SM-32 (Rev. 9 57)

REFERENCE

SHELL OIL COMPANY

APR 12 Rec'd

PRIVATE AND CONFIDENTIAL

DATE APRIL 4, 1973

TO SHELL CHEMICAL COMPANY - ENVIRONMENTAL ENGINEERING - MANAGER

FROM INDUSTRIAL HYGIENIST - DEPARTMENT OF OCCUPATIONAL SAFETY AND HEALTH

SUBJECT WALK-THROUGH INDUSTRIAL HYGIENE SURVEY - HOUSTON CHEMICAL PLANT

PLAINTIFF'S EXHIBIT

SH-1583

This report will summarize the results of the industrial hygiene survey of the Houston Chemical Plant which took place during November 8-10 and 14-15. I appreciate the courtesies extended to me during that time by E. S. Martin, Willard Smith, Charles Bland, and Wesley Neal. I wish to point out that at the time of the final writing of this report, some type of action has been taken on almost every item mentioned in the report. The Houston Plant is to be commended for their fast action.

During the survey it was noted that an extensive air contaminant program had been established. The identification of toxic chemicals on charts in each control room and the revisions to your insulation shop are also noteworthy. The survey consisted of walking through the plant and observing potential exposures to toxic materials. We also talked to operators during the survey in order to become familiar with all the operations they perform. Therefore, in this report we will note exactly what was and was not observed. Both Wesley Neal and I felt that the discussions with operators were of value from an employee relations point-of-view. The only measurements taken during the survey were airflow measurements in laboratory hoods.

Three operations were noted which I would consider high priority items for action. These are:

1. The handling of 35% hydrazine solution and Betz Neutrameen in the chemical injection building in OP II.

2. The handling of brucine and ethyl acrylate in the denaturing area of the "E" unit.

3. The handling and disposal of chemicals in the laboratory warehouse.

These operations are described below.

Chemical Injection Building - OP II

We observed the operator drawing 35% hydrazine solution and Betz Neutrameen from 55 gallon drums into pails. The pails were carried up on a platform and dumped into tanks. Goggles and gloves were worn during the operation which takes place once per shift. No respiratory protection was worn.

In view of the low threshold limit values for these materials (hydrazine - 1 ppm N_2H_4; Neutrameen - 20 ppm morpholine), and because both these materials can be absorbed through the skin, we would recommend the handling of these materials in a closed system. If a completely closed system cannot be implemented, air sampling is recommended. Also, the precautions and procedures shown on material safety data sheets 30198 and 31239 should be followed.

Denaturing Area - "E" Unit

The operator in this area complained about exposure to brucine and Bitrex during the weighing operation. The actual handling of these materials was not observed. The operator also told us he was exposed to brucine dust when it was added to a mixing tank. He also complained that the hand pumps used for ethyl acrylate leaked, and the material got on him. We recommend that you evaluate worker exposure to these materials and institute controls as required. Although a TLV has not been established for brucine, exposure should be minimized because of its relationship to strychnine which has a TLV of 0.15 mg/m^3. The precautions outlined on the material safety data sheet 30188 for brucine should be followed.

Ethyl acrylate has a TLV of 25 ppm. It is also absorbed through the skin. Therefore, skin contact and the breathing of vapors in excess of 25 ppm on an eight-hour time-weighted average basis should be avoided. The ethyl acrylate pumps should be either repaired or replaced if they leak.

A benzene pump was also noted in the denaturing building. Because this pump is in an enclosed space, this area should be checked for benzene levels on a periodic basis.

Laboratory Warehouse Building

Two areas are of concern at the laboratory warehouse: (1) the small laboratory where various reagents are prepared and (2) the back platform area where waste samples are dumped into drums. The small laboratory where reagents are prepared contained an air conditioning unit and an exhaust hood. The employee who works in this laboratory complained that it was necessary at times to turn on the plant air in the laboratory and "purge" the laboratory of gases and vapors that had accumulated. We did not actually observe this condition. However, because of the variety of chemicals handled here, we recommend that employee exposure to vapors in this laboratory be evaluated.

