

CONTROL TECHNOLOGY ASSESSMENT
OF CHEMICAL PROCESSES

Quaker Oats Company
Chemicals Division
Omaha, Nebraska

Preliminary Survey Report
for the Site Visit of
August 19, 1981

Contract No. 210-80-0071

February 2, 1982

Submitted to:

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REPORT NO.:
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I. INTRODUCTION

A. Summary of Visit

The Omaha, Nebraska Plant of the Quaker Oats Company, Chemicals Division was visited by representatives of Enviro Control, Inc. on August 19, 1981 to conduct a preliminary survey of the techniques used to control worker exposure to hazardous substances.

Participants included:

Quaker Oats Company

Lee D. Meyer, Manufacturing Manager

John Curran, Furfural and Unloading Department Manager

John Mutchler, Corporate Director of Health and Safety

Michael Gibson, Technical Manager

Carl Turner, Employee and Community Relations Manager

Richard Klostermeyer, Safety and Training Supervisor

National Institute for Occupational Safety and Health

Harold Van Wagenen, Project Officer

Enviro Control, Inc.

Julius H. Bochinski, Program Manager

Steven L. Bergh, Chemical Engineer

The survey was completed in one day. It included discussions of the processes involved, inspections of the processes and associated control equipment, and detailed discussions of the control techniques of interest. This report summarizes the processes and describes in detail the control techniques observed. All Quaker Oats personnel involved were very cooperative in providing information on the installation and processing equipment, process descriptions, industrial hygiene problems, specific hazards of the chemicals handled, operator training, and safety standards for specific jobs and operations.

B. Background Information on Contract

This visit was conducted as part of the Control Technology Assessment of Chemical Processes, NIOSH Contract No. 210-80-0071. The purpose of this contract is to identify and assess superior control techniques for controlling worker exposure to hazardous substances during chemical processing. This is being done through extensive visits to industrial facilities. Preliminary surveys are intended to generate information about the control strategies used at various facilities and will be used to determine which facilities warrant further, in-depth surveys. Information collected from the visits will be compiled into a control technology reference source to aid in the solution of worker exposure problems in industry.

II. PLANT AND PROCESS DESCRIPTION

This plant produces furfural and furfuryl alcohol (FA) in two separate processes. Agricultural residues such as corn cobs and oat hulls are used to make furfural, the major portion of which is then used to make FA. FA can be sold as is or used to make a variety of products at other processing facilities. The following sections discuss the processes and identify emission points and associated control techniques which are summarized in Figures 1 and 2.

A. Furfural (see Figure 1)

Raw materials used in making furfural (usually corn cobs or oat hulls) arrive at the plant via rail cars or trucks. Corn cobs are unloaded by gravity and subjected to a series of grinding operations before being sent to the furfural plant. Oat hulls require no such pre-processing. Both raw materials are transported by a system of conveyors, vibratory shakers and material elevators and can generate substantial nuisance dust. Control of inhalation exposures to airborne dust is done largely through good housekeeping practices and local exhaust ventilation. The semi-enclosed or isolated nature of the handling operations also contributes. Where workers must attend

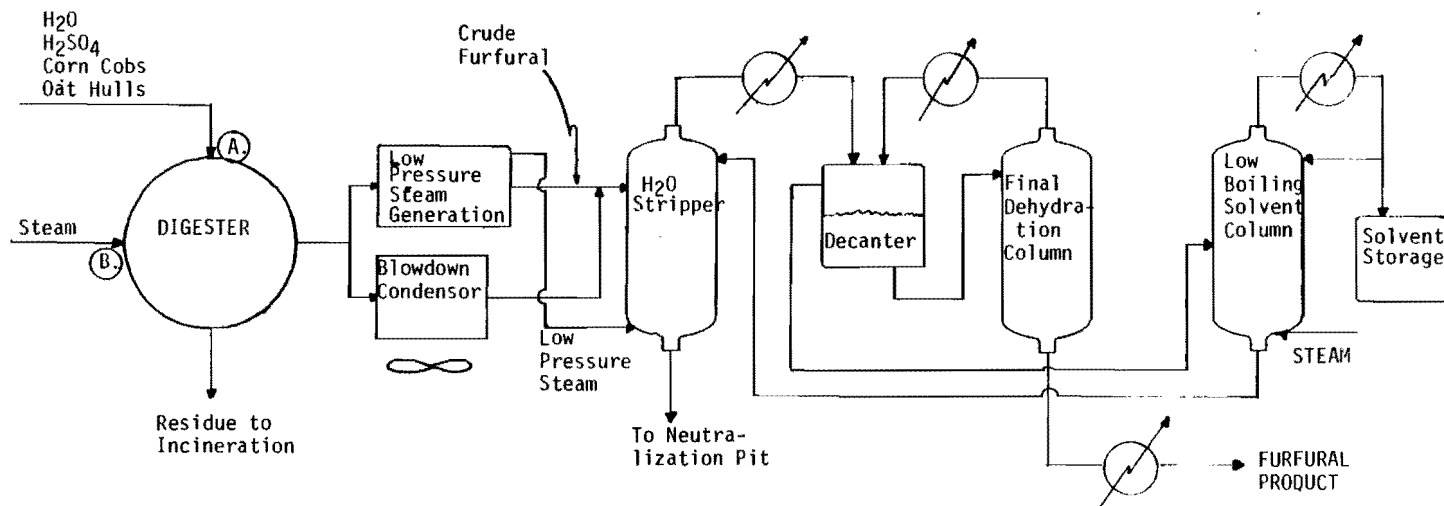
FIGURE 1: FURFURAL

POTENTIAL EMISSION/EXPOSURE POINTS

- (A.) Charging of Raw Materials to Digester
- (B.) Failure of Digester Shaft Seal

CONTROL TECHNIQUES

- (A.) Enclosed Conveyor and Charging Chute
- (B.) Mechanical Packing



POTENTIALLY HAZARDOUS CHEMICALS INVOLVED

Agent	PEL	Chemical and Physical Properties		Health Hazard	
				Route of Entry	Effect
Furfural	5 ppm	M.P.	-34°F	Inhalation	Irritant
		B.P.	323°F	Ingestion	
		V.P.	2 mm	Contact	
		Solubility	8.3%		
H ₂ SO ₄	1 mg/m ³	M.P.	37°F	Inhalation	Irritant
		B.P.	518°F	Ingestion	
		V.P.	<0.001mm	Contact	
		Solubility	Miscible		

to equipment in high dust areas, personal respiratory protection is also employed. The essentially dust-free operation of the facility is impressive.

