators is the least desirable method of controlling worker exposures and should not be used as the primary control method during routine operations. However, NIOSH recognizes that respirators may be required to provide protection in certain situations such as implementation of engineering controls, certain short-duration maintenance procedures, and emergencies. NIOSH maintains that only the most protective respirators should be used involving carcinogens such as propylene oxide and ethylene oxide. These respirators include any self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive-pressure mode, and any supplied air respirator with a full facepiece operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive-pressure mode.

A complete respiratory protection program should include regular training and medical evaluation of personnel, fit testing, periodic environmental monitoring, and maintenance, inspection, and cleaning of equipment. The guidelines for a respiratory protection program can be found in the NIOSH document Guide to Industrial Respiratory Protection (14).

3. A multipoint detection system should be installed in Building 116 to monitor for ethylene oxide and propylene oxide. This system will aid in identifying sources of emissions and warn employees of sudden releases.
4. All reactor vessels in Building 116 should be equipped with mechanical agitator shaft seals rather than the glycerol seals.
5. Short term sampling for ethylene oxide or propylene oxide should be performed during each phase of the process, rather than collecting random short term samples during the workshift.
6. A company policy should be established to prohibit all employees from entering the reactor room, except for essential employees such as reactor room operators, laboratory technicians, and maintenance employees.
7. Based upon observations made during the initial survey, as well as discussions during the industrial hygiene survey, the company should improve efforts to identify and label asbestos containing materials throughout the plant. It was stated by both the company and union that much of the insulating material used in the plant contains asbestos. Unlabeled friable insulating materials were observed in a number of areas of the plant.
8. Because of the large size of the facility, the in-house asbestos identification program should be continued with quality control for asbestos identification.

XI. REFERENCES

1. NIOSH Manual of Analytical Methods, Third Edition, NIOSH, Cincinnati, OH, May 1989.
2. US Department of Labor: OSHA Analytical Methods, Method Number 51, OSHA, Washington DC.
3. NIOSH: Recommendations for Occupational Safety and Health Standards, US Dept of Health and Human Services, 1988.
4. ACGIH: Threshold Limit Values and Biological Exposure Indices for 1989-1990. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1989.
5. OSHA: Air Contaminants - Permissible Exposure Limit (Title 29 Code of Federal Regulations Part 1910.1000) OSHA, US Dept. of Labor, Washington DC, 1989.
6. McLaughlin RS: Chemical burns of the human cornea. Am J Ophthalmol 29: 1355-1362, 1946.
7. Pero RW, Bryngelsson T, Widegren B, Hogstedt B, Welinder H: A reduced capacity for unscheduled DNA synthesis in lymphocytes from individuals exposed to propylene oxide and ethylene oxide. Mutat Res 104: 193-200, 1982.
8. NTP: Toxicology and carcinogenesis studies of propylene oxide in F344/N rats and B6C3F1 mice (inhalation studies). Research Triangle Park NC: National Toxicology Program, NTP 83-020, 1985.
9. NIOSH Current Intelligence Bulletin 51: Carcinogenic Effects of Exposure to Propylene Oxide, NIOSH, Cincinnati, OH, July 13, 1989.
10. NIOSH: Testimony of the National Institute for Occupational Safety and Health on the Occupational Safety and Health Administration's Proposed Rule on Air Contaminants, 29 CFR Part 1910, Docket No. H-020. Presented at the OSHA informal public hearing, August 1, 1988. NIOSH policy statements. Cincinnati, OH: US Dept of Health and Human Services, CDC, NIOSH, 1988.
11. NIOSH Testimony to the US Department of Labor: OSHA proposed rule: occupational exposure to ethylene oxide. NIOSH policy statements, Cincinnati, OH: US DHHS, PHS, CDC, NIOSH.
12. NIOSH: Occupational Respiratory Diseases, DHHS (NIOSH) Publication No. 86-102, Cincinnati, OH, 1986.
13. American Thoracic Society. ATS statement -- Standardization of Spirometry. Medical Section of the American Lung Association. Am Rev Respir Dis 136: 1285-1298, 1987.
14. NIOSH Guide to Industrial Respiratory Protection, NIOSH, Publication No. 87-116, Cincinnati, OH, September 1, 1987.