Waste chemical samples are disposed of at the back porch of the laboratory warehouse. Sample bottles are opened, and the chemicals are dumped into drums. A large fan is available to blow the vapors away from the man dumping the samples. However, the effectiveness of the fan is questionable as it appears to be partially blocked by the windshield at the end of the platform. An actual disposal operation was not observed. However,

because of the variety of chemicals disposed of at this location (allyl alcohol, allyl chloride, epichlorohydrin, DD, etc.), we recommend the evaluation of employee exposure. The installation of local exhaust ventilation may be desirable.

Additional Recommendations

During the survey a number of other operations were either observed or noted by operators. These operations with our recommendations are described below.

Hydrotreater Analytical Building - OP-II

A sample stream containing H_2S is brought through this building for analysis. The building contains an exhaust fan. An alarm in the control room is sounded if the exhaust fan goes off. Despite the controls already installed in this building, we recommend an evaluation of the system considering the possibility of a leak occurring in the building that would not be taken care of by the ventilation system.

AA Unit

Operators complained that allyl alcohol vapors from a nearby vent often get into the A&B control room. We understand that revisions to the vent system, including a scrubber, are already planned to eliminate this exposure.

Petrochem Furnace

We observed there was no drain at the sample location on the #1 PC accumulator (V-3141). The operator complained of exposure to MEK vapors when he sampled at that location. We recommend the installation of a drain at that sample location.

MS&H Unit

Vapors believed to be mesityl oxide and methyl isobutyl carbinol were detected around the pumps in this area. The vapors appeared to be coming from leaking pumps. We recommend these pumps be repaired.

"G" Department - Rock Box

We were advised that ECH and Cl_2 vapors were often noticeable around the rock box. This condition was not detected during the survey. However, we recommend that employee exposure to these vapors be evaluated.

G100/200 Unit

1. HCl vapors were detected in this unit. These vapors were believed to be coming from pump 718. We recommend this pump be repaired.

2. EC-II - We were advised that HCl vapors are generated during the dumping of spent ferric chloride catalyst from the pan dryers. We recommend that operators' exposure to these vapors be evaluated and controls implemented if exposure is excessive.

G300 Unit

Operators complained about vapors (ECH, HCl, AC, Cl_2) coming into the control room. This condition was not detected during the survey. Therefore, we recommend the condition be evaluated by plant personnel. Controls should be implemented if vapors are entering the control room.

Chlor-Alkali Plant

1. Operators complained of chlorine vapors drifting into the cell room when spent sulfuric acid was dumped into an adjoining sewer. This condition was not actually observed. I was advised by W. Neal that this condition has been investigated and is being corrected.

2. An operator complained that 10% caustic solution in the cell liquid drum splashed on him when chlorine from the cells is bubbled through this drum. This operation was not actually observed. We recommend the operation be evaluated and controls instituted to prevent splashing.

Ethyl Alcohol Unit

Benzene is sampled once per shift in this unit. We were advised protective equipment such as gloves and goggles are worn during sampling. The drain at the sample location was plugged causing an amount of benzene to collect in the sink during sampling. We recommend that the operators' exposure to benzene be evaluated during this sampling operation. The clogged drain should be cleaned out.

Government Building

An ethyl acrylate tank and pumps are located in this building. Vapors believed to be ethyl acrylate were detected around the pumps. If these pumps are leaking, they should be repaired. Because the tank and pumps are in an enclosed building, sampling for ethyl acrylate vapors on a periodic basis is recommended. This sampling is especially important in the wintertime when the building is closed up.

A benzene tank is also located in this building. Periodic air sampling to insure that controls are adequate is recommended.

EP Feed Prep

Operators complained that vapors from the vent on the slop caustic tank (Tank 1001) get into the control room. This condition was not actually detected. However, we recommend the matter be evaluated and controls implemented if the condition does exist.

BA Unit

1. An operator complained that an IBA transfer pump (Pump 5431) had to be bled once per shift to the sewer. He pointed out that there was no drain line to the sewer. Consequently, IBA was run out onto the pad exposing the operator to vapors. The operation was not actually observed. We recommend that the operation be investigated and a drain line installed if the complaint is valid.

2. Vapors believed to be n-butyl-aldehydes were very noticeable throughout the BA Unit. We recommend that the vapors be identified and the source eliminated if possible.

Sulfur Plant

The operators in this unit complained of SO_2 and H_2S vapors getting into control rooms during the loading of sulfur trucks. We understand that there are plans to raise the air intake to the pressurized control room to eliminate this problem.