In the next processing step the dry agricultural residues are conveyed to the reactors, or digesters. These are large, spherical, rotating vessels with a manway on top. The dry materials are charged to the digester through this opening by a system of conveyors, hoppers and scales in an enclosed or semi-enclosed environment. A special charging chute and local exhaust ventilation are used in this operation to limit the emission of residual furfural vapor and airborne dust to the workplace during loading of the reactor. The charging chute is discussed further in Section III, A. In addition to the dry materials, dilute sulfuric acid is added to the digester through the charging chute. During reaction the digesters are pressurized with steam to achieve the hydrolysis necessary to convert pentosans in the agricultural residue to furfural. Sulfuric acid is added through permanent or semi-permanent hose arrangements which normally preclude any worker exposure. During the reaction stage, the digesters rotate on large bearings concentric to a mechanically-packed header through which steam is introduced and furfural vapors are extracted. Emission of furfural and worker exposure to it can occur if the packing deteriorates. Details on this packing are presented in Section III, B.

Vapors from the digester are condensed and passed into a stripping column from which an enriched furfural-water distillate is withdrawn. This is condensed, fed to a decanter and separated into two layers. The furfural layer is further enriched in another dehydrating column to obtain the final product. The aqueous layer, containing 8 to 9% furfural is returned to the stripper as reflux after another distillation. The process equipment in this area is totally enclosed and does not normally present exposure problems.

After a reaction cycle is completed the digester opening is uncovered. The vessel is rotated and as it becomes inverted, residue is discharged by gravity into a hopper below the digester. Since residue contains low levels of furfural, acetic acid and formic acid, general dilution ventilation is used to avoid buildup of these vapors in the area.

Exposure to furfural vapors has been determined to be below the OSHA Permissible Exposure Levels of 5 ppm for all personnel involved in the process. 8-hour Time-Weighted Averages (TWA) area samples range from 2.2 ppm to 4.3 ppm. Highest exposure occurs during dumping of the digester residue. A short-term (1 hr) personal sample taken for the digester dumper during the dumping operation showed exposure to be 8.4 ppm. This is below the 1981 American Congress of Government Industrial Hygienists (ACGIH) Short Term Exposure Limit of 10 ppm. In 1981 the ACGIH reduced their recommended 8 hr. TWA level for furfural from 5 ppm to 2 ppm based on experience with respiratory tract and eye irritation of production workers. Quaker Oats has furnished the ACGIH their industrial hygiene data for furfural in support of a higher 8 hr TWA (See Appendix 3.0 for Quaker Oats letter of April 8, 1981 to ACGIH).

B. Furfuryl Alcohol (see Figure 2)

Furfural is converted to furfuryl alcohol (FA) by direct hydrogenation in a continuous processing installation located in a separate, newer building. After preheating and vaporization, the hydrogen and furfural stream is passed through reactors containing a copper-based catalyst bed. The reactor effluent, containing FA and excess hydrogen, is condensed and sent to a holding tank. Excess hydrogen is withdrawn for recycle from this tank. The product FA is then sent to a vacuum dehydrator to distill off any water present before being stored. The totally enclosed nature of the process limits the opportunities for worker exposure during normal operation.

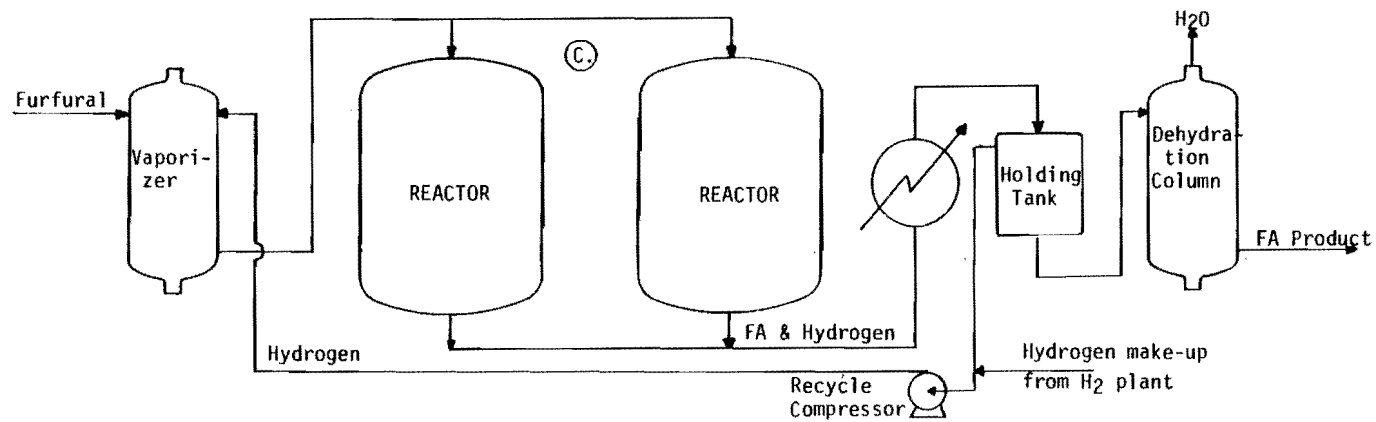
FIGURE 2: FURFURYL ALCOHOL

POTENTIAL EMISSION/EXPOSURE POINTS

- (C.) Dumping and Blowing of Catalyst from Reactors During Changeout

CONTROL TECHNIQUES

- (C.) Catalyst Vacuum System



POTENTIALLY HAZARDOUS CHEMICALS INVOLVED

Agent	PEL	Chemical and Physical Properties		Health Hazard	
				Route of Entry	Effect
Furfural	5 ppm	M.P.	-34°F	Inhalation	Irritant
		B.P.	323°F	Ingestion	
		V.P.	2 mm	Contact	
		Solubility	8.3%		
Furfuryl Alcohol	50 ppm	M.P.	6°F	Inhalation	Irritant Narcotic
		B.P.	338°F	Ingestion	
		V.P.	<1mm	Contact	
		Solubility	miscible		

