HETA 88-340-2048
JUNE 1990
NATIONAL STARCH AND CHEMICAL COMPANY
ISLAND FALLS, MAINE

NIOSH INVESTIGATOR
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## I. SUMMARY

In August 1988, the National Institute for Occupational Safety and Health (NIOSH) received a request from the American Federation of Grain Millers to evaluate exposures to propylene oxide, starch dust, phosphorus oxychloride, epichlorohydrin, and the potential for starch dust explosion at National Starch and Chemical Company in Island Falls, Maine.

NIOSH investigators conducted a site visit on October 12, 1988 and on July 27-29, 1989, to monitor workers' exposure to propylene oxide, epichlorohydrin, and starch dust. Based upon observation of the process, the potential for exposures to phosphorus oxychloride did not appear to be high enough to conduct exposure monitoring. Area propylene oxide air concentrations ranged from less than 0.1 to 10.7 parts per million (ppm) in 15 samples collected in the reactor room and other areas of the plant. Forty-two personal breathing-zone samples were collected from 18 employees on three work shifts over three consecutive days. The employees had 8-hour time-weighted average (TWA) exposures ranging from less than 0.1 to 5.8 ppm. The highest personal breathing-zone exposure occurred when an operator failed to follow operational procedures during the pumping of propylene oxide into a vat. The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for propylene oxide are 20 ppm as an 8-hour TWA. NIOSH recommends that propylene oxide be considered a potential occupational carcinogen and that worker exposures be reduced to the lowest feasible concentrations.

Two personal breathing zone samples for epichlorohydrin were collected from an operator. One sample result collected during the handling of epichlorohydrin was 13.2 ppm for a 16-minute period. A second personal sample collected during this shift (510 minutes) was 0.2 ppm. OSHA has established a PEL for epichlorohydrin of 2 ppm as an 8-hour TWA. NIOSH has recommended that epichlorohydrin be treated as a human carcinogen and exposures be limited to the lowest feasible concentrations.

Five personal breathing-zone sample results for total nuisance dust (starch dust) ranged from an 8-hour TWA of 3.2 to 18.1 milligrams per cubic meter of air ($mg/m^3$). The OSHA 8-hour PEL for total nuisance dust is 15 $mg/m^3$. The ACGIH TLV for starch is 10 $mg/m^3$. In many areas of the plant starch dust is present on surfaces as well as in the air.

Although propylene oxide concentrations are below the OSHA PEL, detectable concentrations were present in the reactor room and other areas of the plant; these should be reduced to the lowest feasible concentration. Controls, such as improving the tightness of equipment seals, and close attention to operational procedures should reduce propylene oxide exposures. The presence of even a fine layer of starch dust on surfaces is a potential fire and explosion hazard, therefore, airborne and surface starch dust should also be reduced to the lowest feasible levels.

KEYWORDS: SIC 2046, wet corn milling, propylene oxide, starch, epichlorohydrin, tapioca, dust

## II. INTRODUCTION

On August 3, 1988, the National Institute for Occupational Safety and Health (NIOSH) received a request from the American Federation of Grain Millers (AFGM) to evaluate exposures to propylene oxide, starch dust, phosphorus oxychloride, epichlorohydrin, and the potential explosion hazard from starch dust at National Starch and Chemical Company in Island Falls, Maine. Field surveys were conducted on October 12, 1988 and on July 27-29, 1989.

## III. BACKGROUND

The facility was built in 1957 and sold to National Starch and Chemical Company in 1977. Originally the plant processed potatoes for starch and dextrin. In 1963, production of tapioca starches for food and industrial uses began. Currently the company utilizes tapioca starch and a limited amount of potato and corn starch to produce 40 different speciality starches. The plant operates three work shifts with 69 hourly and 19 salary employees.