XII. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by: Jane Brown McCammon, MS, C.I.H.
Industrial Hygienist
Industrial Hygiene Section

Bruce Hills, C.I.H.
Industrial Hygienist
Industrial Hygiene Section

David Orgel, MD
Medical Officer
Medical Section
Surveillance Branch

Field Assistants: Dan Almaguer, MS
Industrial Hygienist
Industrial Hygiene Section

Barb Dames, BS
Biologist
Document Development Branch
Division of Standard Development and
Technology Transfer

Eugene Freund, MD
Medical Officer
Medical Section
Surveillance Branch

Analytical Support: UBTL
Salt Lake City, Utah 84108
Measurement Development Section, and
Measurement Support Section
Measurement Research and Support
Branch
Division of Physical Sciences and
Engineering
Cincinnati, Ohio 45226

Originating Office: Hazard Evaluations and Technical
Assistance Branch
Division of Surveillance, Hazard
Evaluations, and Field Studies

XIII. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are temporarily available upon request from NIOSH, Hazard Evaluations and Technical Assistance Branch, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. 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:

1. A.E. Staley Manufacturing Company
2. Allied Industrial Workers of America International Union (AIW)
3. AIW Local No. 837
4. OSHA, Region 5

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table 1

Limits of Detection (LOD) and Limits of Quantitation (LOQ)
of Analytical MethodsA.E. Staley Company
Decatur Illinois

HETA 88-348

| Analyte | Analytical Method | LOD (ug/sample) | LOQ (ug/sample) |
|--|------------------------------|-----------------|-----------------|
| sulfate | NIOSH P&CAM 268 | 0.7 | 2.2 |
| sulfite (on prefilter) | NIOSH P&CAM 268 | 0.5 | 1.7 |
| sulfite on treated filter | NIOSH P&CAM 268 | 3.0 | 9.0 |
| ethylene oxide | NIOSH 1612 | 10 | 30 |
| ethylene oxide | NIOSH 1614 | 0.2 | 0.6 |
| propylene oxide | NIOSH 1612 | 10 | 30 |
| aliphatic amines (as triethylamine) | NIOSH P&CAM 221 | 4 | - |
| mercaptans | Experimental | | |
| ethyl mercaptan | | 54 | - |
| propyl mercaptan | | 16 | |
| hydrogen sulfide | long duration detector tubes | 1.0 | - |
| sulfur dioxide | detector tubes | 0.5 | - |
| silica in bulk | NIOSH 7500 | | |
| quartz | | 0.75% | 1.5% |
| cristobalite | | 0.75% | 1.5% |
| quartz (secondary peak) | 3.8% | 7.5% | |
| cristobalite (secondary peak) | | 3.8% | 7.5% |
| sulfate in bulk | ion chromatography | 20 ug/gram | 38 ug/gram |
| sulfite in bulk | ion chromatography | 20 ug/gram | 54 ug/gram |

Table 2

Environmental Evaluation Criteria

A.E. Staley Company
Decatur, Illinois

HETA 88-348

| Substance | NIOSH | Evaluation Criteria ^a | |
|-----------------|-------------------------------------|---|---|
| | | OSHA | ACGIH |
| Propylene oxide | ^b | 20 ppm | 20 ppm |
| Ethylene oxide | <0.1 ppm 5 ppm 10-min ceiling | 1 ppm 5 ppm 15-min ceiling | 1 ppm |
| Sulfur dioxide | 1.3 mg/m ³ | 5 mg/m ³ 10 mg/m³ STEL | 5 mg/m ³ 10 mg/m ³ STEL |
| Sulfuric acid | 1 mg/m ³ | 1 mg/m ³ | 1 mg/m ³ |
| Vinyl acetate | 4 ppm 15-min ceiling | 10 ppm 20 ppm 15-min ceiling | 10 ppm 20 ppm 15-min ceiling |

^aEvaluation criteria are expressed as time-weighted average concentrations.

^bIn testimony presented to OSHA on August 1, 1988, regarding revision of permissible exposure limits, NIOSH stated that propylene oxide should be labeled as a potential occupational carcinogen. Although no numerical limit was recommended by NIOSH, policy of the Institute has been that exposure to potential carcinogens should be limited to the lowest feasible level.