PDU Building/Epon I Building

1. A variety of toxic chemicals such as ethylenediamine, phenol, epichlorohydrin, and aniline are handled in these buildings. Employee exposure to vapors appears to come primarily from hot liquids in the kettles during the dumping of materials through the kettle manways. Because of the variety of materials handled in these buildings, we recommend that you evaluate the need for local exhaust ventilation at the kettle manways. The installation of ventilation facilities may be cheaper than an extensive air sampling program.

2. Housekeeping in these buildings could be improved. We understand you are currently making an intense effort to do this.

EPON(R) IV

An operator complained that there was no drain line going from the accumulator tank to the sewer. Therefore, when the accumulator overflowed the contents ran to the pad with MIBK vapors being generated. This operation was not observed. We recommend the complaint be investigated and controls implemented if the condition does exist.

EPON III

Operators complained of MIBK vapors coming from an open sump. I was advised by W. Neal that the problem is under study and will be corrected.

EPON II

1. Operators complained of MIBK vapors on the second floor during upsets. They believe these vapors come from an uncovered chute going from the turbofilm to the conveyor belt on the first floor. We recommend the complaint be investigated and controls implemented if the condition does exist.

2. BPA dust was noted on the fifth floor of the EPON II building. An operator complained that the dust control shrouds needed repair and more shrouding was needed. Because BPA production was not in operation during the survey, it was not possible to evaluate the operators' comments. Investigation of the complaint is recommended. An evaluation of employee exposure to BPA is recommended.

P & R Shipping

1. Hopper Car Loading. BPA dust is generated during the loading of the hopper cars. The loading operator and also the employees in the warehouse area are exposed to this dust. I was advised that a project is underway to minimize the amount of dust generated during the loading of hopper cars. An evaluation of employees' exposure to BPA is recommended.

2. Small Container Filling Station. The operator at this location advised us that he fills small containers with a variety of chemicals including allyl glycidyl ether (AGE), phenyl glycidyl ether (PGE), and butyl glycidyl ether (BGE). There is no local ventilation at the station. The operator advised us that he wears a respirator if the vapors get strong. Local exhaust ventilation may be desirable and could be accomplished by running a line to this station from the proposed exhaust system for the drum loading area. We recommend such an installation be evaluated.

3. EPON Resin and BPA Bag Filling Stations. BPA dust was noted in this area. I was advised that a local exhaust system is proposed for the BPA station. Local exhaust is already installed on EPON resin station.

4. Drum Loading Station. EPON 815 (containing BGE) and EPON 820 (containing PGE) are drummed in this area. The area was messy. However, I was advised that the station is being completely revised, including local ventilation.

Phenol Unit

The operator in this area complained that phenol sprays during sampling at the P 2430 sampling station. We recommend investigation of this

complaint and correction of the situation if the complaint is valid. Employee exposure to phenol during sampling should be evaluated.

Main Shop

1. Welding area. The ventilation equipment in the welding area needs repair. We observed a missing hood, a hood that would not stay in place, and dampers that did not work. It appeared that there was one welding table that had no hood. We recommend this ventilation equipment be repaired and supplemented where necessary.

2. Equipment cleaning area. We were advised by an employee that MEK was often used to clean EPON equipment. No local exhaust was noted in this area. We recommend that this operation be investigated and proper controls implemented.

3. Grinders, abrasive cleaners, and a small paint spray booth were noted in the main shop. None of this equipment was in operation during the survey. We understand this equipment is being reviewed by your engineering department for compliance with OSHA standards.

Lead Burning Building

No work was being done in this building during the survey. The lead burner's exposure to lead dust and fumes should be evaluated. The National Institute for Occupational Safety and Health has recently recommended to OSHA that the TLV for inorganic lead be lowered from 0.2 mg/m^3 to 0.15 mg/m^3.

Brick Mason Building

No work was being done in this building during the survey. The brick mason's exposure to silica dust should be evaluated.

Precipitator-Rectifier Building

Employee exposure to ozone in this building should be established. Ozone has a TLV of 0.1 ppm.

Effluent Area

An operator complained of exposure to Rohm & Haas Primafloc which is added to a tank in the secondary treater. The label on the Primafloc bag stated that the material was acidic and should not be inhaled. The exposure of this employee should be evaluated and proper controls implemented.