Propylene oxide is a major ingredient in the production of speciality tapioca starches. The propylene oxide is stored outside the processing building in an underground tank. When propylene oxide is needed, the required amount is pumped to one of five reactor vessels (vats A, B, C, D, and E) in the reactor room where the tapioca starch is processed. The vats all have steel covers with an agitator shaft entering from the top of the vessel with PTFE (polytetrafluoroethylene) packed seals. There is also a hatch door on the top of each vessel to collect samples or to add ingredients. Before pumping the propylene oxide, the lines to the vat are purged with nitrogen to prevent an explosive mixture of oxygen and propylene oxide vapor from forming. The head space of the vats is also blanketed with nitrogen during the reaction cycle to limit oxygen concentrations to below 10%. Fans are located at the top of each vat to exhaust vapors from the head space to outside the building whenever the hatch is opened. This is followed by another nitrogen purge. Once the propylene oxide is added, the starch slurry is heated and mixed for at least one day. During the processing, several of the following chemicals may be added to the slurry depending on the type of product desired: sulfuric acid, hydrochloric acid, hydrogen peroxide, sodium hypochlorite, aluminum sulphate, sodium hydroxide, and phosphorus oxychloride. Although monitoring was not conducted for these substances, exposures appeared to be minimal. The phosphorus oxychloride is stored and weighed on the reactor room mezzanine and manually poured into the vats through the hatch doors. One to three times a month an operator will added 10 to 15 pounds of epichlorohydrin to a single batch of potato starch slurry that will be used for industrial applications. The epichlorohydrin is stored and weighed in a shed outside of the reactor building then hand carried in a plastic container into the building and poured into the vats. After the starch slurry is processed, the slurry should contain only a few parts per million (ppm) propylene oxide. The starch slurry is then pumped out of the vat and undergoes a series of filtering, drying, grinding, blending, and finally bagging in other departments.

The processing of the starch in the reactor room is performed mainly by the operators. Other employees who occasionally enter the reactor room are supervisors, maintenance personnel, and filter operators from the drying department. Food room packers who do not normally enter the reactor room; they bag and package starch in areas adjacent to the reactor room.

## IV. METHODS

NIOSH investigators conducted an initial evaluation of the Island Falls, Maine facility on October 12, 1988. The investigation began with a meeting with management and union representatives on potential health problems within the plant. During this meeting, copies of industrial hygiene records, the OSHA Log and Summary of Occupational Injuries and Illness, a list of employees, flow-through diagrams of the process, a diagram of the plant layout, and a list of all chemicals used in the process were obtained. Following the meeting, a walk-through inspection of the starch modification processes was conducted.

Upon review of the company records and completion of the walk-through inspection, the investigators concluded that there was a potential employee exposure to propylene oxide, epichlorohydrin, and starch dust. Many other chemicals were present in the plant but the potential for exposure was not as great as the above three compounds. A return visit to monitor employees' exposure to these compounds was scheduled. On July 27-29, 1989, environmental monitoring was performed for propylene oxide, epichlorohydrin, and starch dust.

A. Propylene oxide

Personal breathing zone samples were collected from employees who worked in the reactor room, the filter-drying area and the dumping-storage-blending area. Short-term as well as full-shift personal breathing-zone samples were collected from employees in the reactor room since high concentrations of propylene oxide can saturate the charcoal media resulting in propylene oxide breakthrough. In addition, the consecutive short-term samples identified short-term exposures associated with process and job activities. Area air samples were also collected in the reactor room.

Sampling began on July 27th at 0710 hours and continued during all shifts until July 29th at 1500 hours. Personal breathing-zone samples were collected from seven reactor operators, three supervisors, three maintenance workers, three filter operators, and two tag dumpers (packers). Fifteen area samplers were placed in the reactor room on the mezzanine and on vats B, D, and E.

The addition of propylene oxide to the vats has typically been the period of greatest propylene oxide emissions into workroom air. Propylene oxide was added to vat C on July 27th at 1520, to vat E on July 28th at 0500, to vat B on July 28th at 1230, and to vat D on July 29th at 0430.

The propylene oxide air samples were collected on 100/50 mg charcoal tubes at a flow-rate of 0.2 liters per minute. All collected samples were stored below 0ºC until analysis. The samples were then desorbed with carbon disulfide and analyzed by gas chromatography according to NIOSH Method No. 1612.(1) The limit of detection was 0.01 mg per sample.