A potential for exposure does exist when the catalyst in the reactors loses its activity and must be replaced. On average, the catalyst must be changed every 28 days and a special vacuum arrangement is used to ensure that exposure to catalyst fines is limited. This is described in Section III, C.

III. CONTROL TECHNIQUES

A. Digester Charging System

The Furfural Digesters operate batchwise with a cycle time of several hours. The cycle starts with the charging of raw materials to the digester. These include dilute sulfuric acid, and either pulverized corn cobs or oat hulls. All are charged into the digesters through a manway on top. Because the digesters rotate during the reaction cycle no permanent charging connections can be made. However, the present charging system has been designed to minimize opportunities for worker exposure to both dusts and sulfuric acid.

The corn cobs and oat hulls are transferred from staging areas to a conveyor system running directly over the top of all 12 digesters in the plant. From the conveyor system a square duct drops to the floor above each digester. A hinged door on the duct is opened allowing a portable digester charging chute (see Figures 3 and 4) to be inserted through a hole in the floor and into the open manway. A lip on the top of the chute prevents it from falling into the digester. With the door of the square duct closed the digester can be charged. From the conveyor system oat hulls and corn cobs are delivered through the square duct, the loading chute and into the digester. Dilute sulfuric acid is also introduced to the digesters via the loading chute by a fill pipe extending into the square duct. Clearances between the loading chute and manway are small enough that emission of dusts and vapors is limited. Local exhaust ventilation connected to the square duct creates a slight negative pressure during charging to also limit the emission of any dusts or vapors generated.

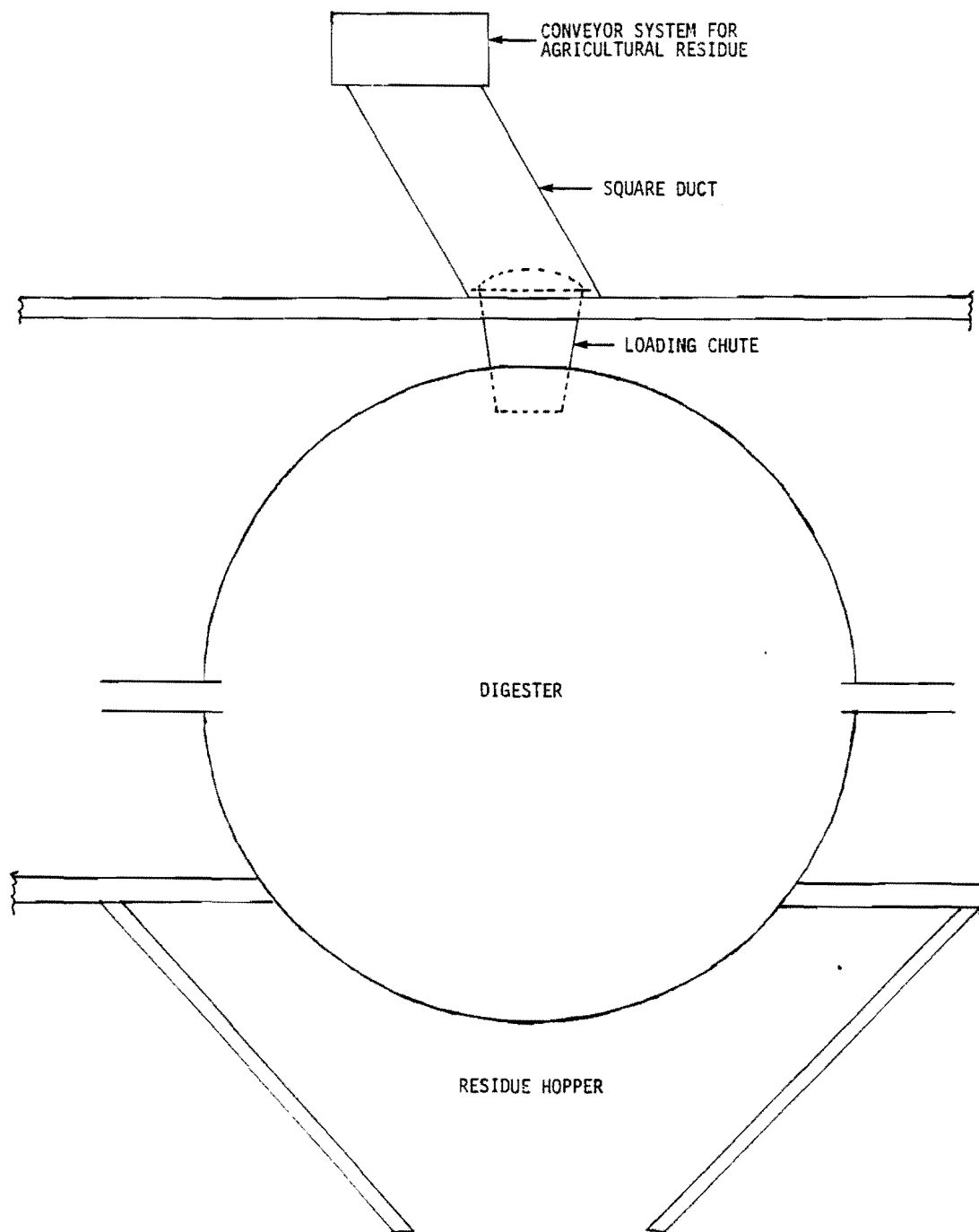
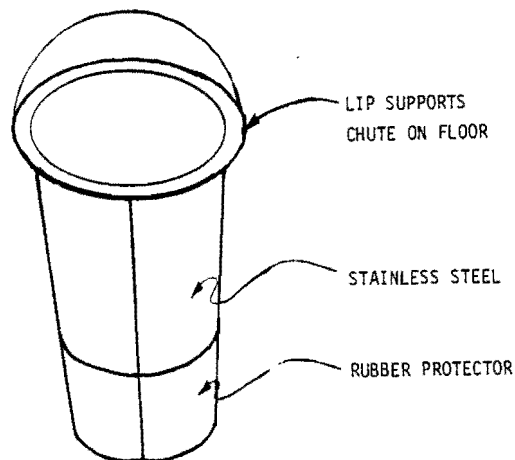