STEL = Short term exposure limit

Table 3
 Airborne Concentrations of Propylene Oxide and Ethylene Oxide
 A. E. Staley Company
 Decatur, Illinois
 March 14, 1989 / Starch Processing / 1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|-------------------------|---------------------------|--------------------|-----------------|--------|----------------|--------|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Mechanic 1 | 0745-0830 | 0.0050 | 1500* | 630* | 22* | 12* |
| | 0830-0959 | 0.0066 | 11 | 4.6 | ND | ND |
| | 0959-1406 | 0.028 | ND | ND | ND | ND |
| Machinist | 0745-0855 | 0.017 | 100 | 42 | ND | ND |
| | 1207-1237 | | | | | |
| Mechanic 2 | 0740-0855 | 0.010 | 81 | 34 | ND | ND |
| | 1205-1235 | | | | | |
| Operator 1 | 0725-1112 | 0.022 | 110 | 46 | ND | ND |
| | 1112-1345 | 0.014 | ND | ND | ND | ND |
| Operator 1 | 0725-0825 | 0.0066 | 330 | 140 | ND | ND |
| | 0825-0949 | 0.0083 | 170 | 72 | ND | ND |
| | 0949-1112 | 0.0082 | (2.4) @ | (1.0) | ND | ND |
| | 1112-1233 | 0.0070 | ND | ND | ND | ND |
| | 1233-1335 | 0.0071 | ND | ND | ND | ND |
| | | | | | | |
| NIOSH 1 | 0730-0847 | 0.0081 | 530 | 220 | ND | ND |
| | 0849-1114 | 0.014 | 15 | 6.3 | ND | ND |
| NIOSH 2 | 0730-0852 | 0.0082 | 90 | 38 | ND | ND |
| | 1043-1115 | 0.0030 | ND | ND | ND | ND |
| | | | | | | |
| Engineer 1 | 1322-1401 | 0.0035 | (8.6) | (3.6) | (5.7) | (3.2) |
| Engineer 2 | 1322-1401 | 0.0039 | (7.7) | (3.2) | (5.1) | (2.8) |
| Salesman | 1322-1401 | 0.0039 | (7.7) | (3.2) | (5.1) | (2.8) |
| Reactors - upper level | | | | | | |
| Between 5 & 6 | 0735-0830 | 0.0061 | 5100* | 2100* | ND | ND |
| Center room | 0735-0830 | 0.0061 | 5600* | 2400* | ND | ND |
| Beside 7 | 0735-0830 | 0.0061 | 4800* | 2000* | ND | ND |
| | 0830-0927 | 0.0053 | 2800* | 1200* | ND | ND |
| Center room | 0830-0927 | 0.0052 | 2700* | 1100* | ND | ND |
| Beside 5 | 0830-0927 | 0.0052 | 2300* | 1000* | ND | ND |
| Beside 7 | 0937-1123 | 0.011 | (2.7) | (1.1) | 3.8* | 2.1* |
| Center room | 0937-1123 | 0.011 | 4.5 | 1.9 | 3.8* | 2.1* |
| Beside 5 | 0937-1123 | 0.011 | 5.6 | 2.4 | (2.8)* | (1.6)* |
| Beside 7 | 1125-1525 | 0.017 | (0.59) | (0.25) | 48* | 27* |
| Center room | 1125-1525 | 0.018 | (1.0) | (0.42) | 28* | 16* |
| Beside 5 | 1125-1525 | 0.019 | (1.0) | (0.42) | 59* | 33* |
| Reactors - ground level | | | | | | |
| Beside 7 | 0732-0830 | 0.0066 | 4700* | 2000* | ND | ND |
| Beside 7 | 0937-1123 | 0.011 | 3.6 | 1.5 | ND | ND |
| Beside 7 | 1130-1535 | 0.018 | (0.56) | (0.24) | 34* | 19* |
| Control room | 0730-1400 | 0.037 | 21 | 8.8 | ND | ND |

*Indicates that the backup section of the sampling tube contained greater than 30% of the reported analytical result.

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

@Bracketed values reflect analytical results which are between the LOD and the LOQ.