B. Epichlorohydrin

Epichlorohydrin was added to a vat on July 27 at 1420 by Operator 1. Two breathing zone samples were collected from this worker, one for 16 minutes during the weighing, transporting, and pouring of the epichlorohydrin, and a second for the entire 510 minutes of his work shift. The two samples were collected on 100/50 mg charcoal tubes at a flow-rate of 0.2 liters per minute and stored below 0ºC until analyzed The samples were then desorbed with carbon disulfide and analyzed by gas chromatography according to NIOSH Method No. 1010.(1) The limit of detection was 0.01 mg per sample.

C. Total Dust

On July 28th, personal breathing zone samples were collected for total nuisance dust from 5 Food Packers who worked in the drying and dumping-storage-blending departments. All samples were collected on pre-weighed 37-mm, 5-um pore size, polyvinyl chloride membrane filters at a flow-rate of either 2 or 3 liters per minute. Gravimetric analysis of the samples was performed according to NIOSH Method No. 0500.(1)

## V. EVALUATION CRITERIA

### A. 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.(2) Exposure to propylene oxide can also result in a reduced capacity to repair DNA lesions. Twenty-three workers exposed to propylene oxide in a factory producing alkylated starch had reduced capacity for unscheduled DNA synthesis following the in vitro induction for DNA damage to their blood lymphocytes.(3) 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.(4) 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.(5)

The Occupational Safety and Health Administration (OSHA) has recently established an 8-hour time-weighted average (TWA) PEL of 20 ppm for propylene oxide to protect workers against the risk of primary irritation and central nervous system depression.(6) However, during the OSHA rule-making process, NIOSH disagreed with the proposed permissible exposure limit (PEL), recommending that propylene oxide be designated as a potential occupational carcinogen.(7)

The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) is 20 ppm as an 8-hour TWA.(8) The ACGIH TLV TWA is based on the acute toxicity of propylene oxide and its "lesser toxicity in relation to ethylene oxide".(9)

### B. Epichlorohydrin

Epichlorohydrin is a colorless liquid with an irritating, chloroform-like odor. Worker exposure to epichlorohydrin may occur by either ingestion, inhalation, or dermal contact. The International Agency for Research on Cancer reported that there is sufficient evidence for the carcinogenicity of epichlorohydrin in experimental animals, however, there is inadequate evidence for the carcinogenicity of epichlorohydrin in humans.(10) OSHA has established a PEL for epichlorohydrin of 2 ppm as an 8-hour TWA. NIOSH has recommended that epichlorohydrin be treated as a human carcinogen and exposure be limited to the lowest level possible.(11)

### C. Total Nuisance Dusts (corn, tapioca, and potato starches)

Airborne nuisance dusts, which include corn, tapioca, and potato starches, are supposedly dusts which have few adverse effects on the lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. OSHA's 8-hour PEL for nuisance dust is 5 $mg/m^3$ for respirable dust and 15 $mg/m^3$ for total dust.(8) The ACGIH recommends that exposure to starch not exceed 10 $mg/m^3$.(9) NIOSH has not recommended an exposure level for nuisance dust.

Although starches are considered non-toxic, starch dust is a fire and explosion hazard. The Bureau of Mines has classified most starches as having a "severe" explosion potential. The National Fire Protection Association has detailed standards for the manufacturing and handling of starch.(12) The standards include requirements for structural features, ventilation, explosion protection, equipment, starch dryers, dust control, house keeping, electrical, fire protection, cutting, welding, spark-operations, and other topics.