Figure 3. Digester Charging System Layout

FIGURE 4: PORTABLE DIGESTER LOADING CHUTE



B. Digester Shaft Seal

During the reaction cycle the digesters rotate to thoroughly mix all the reactants. Each digester rotates on bearings concentric to a large mechanically-packed header which extends into each end of the digester. Through one end, steam is injected to pressurize the vessel and strip the furfural from the agricultural residue. During the reaction, crude furfural vapors are extracted through the other end (see Figure 5). Mechanical packing is used to seal the header.

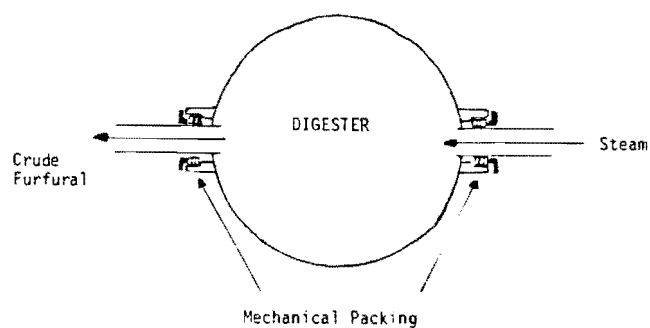


FIGURE 5: FURFURAL DIGESTERS

If the integrity of the packing decreases there is a chance for intermittent furfural exposure. The design of the stuffing box and packing gland are not unique. However it has been found that different packing materials work best for either end of the header. As detailed in Figure 6, Garlock 5888 is used on the cooler, furfural vapor end of the header. On the other end, where relatively hotter steam is introduced, Garlock 731 is used. This combination of packing materials, coupled with daily preventive maintenance ensures that the header stays sealed. It should be noted that this combination works well for this particular situation but should not be applied indiscriminately to other situations. Other similar situations should be carefully evaluated to determine what combination will work best.

C. Catalyst Vacuum System

The furfuryl alcohol process is totally enclosed so opportunities for exposure to hazardous substances are limited. However, about every month the copper-based catalyst in the continuous reactors must be replaced because of reduced activity.

After the process is shut down and thoroughly purged, the bottoms of the reactors are removed to allow the catalyst to fall out. It is then regenerated to be used again. Occasionally, some of the catalyst will not fall freely out of the reactor tubes. When this happens, a high pressure air lance is inserted into the top of the tube to blow the blockage out. This air blast can create large amounts of catalyst dust which is harmful if inhaled.

To reduce the amount of dust released to the work area, a mechanical suction device is placed over the tube(s) being blown, as shown in Figure 7. The circular device has no top, allowing the air lance to be inserted into the blocked tube. Air is exhausted from a screened annulus inside the device carrying away any dust and catalyst fines generated.