Table 4

Airborne Concentrations of Propylene Oxide and Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
March 14, 1989

Starch Processing
2nd Shift

| Job title/ Area | Time of sample <u>collection</u> | Sample volume <u>(M3)</u> | Propylene oxide | | Ethylene oxide | |
|-------------------------|--|---------------------------------|--------------------|------------|-------------------|------------|
| | | | <u>mg/M3</u> | <u>ppm</u> | <u>mg/M3</u> | <u>ppm</u> |
| Operator | 1515-1855 | 0.023 | ND | ND | (0.43) @ | (0.24) |
| Reactors - upper level | | | | | | |
| Beside 7 | 1530-1855 | 0.020 | ND | ND | ND | ND |
| Center room | 1530-1855 | 0.020 | ND | ND | ND | ND |
| Beside 5 | 1530-1855 | 0.020 | ND | ND | ND | ND |
| Reactors - ground level | | | | | | |
| Beside 7 | 1530-1855 | 0.021 | ND | ND | ND | ND |

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

@Bracketed values reflect analytical results which are between the limit of detection and the limit of quantitation for the method.

Table 5

Airborne Concentrations of Propylene Oxide and Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
March 15, 1989

Starch Processing
1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|---|---------------------------------|--------------------------|--------------------|---------|-------------------|--------|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Mechanic 1 | 0946-1127 | 0.011 | ND/ | ND | ND | ND |
| Mechanic 2 | 0946-1127 | 0.010 | (3.0) | @ (1.3) | ND | ND |
| Engineer | 1122-1134 | 0.0012 | ND | ND | ND | ND |
| Ground level, between tanks 1,2,3,4 | 1154-1345 | 0.0083 | ND | ND | (13)* | (7.2)* |
| Ground level, between tanks 5,6,7,8 | 1154-1343 | 0.0086 | ND | ND | ND | ND |
| Control room | 1157-1342 | 0.0080 | ND | ND | ND | ND |

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

@Bracketed values reflect analytical results which are between the LOD and the LOQ.

*Indicates that the backup section of the sampling tube contained greater than 30% of the reported analytical result.

Table 6

Airborne Concentrations of Propylene Oxide and Ethylene Oxide

A. E. Staley Company
Decatur, Illinois
March 16, 1989

Starch Processing
1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|--------------------|---------------------------------|--------------------------|--------------------|-----|-------------------|-----|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Operator 1 | 1310-1437 | 0.0088 | ND | ND | ND | ND |
| Operator 1 | 1310-1437 | 0.0088 | ND | ND | ND | ND |

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

Table 7

Airborne Concentrations of Propylene Oxide and Ethylene Oxide
A. E. Staley Company

Decatur, Illinois
March 16, 1989

Starch Processing
2nd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|-------------------------|---------------------------------|--------------------------|--------------------|-------|-------------------|---------|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Operator 1 | 1507-2032 | 0.032 | 5.0 | 2.1 | ND | ND |
| Operator 1 | 1507-1634 | 0.0086 | ND | ND | ND | ND |
| Operator 1 | 1635-1752 | 0.0076 | (2.6) @ | (1.1) | ND | ND |
| Operator 1 | 1754-2032 | 0.016 | 9.4 | 4.0 | ND | ND |
| Reactors - upper level | | | | | | |
| Reactor 7 | 1520-2046 | 0.034 | 330 | 140 | ND | ND |
| Reactor 8 | 1520-1630 | 0.0069 | ND | ND | ND | ND |
| Reactor 8 | 1631-1752 | 0.0081 | 23 | 9.7 | ND | ND |
| Reactor 5 | 1520-1627 | 0.0066 | ND | ND | ND | ND |
| Reactor 5 | 1628-1752 | 0.0083 | 6.0 | 2.5 | ND | ND |
| Reactor 8 | 1801-2046 | 0.017 | 110 | 46 | ND | ND |
| Reactor 5 | 1801-2046 | 0.016 | 34 | 14 | (1.2)* | (0.67)* |
| Reactors - ground level | | | | | | |
| Far | 1520-2046 | 0.031 | 100 | 42 | ND | ND |
| Middle | 1520-1625 | 0.0059 | ND | ND | ND | ND |
| Middle | 1635-1752 | 0.016 | 94 | 40 | ND | ND |
| Middle | 1801-2046 | 0.016 | 94 | 40 | (0.63) | (0.35) |

*Indicates that the backup section of the sampling tube contained greater than 30% of the reported analytical result.

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

@Bracketed values reflect analytical results which are between the LOD and the LOQ.