Laboratories - Administration Building

1. ICD Laboratory - Acid Dumping Sink. Acid vapors were noticeable when waste acids were dumped into this sink. Employee exposure to these vapors should be evaluated. Local exhaust ventilation may be desirable.

2. Polymers Laboratory.

   a. Solvent vapors (acetone, MEK) were noticeable at the solvent washing sink. An employee complained he often developed a headache when washing with solvents. Employee exposure to these vapors should be evaluated. Local exhaust ventilation may be desirable in view of the employee's complaint.

   b. Benzene and phenol are used in this laboratory. We recommend that employee exposure to these materials be evaluated as we understand they are not always used under laboratory hoods. Using these materials under hoods would, of course, be desirable.

3. OP-II/VCM Wet Laboratory. Carbon tetrachloride is used in this laboratory. We recommend that this material be used under a hood. If this is not possible, we recommend that air sampling be done to evaluate employee exposure.

4. Environmental Laboratory. Carbon tetrachloride is also used in this laboratory. Employee exposure to this material should be evaluated if it is not used under a laboratory hood.

5. Steam Ejector System. This system is used to vent waste gaseous samples to the atmosphere. A comment was made during the survey that the vent on the system is not high enough to prevent the waste gases from being sucked back into the air conditioning system. We recommend that the need for raising this vent be evaluated.

6. General Comment on Laboratory Hoods. The American Conference of Governmental Industrial Hygienists recommends a minimum flow rate of 100 feet per minute at the open face of laboratory hoods. Most of the laboratory hoods did not meet this criteria unless the hood doors were lowered to within 3-4 inches from the bottom. Therefore, we recommend that the hoods be used with the doors lowered as far down as possible. We understand you have done air sampling around some of the hoods and have found the ventilation capacity sufficient.

Unit Control Rooms

Many unit control rooms contain small laboratories with no local or general exhaust ventilation other than an air conditioning system. As operators spend significant time in these control rooms, we recommend that employee exposure to toxic chemicals in these rooms be evaluated.

It was also noted during the survey that laboratories and eating facilities are adjacent to one another in many control rooms. Section 1910.141(g)(3)(i) of the OSHA standard states that "No food shall be stored or eaten where there are present any toxic materials or substances that may be injurious to health." In view of this standard, we recommend that the proximity of eating and laboratory facilities in control rooms be carefully reviewed to determine if any hazardous situations actually do exist.

Polynuclear Aromatics

Employee exposure to polynuclear aromatics in OP-II will have to be evaluated. This department will be supplying more information on this matter.

General Recommendation

Your current air contaminant sampling program is quite extensive. To date most of the testing has been with detector tubes. This is understandable in view of the multitude of materials used or produced in the plant. We do wish to point out, however, that detector tubes are primarily screening devices. If the accuracies of the tubes ($\pm$ 25% at best) make questionable whether or not employees are overexposed, more accurate methods of sampling and analysis would be required. We also wish to recommend that if you suspect employees are exposed to a toxic material, and no detector tube is available, you develop an appropriate sampling and analytical technique for that material. It will be a long time before full standards, including sampling and analytical techniques, will be incorporated into the OSHA standards. This department is available to assist you in the development of appropriate sampling and analytical techniques. Information on sampling and analysis for epichlorohydrin is attached per request of the Houston Chemical Plant.

D. P. Atwood

D. P. Atwood

Attachment

cc - (w/attachment)
Shell Chemical Company - General Manager Manufacturing
Industrial Hygiene - Manager
Shell Chemical Company - Houston Plant - Plant Manager

1,1-Dimethylhydrazine

Pinkerton, M. K., J. M. Lauer, P. Diamond, and A. A. Tamas. **A Colorimetric Determination for 1,1-Dimethylhydrazine (UDMH) in Air, Blood and Water,** Am. Ind. Hyg. Assoc. J. **24,** 239 (1963).

1,1-Dimethylhydrazine (UDMH), in concentrations from 2.5–50 ppm, can be determined with this method. The range can be extended by proper dilution techniques. The sample is collected in a polyethylene bubbler containing a buffer solution citric acid and disodium phosphate in water. Trisodium pentacyanoamino ferroate is added to an aliquot of the sample. The resulting red-orange color is allowed to develop for 1 hour and the optical density at 500 mμ is determined with a spectrophotometer. The concentration is determined by comparison with a standard curve and the airborne concentration is calculated.