FIGURE 6: DIGESTER SHAFT PACKING

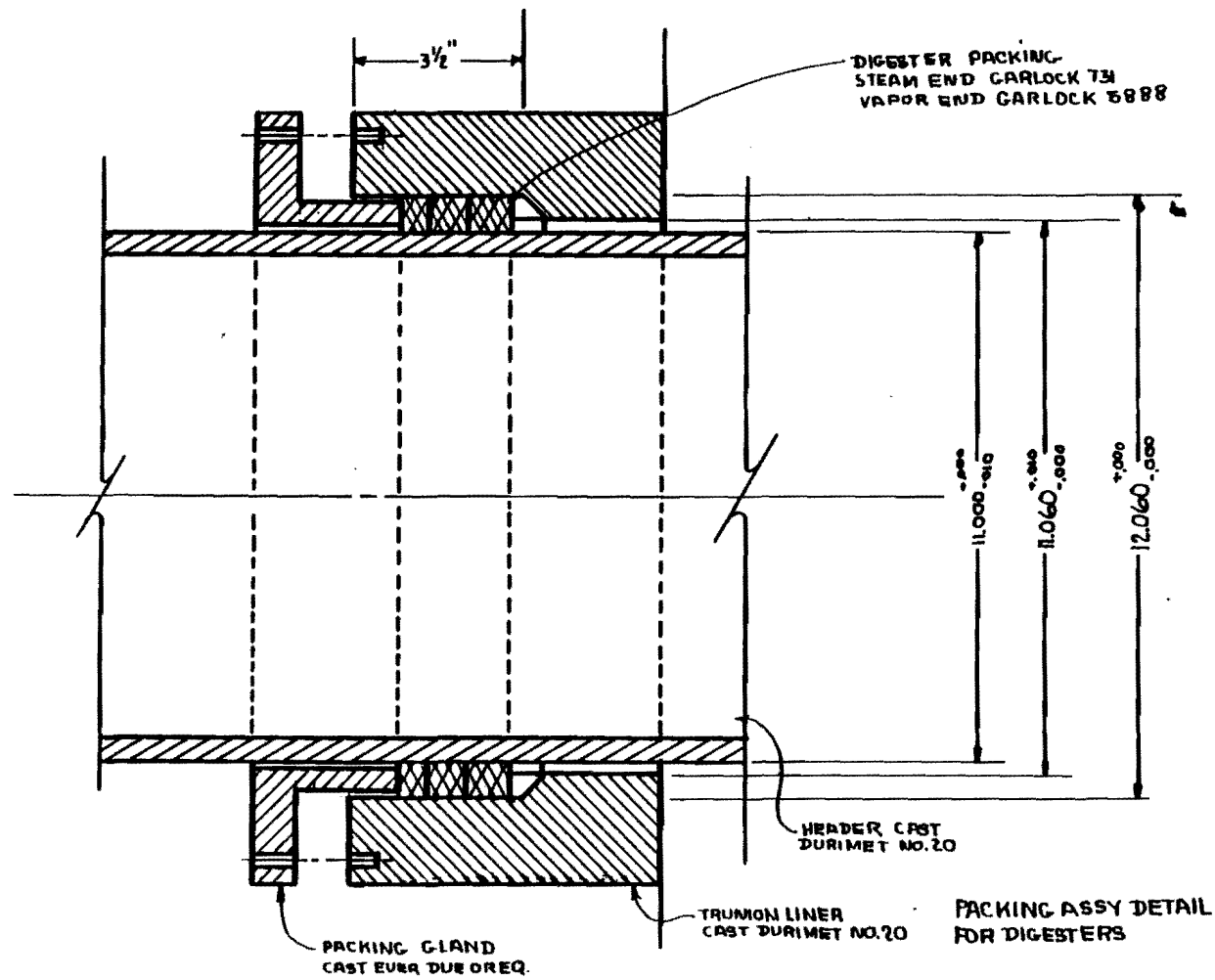
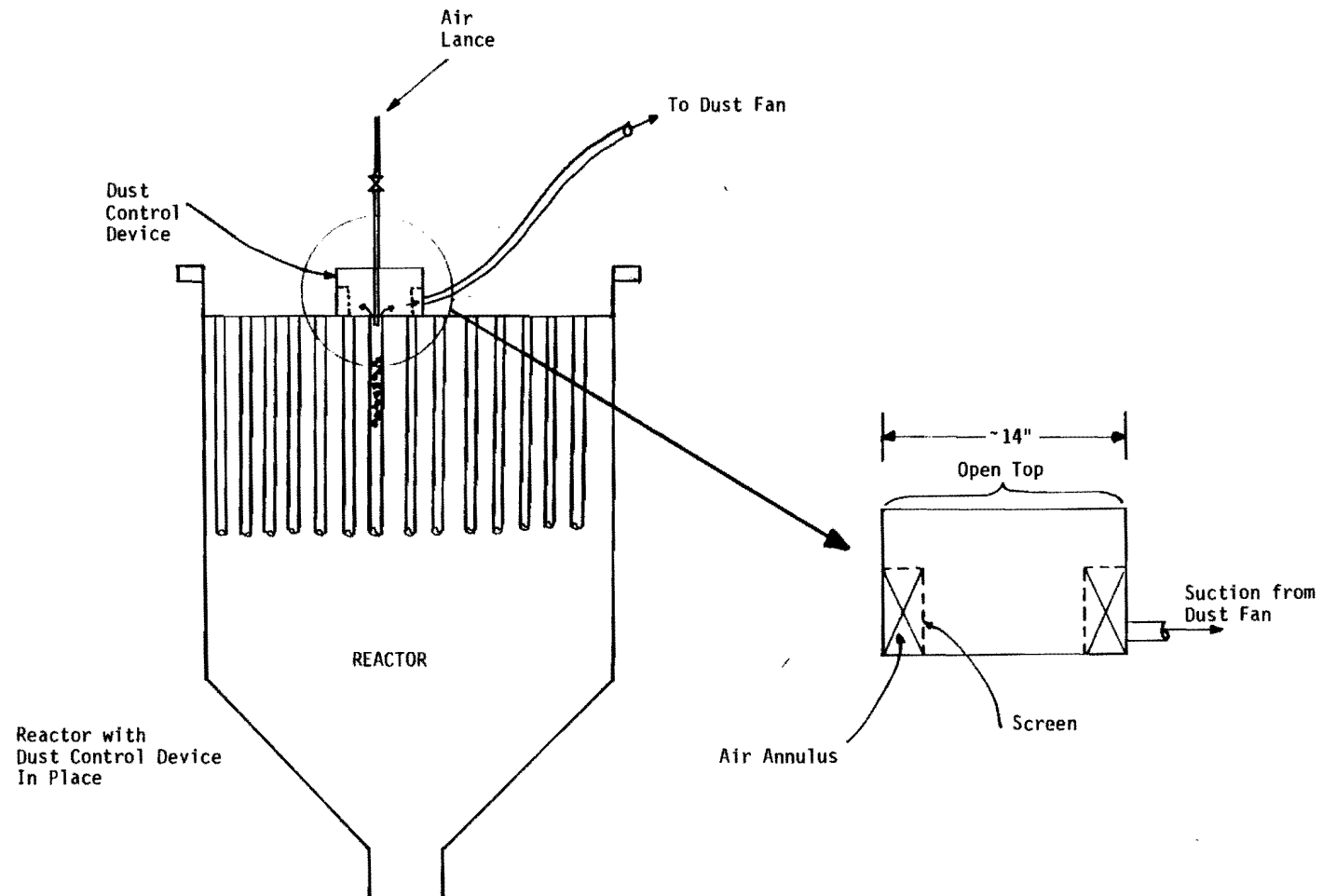