Table 8

Airborne Concentrations of Propylene Oxide and Ethylene Oxide
A. E. Staley CompanyDecatur, Illinois
March 16, 1989Starch Drying
Building 16
1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|--------------------|---------------------------------|--------------------------|--------------------|-----|-------------------|-----|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Reactor 28 | 0943-1354 | 0.025 | ND | ND | ND | ND |
| Reactor 28 | 0943-1354 | 0.026 | ND | ND | ND | ND |

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

Table 9

Airborne Concentrations of Propylene Oxide and Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
March 16, 1989

Flash Drying (Building 26)
2nd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Propylene oxide | | Ethylene oxide | |
|---|---------------------------------|--------------------------|--------------------|-----|-------------------|-----|
| | | | mg/M3 | ppm | mg/M3 | ppm |
| Relief operator | 1704-2137 | 0.027 | ND | ND | ND | ND |
| Product col- lection tank 4th floor | 1706-2137 | 0.023 | ND | ND | ND | ND |
| Paddle mixer- mezzanine | 1720-2130 | 0.025 | ND | ND | ND | ND |
| Near vibrating screens-3rd floor | 1726-2126 | 0.024 | ND | ND | ND | ND |
| Above chemical tank-Flash 2 | 1710-2123 | 0.025 | ND | ND | ND | ND |

/ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample for each analyte. The limit of quantitation (LOQ) was 0.03 milligrams per sample for each analyte.

TABLE 10

Airborne Concentrations of Vinyl Acetate
A. E. Staley Company
Decatur, Illinois
March 15, 1989

Waste Water Treatment Plant

| Job title/ Area | Time of sample collection | Sample volume (M3) | mg/M3 | ppm |
|---------------------------------------|---------------------------|--------------------|--------|--------|
| Operator 1 | 1647-1932 | 0.016 | 20 | 5.7 |
| Operator 2 | 1647-1932 | 0.015 | 4 | 1.1 |
| Operator 3 | 1347-1415 | 0.0031 | ND | ND |
| Filter tank | 1648-1940 | 0.016 | 26 | 7.4 |
| Filter downspout | 1650-1940 | 0.015 | 24 | 6.8 |
| Near filter | 1649-1940 | 0.016 | 20 | 5.7 |
| On press | 1717-1945 | 0.014 | 69 | 20 |
| Near the point of waste water removal | 1732-1945 | 0.013 | 62 | 18 |
| Tank 5-on ladder | 1340-1445 | 0.0063 | (4.8)@ | (1.4) |
| Tank 5-top near stairs | 1340-1445 | 0.0061 | (3.3) | (0.94) |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.01 milligrams per sample. The limit of quantitation (LOQ) was 0.03 milligrams per sample.

@Bracketed values reflect analytical results which are between the LOD and the LOQ.

Table 11

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 10, 1989

Starch Processing
2nd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|------------------------|---------------------------------|--------------------------|-------------------|------|
| | | | mg/M3 | ppm |
| Operator 1 | 1536-2237 | 0.023 | 0.17 | 0.09 |
| Operator 1 | 1536-2237 | 0.041 | 0.18 | 0.10 |
| Reactors - upper level | | | | |
| Tank 5 | 1550-2250 | 0.019 | 0.41 | 0.22 |
| | 1550-2250 | 0.039 | 0.62 | 0.34 |
| Tank 6 | 1550-2250 | 0.018 | 0.39 | 0.21 |
| | 1550-2250 | 0.040 | 0.22 | 0.12 |
| Tank 6 | 1550-2250 | 0.020 | 1.6 | 0.88 |
| | 1550-2250 | 0.039 | 1.9 | 1.0 |
| Reactors - lower level | | | | |
| Tank 5 & 6 | 1610-2250 | 0.039 | 0.02 | 0.01 |
| | 1610-2250 | 0.017 | 0.05 | 0.03 |
| Center room | 1614-2250 | 0.018 | 0.04 | 0.02 |
| | 1614-2250 | 0.038 | 0.09 | 0.05 |
| Control room desk | 1611-2237 | 0.019 | 0.13 | 0.07 |
| | 1611-2237 | 0.039 | 0.12 | 0.07 |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 12