## VI. RESULTS

### A. Propylene Oxide

Forty-two personal breathing zone samples were collected from seven reactor operators, three supervisors, three maintenance workers, three filter operators, and two tag dumpers (packers) (Table 1). The operators had 8-hour TWA propylene oxide exposures ranging from less than 0.1 to 5.8 ppm. The highest exposure (5.8) ppm occurred to Operator 5 on July 28-29 on the 3rd shift. During the same period an area sample collected in the mezzanine measured 10.7 ppm. Some factors that may have contributed to these levels are; propylene oxide was pumped into vat D at 0430, the sodium hydroxide valve on vat D was left open, possibly allowing propylene oxide vapor to be released into the reactor room, the hatch door to vat D was not closed tightly, and the ceiling fan above the vessels used to vent fumes and vapors was turned off during the shift. The supervisors, maintenance personal, filter operators, and tag dumpers had 8-hour TWA exposures ranging from less than 0.1 to 0.7 ppm. The highest short-term exposure amoung this group was also 0.7 ppm which occurred on July 27th between 0725 and 0752 when a maintenance employee was in the reactor room. Fifteen area samples collected in the reactor room ranged from less than 0.1 to 10.7 ppm (Table 2).

### B. Epichlorohydrin

Epichlorohydrin was added to a vat on July 27 at 1420 by Operator 1. The operator wore a neoprene apron, gloves, boots, a face shield, and a 3M half face cartridge respirator (TC 23C-443). The operator was qualitatively fit tested for this respirator and also wears it during the weighing and pouring of phosphrous oxychloride. Two breathing zone samples were collected from this workers (outside of his respirator) (Table 3). One sample collected during the handling of epichlorohydrin measured 13.2 ppm for a 16 minute period. Assuming that no further exposure to epichlorohydrin occurred during the shift, his 8-hour TWA exposure would be 0.7 ppm. A second personal sample collected during his shift (510 minutes) measured 0.2 ppm.

### C. Total Dust

On July 28th, personal breathing zone samples for total nuisance dust were collected from 5 Food Packers who worked in the drying and dumping-storage-blending departments. The 8-hour TWA exposures ranged from 3.2 to 18.1 $mg/m^3$ which is in excess of the OSHA total dust standard of 15 $mg/m^3$. Exposures were greatest during the bagging of the starch.

## VII. CONCLUSIONS

Propylene oxide vapor is present in the reactor room and possibly at low concentrations in other areas of the plant. Propylene oxide concentrations were approximately 10 times greater on July 28-29 during pumping of propylene oxide into vat D than on the other shifts. The cause of this excursion was mainly due to propylene oxide being pumped into a vat when the sodium hydroxide valve on was left open, the hatch door not closed tightly, and the ceiling fan above the vessels used to vent fumes and vapors was turned off during the shift.

Although propylene oxide concentrations are below the OSHA PEL, there are still low levels present in the work area. Since propylene oxide is considered by NIOSH to be a potential occupational carcinogen, employee exposures should be reduced to the lowest feasible level.

Exposure to epichlorohydrin should be minimal because the operators wear respirators during the weighing, transporting, and pouring. Since epichlorohydrin is a regulated carcinogen, automating the addition of epichlorohydrin to the process would most likely further reduce employees' exposure to epichlorohydrin.

Two of the five food packers monitored were exposed to starch levels in excess of the ACGIH TLV of 10 $mg/m^3$. One of these employees was exposed to total nuisance dust (starch) level in excess of the OSHA PEL on 15 $mg/m^3$.

Starch dust on surfaces is common throughout most areas of the plant. Although the complete removal of all fugitive starch is extremely difficult, the presence of even a fine layer of starch dust on surfaces is a potential fire or explosion hazard.

## VIII. RECOMMENDATIONS

1. To further reduce propylene oxide exposures in the plant atmosphere, the following steps should be taken:

    a. Agitator shaft seals on the vats should be routinely inspected.

    b. Seals on the hatch doors should be routinely checked.

    c. Propylene oxide in the starch slurry should be completely reacted before the slurry is pumped to the filtering and drying department.

    d. Access to the reactor room should be limited to only essential employees.

    e. Operators need to review operational procedures to prevent the escape of propylene oxide vapors into the work area.

2. The hood used to provide local ventilation during the weighing of phosphorus oxychloride should be improved. Enclosing the weighing station with a booth would be more effective.

3. Starch dust levels should be reduced in the food packing area to levels below the ACGIH TLV of 10 $mg/m^3$. All efforts to reduce airborne starch dust, through housekeeping and engineering controls, will also reduce the potential for fire or explosion.