FIGURE 7: CATALYST VACUUM DEVICE



D. Work Practices

The company has a very effective work practices program which is reflected in the excellent housekeeping throughout the plant areas. The considerations that make the program effective are:

- Training of operators and maintenance personnel--operators are trained for each operation and task they will encounter during plant operation. It is the foreman's and Plant Inspector's responsibility to make certain the person being trained fully understands the job procedures, modes of release of chemical substances and potential hazards involved, and control techniques to be used.
- Documented training material for each job classification.
- Plant safety standards that address:
 - health hazards of chemical agents
 - mode of emission of chemical agents
 - control techniques to be used
- Management follow-up and monitoring to ensure consistent application of work practices by the various plant operators

E. Personal Protective Equipment

Disposable respirators (NIOSH approval number TC-21C) are provided for all employees to avoid exposure to dust generated by handling of agricultural residues. Certain job functions require the use of respirators and plant management is charged with the responsibility of ensuring that they are used properly. Local exhaust and general dilution ventilation supplements the protection afforded by respirators in areas that are enclosed.

Furfural and furfuryl alcohol are not considered highly toxic chemicals. However, exposure to vapors may induce nausea, burning of the eyes, and in high concentrations, narcotic effects. When this situation exists, (i.e., tank or equipment cleaning or repair) chemical safety goggles and proper respiratory protection are used. Generally though, workers do not encounter high vapor concentrations of either

of the chemicals. When workers do come into contact with them it is at a relatively low temperature, and vapor pressures are minimal. Dermal exposure is the main concern in this case as both chemicals readily penetrate and stain the skin. Neoprene or rubber gloves, aprons and boots are provided for any employee doing an operation that may cause direct contact with the liquids.

1.0 Plant Description

This facility is located in the city of Omaha, Nebraska at 302 Pierce Street, which is not far from the center of town. The climate in Omaha is very warm and humid in the summer and cold and snowy in the winter. The furfural plant was built in the early 1950's with the furfuryl alcohol units added in the early 1960's. It is a medium-sized plant with 40 salaried employees and 100 hourly employees working 3 shifts daily. The plant consists of several multi-story buildings which house the major processes. Storage, loading and unloading facilities are outdoors.

2.0 Description of Programs

A corporate industrial hygiene staff is available for this plant on an as-needed basis to perform surveys and provide services. There is no full time industrial hygienist or medical doctor stationed at the plant. An on-call doctor gives each hourly employee a complete medical examination annually (including blood tests). When industrial hygiene surveys are performed, there are four substances of concern. They are:

- Dust from agricultural residue ("nuisance dust") - exposures to dusts are measured by conventional particulate sampling techniques, including filtration with low flow rates for both total airborne and respirable concentrations.
- Furfural vapors - exposures are measured with samples collected from the breathing zones of employees by attaching a small battery-operated pump to the belt of the employee and drawing air through a glass tube containing activated charcoal, positioned in the breathing zone and attached to the employee's lapel. Samples are taken using calibrated pumps operating at approximately 0.1 liter per minute. The analytical technique includes desorption with high-purity pyridine followed by gas chromatography and detection using flame ionization.

- Copper based catalyst dusts - Again, exposures to dust can be measured by conventional particulate sampling techniques, including filtration with low flow rates for both total airborne and respirable concentrations. One useful configuration for sampling in this instance includes tared cellulose-ester filters with 0.45 micron pore size. On each filter, the weight gain is measured with conventional gravimetric methods. Copper can be determined using standard atomic absorption techniques. For employees who have a possibility of exposure to catalyst dust, a blood serum test for copper is done in addition to the annual physical they receive along with all the other employees at the plant.
- Furfuryl alcohol vapors - exposures are measured with samples collected from the breathing zones of employees by attaching a small battery-operated pump to the belt of the employee and drawing air through a glass tube containing activated charcoal, positioned in the breathing zone and attached to the employee's lapel. Samples are taken using calibrated pumps operating at approximately 0.1 liters per minute. The analytical technique includes desorption with high-purity pyridine or carbon disulfide, followed by gas chromatography using flame ionization.

3.0 Threshold Limit Value for Furfural

The following is the text of a letter written by the Quaker Oats Company to the Threshold Limit Value (TLV) Committee of the American Congress of Governmental Industrial Hygienists in support of maintaining the TLV for furfural at an 8-hr time-weighted-average of 5.0 ppm.

April 8, 1981

Threshold Limit Value Committee
American Conference of Governmental
Industrial Hygienists
P.O. Box 1937
Cincinnati, OH 45201

Re: THRESHOLD LIMIT VALUE FOR FURFURAL

Gentlemen:

This letter and enclosures convey our latest information and current understanding as to the most appropriate value for a threshold limit for furfural. We forward this information knowing that the TLV for furfural has been under review by the Committee and a revision is now pending.

The Quaker Oats Company has produced furfural commercially for more than 50 years. As the world's leading producer, we have accumulated substantial information regarding the properties of furfural, including its toxicology and potential health effects.

Two years ago, Quaker began a systematic, in-house epidemiologic study (retrospective and prospective) of former and current employees working with furfural, including mortality and morbidity analyses. Although progressing well, this on-going project is not sufficiently developed to provide substantial input with respect to the TLV for this substance. Nevertheless, we agree fully with the notion that the threshold limit for furfural should be set on the basis of subjective sensory response, given the capacity of furfural to cause irritation of mucous membranes at low-to-moderate levels. Therefore, we take this opportunity to summarize our current position on this issue in order to provide constructive input to the Committee in its present deliberations.

We believe the primary basis for the 1979-proposed revision in the TLV to be insufficient. We trust the information conveyed now will further clarify the appropriate level for a TLV for furfural based on sensory irritation. More importantly, we believe the TLV Committee should not make a final decision on a furfural limit for at least another year, at which time we should have sufficient analyses completed in our epidemiologic study to comment more conclusively on a chronic exposure limit for this substance.