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 10, 1989

Starch Drying

2nd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|--|---------------------------------|--------------------------|-------------------|---------|
| | | | mg/M3 | ppm |
| Building 16 above overflow hole, tank #2 | 1540-2320 | 0.021 | (0.01) | (0.01) |
| | 1540-2320 | 0.044 | 0.02 | 0.01 |
| Downstairs at pump to send batch to bldg 12, under tank #2 | 1545-2324 | 0.022 | ND | ND |
| | 1545-2324 | 0.043 | (0.01) | (0.004) |
| Building 12, 1 & 2 receiving tank on top | 1603-2339 | 0.024 | 1.5 | 0.82 |
| | 1603-2339 | 0.041 | 2.3 | 1.3 |
| Building 12, 3rd floor belt dryer | 1647-2337 | 0.036 | 0.04 | 0.02 |
| | 1647-2337 | 0.015 | (0.02) | (0.01) |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Bracketed values reflect analytical results which are between the LOD and the LOQ.

Table 13

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 10, 1989

Starch Processing
3rd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|------------------------|---------------------------------|--------------------------|----------------|------|
| | | | mg/M3 | ppm |
| Operator | 2245-0630 | 0.024 | 0.27 | 0.15 |
| | 2245-0630 | 0.052 | 0.40 | 0.22 |
| Reactors - upper level | | | | |
| Tank 1 | 2154-0705 | 0.023 | 5.7 | 3.1 |
| | 2154-0705 | 0.053 | 5.3 | 2.9 |
| Tank 2 | 2244-0704 | 0.048 | 2.0 | 1.1 |
| | 2244-0704 | 0.025 | 3.0 | 1.6 |
| Reactors - lower level | | | | |
| Tank 1 | 2152-0707 | 0.026 | 1.6 | 0.88 |
| | 2152-0707 | 0.053 | 0.94 | 0.52 |
| Tank 2 | 2244-0704 | 0.051 | 0.63 | 0.34 |
| | 2244-0704 | 0.024 | 0.36 | 0.20 |
| Control room desk | 2245-0702 | 0.026 | 0.25 | 0.14 |
| | 2245-0702 | 0.052 | 0.40 | 0.22 |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 14

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 11, 1989

Starch Processing
1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|------------------------|---------------------------------|--------------------------|-------------------|------|
| | | | mg/M3 | ppm |
| Operator | 0712-1522 | 0.029 | 0.08 | 0.04 |
| | 0712-1522 | 0.048 | 0.08 | 0.04 |
| Reactors - upper level | | | | |
| Tank 1 | 0728-1525 | 0.045 | 0.36 | 0.19 |
| | 0728-1525 | 0.021 | 0.42 | 0.23 |
| Tank 2 | 0732-1524 | 0.045 | 0.07 | 0.03 |
| | 0732-1524 | 0.022 | 0.10 | 0.06 |
| Reactors - lower level | | | | |
| Tank 1 | 0724-1525 | 0.046 | 0.07 | 0.04 |
| | 0724-1525 | 0.022 | 0.07 | 0.04 |
| Tank 2 | 0730-1525 | 0.044 | 0.25 | 0.14 |
| | 0730-1525 | 0.022 | 0.27 | 0.15 |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 15

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 11, 1989

Starch Drying
1st Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|---|---------------------------------|--------------------------|-------------------|------|
| | | | mg/M3 | ppm |
| Building 16, tank 12, second floor above open cap top | 0805-1614 | 0.044 | 0.32 | 0.17 |
| | 0805-1614 | 0.018 | 0.61 | 0.33 |
| Building 16, bottom floor tank 12 | 0809-1615 | 0.02 | 0.03 | 0.02 |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 16

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 11, 1989

Starch Processing
2nd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|------------------------|---------------------------------|--------------------------|-------------------|------|
| | | | mg/M3 | ppm |
| Operator | 1522-2203 | 0.039 | 0.04 | 0.02 |
| | 1522-2203 | 0.02 | 0.04 | 0.02 |
| Reactors - upper level | | | | |
| Tank 5 | 1527-2230 | 0.038 | ND | ND |
| | 1527-2230 | 0.010 | ND | ND |
| Tank 6 | 1528-2230 | 0.042 | ND | ND |
| | 1528-2230 | 0.019 | ND | ND |
| Reactors - lower level | | | | |
| Tank 5 | 1527-2230 | 0.040 | ND | ND |
| | 1527-2230 | 0.020 | ND | ND |
| Tank 6 | 1527-2230 | 0.038 | ND | ND |
| | 1527-2230 | 0.020 | ND | ND |
| Control room desk | 1522-2203 | 0.039 | 0.04 | 0.02 |
| | 1522-2203 | 0.020 | 0.03 | 0.02 |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 17