## IX. REFERENCES


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## X. AUTHORSHIP AND ACKNOWLEDGEMENTS


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## XI. DISTRIBUTION AND AVAILABILITY OF REPORT

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1. National Starch and Chemical Company
2. American Federation of Grain Millers, Local 234
3. American Federation of Grain Millers, International
4. NIOSH, Boston Region
5. OSHA, Region I

In order to comply with NIOSH's regulations regarding informing affected employees (CFR, Title 42, Part 85a, Section 85.11), 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

Personal Breathing Zone Samples for Propylene Oxide

National Starch and Chemical Company
Island Falls, Maine
HETA 88-340

July 27-29, 1989

| Job Titles | Sample No. | Date July | Time Hours | 8-Hour TWA ppm | 8-Hour TWA in ppm |
|---|---|---|---|---|---|
| Operator 1 | C2 | 27 | 0710-1050 | 0.8 | |
| | C11 | 27 | 1050-1416 | 2.4 | |
| | C17 | 27 | 1432-1446 | ND | |
| | C12 | 27 | 1416-1432 | ND | 1.4 |
| Operator 1 | C18 | 27 | 0715-1545 | 1.7 | 0.8 |
| Operator 2 | C3 | 27 | 0715-1055 | 0.2 | |
| | C16 | 27 | 1055-1440 | 0.1 | 0.1 |
| Operator 2 | C15 | 27 | 0715-1439 | 0.2 | 0.2 |
| Operator 3 | C6 | 27 | 0720-1120 | 0.6 | |
| | C14 | 27 | 1120-1435 | 0.5 | 0.5 |
| Operator 3 | C13 | 27 | 0720-1434 | 0.6 | 0.5 |
| Operator 4 | C23 | 27 | 1515-1555 | ND | |
| | C26 | 27 | 1555-2245 | ND | ND |
| Operator 4 | C27 | 27 | 1502-2245 | 0.1 | 0.1 |
| Operator 4 | C61 | 29 | 1500-2250 | 2.4 | 2.1 |
| Operator 5 | C30 | 27-28 | 2300-0645 | 0.2 | 0.2 |
| Operator 5 | C48 | 28-29 | 2300-0645 | 5.9 | 5.8 |
| Operator 6 | C38 | 28 | 0815-1450 | ND | ND |
| Operator 7 | C36 | 28 | 0702-1500 | 0.2 | 0.2 |
| Operator 7 | C55 | 29 | 0704-1500 | 1.1 | 1.1 |

continued

TABLE 1 (continued)

Personal Breathing Zone Samples for Propylene Oxide

National Starch and Chemical Company
Island Falls, Maine
HETA 88-340

July 27-29, 1989

| Job Titles | Sample No. | Date July | Time Hours | 8-Hour TWA ppm | 8-Hour TWA in ppm |
|---|---|---|---|---|---|
| Supervisor 1 | C7 | 27 | 0715-1120 | ND | |
| | C19 | 27 | 1120-1500 | 0.5 | 0.2 |
| Supervisor 1 | C24 | 27 | 0715-1900 | 0.1 | 0.2 |
| Supervisor 2 | C31 | 27-28 | 2300-0645 | ND | ND |
| Supervisor 2 | C47 | 28-29 | 2250-0645 | ND | ND |
| Supervisor 3 | C39 | 28 | 0802-1500 | ND | ND |
| Supervisor 3 | C57 | 28 | 0820-1530 | 0.1 | 0.1 |
| Maintenance 1 | C1 | 27 | 0725-0752 | 0.7 | 0.1 |
| Maintenance 2 | C5 | 27 | 0715-1116 | ND | |
| | C9 | 27 | 1116-1445 | ND | ND |
| Maintenance 2 | C10 | 27 | 0715-1445 | ND | ND |
| Maintenance 3 | C51 | 29 | 0920-0935 | ND | ND |
| Maintenance 3 | C56 | 29 | 1132-1500 | ND | ND |
| Filter Operator 1 | C8 | 27 | 0715-1120 | ND | |
| | C21 | 27 | 1120-1510 | 0.4 | 0.2 |
| Filter Operator 1 | C25 | 27 | 0715-1900 | 0.1 | 0.1 |
| Filter Operator 2 | C29 | 27-28 | 2300-0645 | 0.2 | 0.2 |
| Filter Operator 3 | C41 | 28 | 0920-1700 | 0.1 | 0.1 |
| Filter Operator 3 | C62 | 29 | 0922-1900 | 0.6 | 0.7 |
| Tag Dumper 1 | C37 | 28 | 0705-1445 | ND | ND |
| Tag Dumper 1 | C54 | 29 | 0740-1500 | ND | ND |
| Tag Dumper 2 | C46 | 28 | 0700-1500 | 0.1 | 0.1 |