Sampling Procedures

The sampling rate through the bubbler can be 1 lpm for 2 minutes. Longer sampling times can be used but the sample must be diluted to fall into the range of the determination.

Interferences

Nitrogen dioxide may interfere with the determination by somewhat reducing the color produced.

This method is applicable to industrial hygiene analysis and requires 2–3 hours for a complete analysis. The method is not sensitive enough for air pollution work.

Epichlorohydrin

Hanson, N. W., D. A. Reilly, and H. E. Stagg, Eds. *The Determination of Toxic Substances in Air* (Cambridge, England: W. Heffer and Sons, Ltd., 1965), p 121.

See Also

1. Nash, T. Biochem. J. 55, 416 (1953).
2. Gage, J. C. Brit. J. Ind. Med. 16, 11 (1959).

Epichlorohydrin, in concentrations from 2.5–20 ppm in a 1-liter air sample, can be determined by this method. The air sample is collected

in two midget impingers containing 8 ml of water and connected in series. After collection, the sample is heated for 1 hour to open the epoxide ring, producing glycerol chlorohydrin which is then oxidized with periodic acid to produce formaldehyde. Sodium arsenite and a solution of acetylacetone in acetic acid and ammonium acetate is added to the sample and heated for several minutes. The optical density of the resulting yellow-stained solution is read in a spectrophotometer at 412 mμ. The quantity of epichlorohydrin present in the sample is read from a previously prepared calibration curve and the airborne concentration is calculated.

Sampling Procedure

The sampling rate through the two midget impingers should be approximately 1 lpm. If 1 liter of air is sampled, the method can be expected to determine 2.5–20 ppm. An increase or decrease in the sampling time will provide an increase or decrease of the sensitivity limits obtainable.

Interferences

Formaldehyde, other aldehydes, and substances yielding aldehydes when exposed to the reagents used in this analysis can be expected to interfere with this determination.

The method is simple and requires approximately 3 hours for complete analysis. It is applicable to industrial hygiene work but is not considered sufficiently sensitive for air pollution work.

Daniel, J. W., and J. C. Gage. **The Determination of Epichlorohydrin in Air,** Analyst 81, 594 (1956).

Epichlorohydrin, in concentrations above 10 mg/m^3, can be determined by this method. The sample is collected in a specially constructed bubbler containing 8 ml distilled water. The sample is diluted to 10 ml with distilled water and quantitatively transferred to a flask. Periodic acid is added and the solution heated in a water bath for 20 minutes. Arsenite solution and a solution consisting of a mixture of ammonium acetate, glacial acetic acid and acetylacetone are added to the sample. The optical density of the resulting stained solution is read in a spectrophotometer at a wavelength of 412 mμ.

Sampling Procedure

The sample is collected in a specially constructed bubbler containing 8 ml of distilled water. A sampling rate of 0.5 lpm for 5 minutes will usually provide an adequate sample.

Interferences

Formaldehyde, formaldehyde-producing substances, ethylene oxide, and ethylene glycol will interfere with this determination. The method requires less than 2 hours for analysis and is suitable for industrial hygiene work. It is not sufficiently sensitive for air pollution work.

Ethyl Acetate

Goddu, R. F., N. F. Le Blanc, and C. M. Wright. **Spectrophotometric Determination of Esters and Anhydrides by Hydroxamic Acid Reaction,** Anal. Chem. 27, 1251 (1955).

See Also

Hill, V. T. Ind. Eng. Chem., Anal. Ed. 18, 317 (1946).

Ethyl acetate, in concentrations above approximately 20 ppm in a 25-liter air sample, can be determined by this method. The sample is collected in two fritted bubblers connected in series, each containing ethyl alcohol. The sample is reacted with an alkaline hydroxylamine solution. The addition of ferric ion to this mixture produces a highly-colored product. The absorbance of this product is read at a wavelength of 530 mμ, and the quantity of ester present is read from a calibration curve. The airborne concentration is calculated.

Sampling Procedure

The air sample is collected in two fritted bubblers connected in series, each containing 10 ml ethyl alcohol. The sampling rate should be approximately 1–2 lpm until at least 25 liters of air have been sampled.

Interferences

Any other ester, anhydrides, aldehydes, and isocyanates will interfere with this determination.

This method requires approximately 2 hours for complete analysis. The method is applicable to industrial hygiene work but is not sufficiently sensitive for air pollution work.