In the meantime, we suggest that a TLV based on sensory irritation be continued at 5.0 ppm for furfural on a time-weighted average basis (with "skin" notation) and 15 ppm as a short-term exposure limit (STEL).

Attached for your review are the following documents that support our recommendations:

- Exhibit I - An analysis of the NIOSH study on which the TLV revision is based.
- Exhibit II - A Summary of recent exposure data and the subjective responses documented by Quaker's professional industrial hygienists.
- Exhibit III - A summary of environmental sampling and sensory responses accumulated by our Chemicals Division staff and Customer Service Technical Specialists.

We find, on the strength of all this information and our current understanding, no basis for the furfural TLV to be lowered to 2.0 ppm. We believe the evidence does not support a level less than 5.0 ppm. Therefore, in light of continuing epidemiologic investigation, we recommend that the TLV be continued tentatively or reestablished at 5.0 ppm on a time-weighted average basis and 15 ppm as a STEL.

We appreciate the opportunity to offer this data, and trust the Committee will find it useful.

John E. Mutchler
Director - Health Safety
The Quaker Oats Company

JEM/kam/
Enclosures

EXHIBIT I

CRITIQUE OF NIOSH STUDY USED AS A BASIS FOR FURFURAL TLV REDUCTION

In the report of a NIOSH Health Hazard Evaluation at Pacific Grinding Wheel Company (1), the investigators suggest that a Threshold Limit Value (TLV) of five parts per million (ppm) for furfural may not be low enough to protect workers from sensory irritation. We disagree that the measurements and observations during this study justify such a conclusion, for the following reasons:

1. Because of technical difficulties with charcoal-tube sampling, the NIOSH investigators collected general-area measurements to profile workplace furfural concentrations using a Wilks Miran Portable Infrared Analyser. Although this technique can provide a reliable estimate of air concentrations, the samples were not actually collected from the breathing zones of workers. Furthermore, the report of the study does not offer the reader enough information to judge whether these measurements provide an accurate estimate of worker exposure.
2. As a part of this evaluation, a NIOSH physician conducted a medical evaluation on March 19, 1974, consisting of personal interviews and a limited examination of employees exposed to furfural. The environmental measurements, however, were collected on August 21 and December 5-6, 1973, several months prior to the medical evaluations. Although we do not know the specific questions asked by the investigators, it would seem more appropriate to question the workers soon after (or during) workplace monitoring. If measurements had been taken on March 19, 1974, the day of the medical evaluation, or if the medical evaluation had been conducted on the same day as environmental monitoring in 1973, one could place a significantly higher level of confidence on the relationship between exposures and subjective irritation.
3. Almost all reported furfural-in-air concentrations exceeded five ppm during the NIOSH study, and it is possible that reports of irritation could have been related to exposure periods above five ppm. Even on December 6, 1973, when night-shift measurements averaged 5.1 and 5.9 ppm, the "ten-minute furfural concentration averages" during the same time period showed concentrations up to 7.8 ppm. Did the irritation occur only during the 10-minute intervals where exposures exceeded five ppm? Or, did the irritation responses also occur during the lower 10-minute concentration averages?

Using the data in Table I of the NIOSH study, the time-weighted average furfural concentration for the 1390 minutes of monitoring is 8.2 ppm. These data confirm that irritation can result at the highest concentrations. Yet, very few of the readings were below five ppm. Prior to reducing the furfural TLV from five ppm on the basis of sensory irritation, we believe that more data needs to be evaluated in the 2-5 ppm concentration range. Exhibits II and III provide such information.

References

1. Arvin G. Apol, "Toxicity Determination Report 73.18.171, Pacific Grinding Wheel Company," Health Hazard Evaluation, National Institute for Occupational Safety and Health, Cincinnati, January, 1975.

EXHIBIT II

CORRELATION OF SENSORY IRRITATION WITH FURFURAL EXPOSURES

BY QUAKER INDUSTRIAL HYGIENISTS

PLANT A

During a five-day industrial hygiene study at Plant A, eight-hour, time-weighted average exposures to furfural ranged from 0.1 to 1.7 parts per million (ppm). These employees occasionally worked in a control room and other area of the plant, however, where furfural was not present. General-areas samples were also taken simultaneously at two centrally-located positions (each sample lasting for approximately five hours) to determine the typical daily furfural concentrations in areas where worker exposures would most likely occur. These two samples indicated furfural concentrations of 2.7 and 4.6 ppm. During this time, the industrial hygienist worked in the same area, observing workers and the general operations, without experiencing any discomfort. In addition, workers present at these locations did not express any symptoms of irritation.

Workers did experience brief periods of eye irritation while opening process vessels. Although this operation occurred several times per shift for 5-7 minutes each, operators avoided the visibly vaporous emission, which included acetic acid. No air samples were taken to quantify peak exposures for this task, but from other similar studies we know the levels can range up to 50 ppm.

PLANT B

During a five-day industrial hygiene study at Plant B, eight-hour, time-weighted average furfural exposures ranged from 1.1 to 5.3 ppm, with no reports of sensory irritation by workers or the hygienist. Using Drager-tube sampling techniques, workplace acetic acid levels ranged from one to three ppm at the same time.

As at Plant A, workers can experience eye and respiratory tract irritation while opening process vessels, an operation which normally occurs several times per shift, although operators need not encounter the vaporous stream directly. While performing this task, with its potential for the highest, short-term exposures, air samples were collected using the standard procedure. The results indicate a wide variation in exposure levels, ranging from 2.5 to 17.8 ppm for the 6-7 minute duration of the task. During these cycles, operators did not complain of sensory irritation unless standing directly in emission stream. An air sample taken in the stream of vapors indicated a furfural concentration of 43 ppm. Drager-tube measurements, also taken in the emissions stream, indicated acetic acid levels of 80 to 100 ppm - well above the current TLV and within the sensory irritations range. The investigator collecting these air samples also experienced an immediate onset of transitory eye, nose, and throat irritation while standing in the vaporous emissions during vessel opening.