Airborne Concentrations of Ethylene Oxide
A. E. Staley Company
Decatur, Illinois
July 11, 1989

Starch Processing
3rd Shift

| Job title/ Area | Time of sample collection | Sample volume (M3) | Ethylene oxide | |
|---------------------------------------|---------------------------------|--------------------------|-------------------|--------|
| | | | mg/M3 | ppm |
| Operator 1 | 2245-0630 | 0.044 | 0.04 | 0.02 |
| | 2245-0630 | 0.022 | 0.03 | 0.02 |
| Reactors - upper level | | | | |
| Tank 5 | 2248-2315 | 0.002 | ND | ND |
| | 2315-2329 | 0.001 | (0.20) | (0.11) |
| Tank 6 | 2246-0730 | 0.025 | 0.15 | 0.08 |
| Reactors - lower level | | | | |
| Tank 5 & 6 | 2235-0720 | 0.028 | 0.13 | 0.07 |
| | 2235-0720 | 0.048 | 0.21 | 0.11 |
| Tank 5 | 2235-0730 | 0.026 | 0.15 | 0.08 |
| | 2235-0730 | 0.052 | 0.13 | 0.07 |
| Control room desk | 2337-0630 | 0.045 | 0.02 | 0.01 |
| | 2337-0630 | 0.022 | ND | ND |
| Outside hood sash in laboratory | 2240-0725 | 0.031 | (0.01) | (0.01) |

ND = non-detectable. The limit of detection (LOD) for these samples was 0.2 micrograms per sample. The limit of quantitation (LOQ) was 0.6 micrograms per sample.

Table 18

PREVALENCE OF WORK RELATED SYMPTOMS AMONG 66 EMPLOYEES:
 A. E. Staley Company
 Decatur, Illinois

| <u>SYMPTOM</u> | <u>ANY WORK</u> | <u>FUMES ONLY</u> |
|-----------------|-----------------|-------------------|
| Headache | 49 (74%)* | 31 (47%) |
| Sneezing | 47 (71%) | 21 (32%) |
| Cough | 39 (59%) | 22 (33%) |
| Post-nasal drip | 34 (51%) | 25 (38%) |
| Fatigue | 33 (50%) | 19 (29%) |
| Dyspnea | 29 (44%) | 14 (21%) |
| Dizziness | 27 (41%) | 16 (24%) |
| Muscle aches | 27 (40%) | 13 (20%) |
| Chest tightness | 22 (33%) | 9 (14%) |
| Hoarseness | 21 (30%) | 8 (12%) |
| Wheezing | 19 (29%) | 8 (12%) |
| Rash | 26 (24%) | 13 (20%) |
| Joint pain | 26 (24%) | 11 (17%) |
| Bronchitis | 14 (21%) | 6 (9%) |
| Fevers/chills | 13 (20%) | 5 (8%) |
| Numbness | 11 (17%) | 5 (8%) |
| Nausea/vomiting | 11 (17%) | 10 (15%) |
| Swelling | 7 (11%) | 2 (3%) |

* Number and (%) with symptoms

Table 19
DISTRIBUTION OF THOSE QUESTIONED BY BUILDING

A. E. Staley Company
Decatur, Illinois

BUILDING

| | |
|---------------------|-----------|
| 17 (Packing house) | 19 (30%)* |
| 16 (Bleach) | 13 (20%) |
| 54 (Maintenance) | 13 (20%) |
| 5/10 (Syrup) | 10 (16%) |
| 2 (Engine room) | 6 (9%) |
| 19 (Waste operator) | 2 (3%) |
| 6 | 1 (2%) |

* Number and (%) with symptoms.

Table 20
DISTRIBUTION OF THOSE QUESTIONED BY OCCUPATION

A. E. Staley Company
Decatur, Illinois

JOB

| | |
|-------------|-----------|
| Operator | 37 (56%)* |
| Maintenance | 26 (39%) |
| Supervisor | 2 (1%) |
| Unknown | 2 (1%) |

* Number and (%) with symptoms.