ND = non-detectable (less than 0.01 mg per sample)
OSHA PEL for propylene oxide is 20 ppm (parts per million) as an 8-hour TWA.
NIOSH recommends that exposures be reduced the lowest feasible level.

TABLE 2

Area Air Samples for Propylene Oxide

HETA 88-340

National Starch and Chemical Company
Island Falls, Maine

July 27-29, 1989

| Location | Sample No. | Date-July | Time-hours | ppm |
|---|---|---|---|---|
| Mezzanine | C4 | 27 | 0805-1100 | 1.8 |
| Mezzanine | C20 | 27 | 1100-1505 | 1.2 |
| Mezzanine | C22 | 27 | 1505-1550 | 2.1 |
| Mezzanine | C28 | 27 | 1550-1055 | 3.6 |
| Mezzanine | C32 | 27-28 | 2255-0645 | 0.7 |
| Mezzanine | C40 | 28 | 0817-1502 | 2.4 |
| Vats G & F | C43 | 28 | 1400-2300 | 0.7 |
| Vat B | C44 | 28 | 1400-2300 | 0.7 |
| Mezzanine | C49 | 28-29 | 2245-0700 | 0.7 |
| Mezzanine | C50 | 28-29 | 2245-0700 | 10.7 |
| Vat B | C52 | 29 | 0710-1450 | 1.9 |
| Vat D | C53 | 29 | 0710-1455 | 1.1 |
| Vat E | C60 | 29 | 1455-1550 | ND |
| Vat B | C63 | 29 | 1450-2250 | 1.3 |
| Vat E | C64 | 29 | 1550-2250 | 3.9 |

ND = non-detectable (less than 0.01 mg per sample)

TABLE 3

Personal Breathing Zone Samples for Epichlorohydrin

HETA 88-340

National Starch and Chemical Company
Island Falls, Maine

July 27-29, 1989

| Job Titles | Sample No. | Date July | Time Hours | ppm | 8-Hour TWA in ppm |
|---|---|---|---|---|---|
| Operator 1 | C12 | 27 | 1416-1432 | 13.2 | 0.7 |
| Operator 1 | C18 | 27 | 0715-1545 | 0.2 | 0.2 |

OSHA PEL for epichlorohydrin is 2 ppm (parts per million) as an 8-hour TWA (time-weighted average).

NIOSH recommends that exposures be reduced the lowest feasible level.

TABLE 4

Personal Breathing Zone Samples for Total Dust

HETA 88-340

National Starch and Chemical Company
Island Falls, Maine

July 28, 1989

| Job Title | Sample No. | Time (minutes) | $mg/m^3$ | 8-Hour TWA $mg/m^3$ |
|---|---|---|---|---|
| Packer 1 | 6260 | 435 | 20.0 | 18.1 |
| Packer 2 | 6262 | 379 | 11.6 | 9.1 |
| Packer 3 | 5940 | 380 | 14.4 | 11.4 |
| Packer 4 | 6270 | 375 | 5.7 | 4.5 |
| Packer 5 | 5957 | 380 | 4.0 | 3.2 |

The ACGIH TLV for total nuisance dust and starch is 10 $mg/m^3$ as an 8-hour TWA.

The OSHA PEL for total nuisance dust is 15 $mg/m^3$ as an 8-hour TWA.