PLANT C

A two-day study of furfural exposures at Plant C showed time-weighted concentrations ranging from 1.0 to 4.3 ppm for three job classifications. Although mild and moderate odors typical of furfural were noticeable to the industrial hygienist during these sampling periods, there was no indication by the workers or the investigator of sensory irritation.

Two shorter samples at fixed locations near suspected process sources, lasting three and four hours, showed concentrations of 5.6 and 11.1 ppm, respectively. The hygienist noted a strong odor but no irritation during frequent attendance of the sampling apparatus during the 3-hour sample. Mild irritation of the eyes and nose was recorded once by the hygienist while attending the equipment during the 4-hour sample.

During another four-day study at Plant C, time-weighted average exposures to furfural ranged from 0.3 to 3.5 ppm, with no reports of sensory irritation from operators except during one brief, intermittent operations.

One employee periodically moves process materials while driving a small tractor with a front-end scoop. This operation does not occur each day, but when it occurs, it lasts from 15 minutes to four hours each shift. The damp material contains furfural and other substances, including acetic acid. This operation always occurs outdoors, and consequently, vapor exposures to the operator vary momentarily depending on local wind conditions and the worker's position. Breathing zone results for 15-to 35-minute periods show exposure ranging from 1.4 to 17.3 ppm. The operator periodically experiences eye irritation when the odor become very strong.

SUMMARY

Quaker maintains an industrial hygiene program, using board-certified professionals, to provide current documentation of worker exposures to furfural in all plants. We have measured many full-shift, time-weighted average exposures, all ranging between 0.3 and 5.3 ppm, with no corresponding reports of sensory irritation. Intermittent peak exposures occur at a few of our operations, and sometimes result in transient sensory irritation. Although we have not fully characterized the exposure levels which elicit an irritating response, it certainly appears that such exposures must exceed five ppm by a substantial margin.

EXHIBIT III

OTHER STUDIES BY QUAKER PERSONNEL

In addition to the industrial hygiene studies conducted within Quaker, our Customer Services Group in the Chemicals Division routinely conducts air quality and process-related air sampling in the workplaces of other firms using furfural. These measurements are conducted by standard methods, using battery-operated sampling pumps and activated charcoal, and include both breathing-zone and general-area samples. A representative compilation of results from such studies is shown in the attached Table III. In this summary of results, furfural-in-air concentrations and subjective responses have been noted by eight different, experienced Quaker investigators.

These data show clearly that, although odors can be present with very low concentrations of furfural, sensory irritation has not been observed at concentrations less than 6.4 ppm.

TABLE III
SUMMARY OF SENSORY RESPONSE CRITERIA
FURFURAL-IN-AIR CONCENTRATIONS

EXPOSURE LEVEL (ppm)	SAMPLE DURATION (minutes)	SUBJECTIVE RESPONSE	OBSERVER
0.1	448	No Odor	A
0.1	454	Faint Odor	A
0.1	360	Some Odor/Non-Irritating	B
0.2	210	Faint Odor	A
0.3	240	Marginal Odor	C
0.5	240	Marginal Odor	C
0.6	120	Odor in Area/Non-Irritating	B
0.7	180	Faint Odor (Due to open container)	A
1.1	240	Mild Odor	C
1.2	30	Strong Odor/Non-Irritating	B
1.2	240	Mild Odor	C
1.4	240	Mild Odor	C
1.8	450	Odor/Non-Irritating	A
2.4	210	Strong Odor	D
3.1	206	Odor Detected, With Increased Intensity as Additional Liquid Added	D
3.2	240	Mild Odor	C
3.3	220	Strong Odor	D
3.5	180	Medium Odor	E
3.6	468	Odor/Non-Irritating	A
3.8	180	Strong Odor	E
4.1	240	Mild Odor	C
5.0	207	Medium Odor	E
5.8	180	Strong Odor	E
6.4	480	Strong Lingering Odor/Non-Irritating	A
6.0-6.4	480	Strong Lingering Odor	A
6.1	120	Medium Odor	E
6.2	10	Odor/No Discomfort	F
6.2	10	Strong Odor	G
6.4	480	Strong Lingering Odor/Non-Irritating	A
6.4	56	Odor Uncomfortable at Times/Nasal, Eye Irritation	D
6.5	480	Strong Lingering Odor	A
7.0	240	Mild to Strong Odor	C
7.5	240	Mild to Strong Odor	C
7.9	10	Odor/No Discomfort	F
8.8	240	Moderate to Strong Odor	C
10.0	120	Strong Odor	E
10.1	480	Strong Lingering Odor	A

TABLE III (Continued)

EXPOSURE LEVEL (ppm)	SAMPLE DURATION (minutes)	SUBJECTIVE RESPONSE	OBSERVER
10.3	240	Moderate to Strong Odor	C
13.9	78	Odor Uncomfortable at Times/Nasal, Eye Irritation	D
15.8	240	Strong Odor/Non-Irritating	C
16.4	120	Strong Odor	E
17.4	240	Strong Odor/Non-Irritating	C
18.9	240	Strong Odor/Non-Irritating	C
20	240	Strong Odor/Non-Irritating	C
38-70	12	Very Strong Odor/Red Watering Eyes	H
50	12	Choking/Coughing Sensation/Taste in Mouth/Odor Intense	H
50-60	54	Eye Irritation	A
54	480	Eyes Teared/No Employees in Area	A
56	12	Choking/Coughing Sensation/Taste in Mouth/Odor Intense	H
61	480	Eyes Teared/Very Irritating/No Employees In Area	A
66	12	Choking/Coughing Sensation/Taste in Mouth/Odor Intense	H
71	12	Choking/Coughing Sensation/Taste in Mouth/Odor Intense	H