This Health Hazard Evaluation (HHE) report and any recommendations made herein are for the specific facility evaluated and may not be universally applicable. Any recommendations made are not to be considered as final statements of NIOSH policy or of any agency or individual involved. Additional HHE reports are available at http://www.cdc.gov/niosh/hhe/reports

HAZARD EVALUATION AND TECHNICAL ASSISTANCE REPORT
HETA 90-198-L2060
GENCORP POLYMER PRODUCTS
MOGADORE, OHIO
AUGUST 1990

Hazard Evaluation and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations, and Field Studies
National Institute for Occupational Safety and Health
4676 Columbia Parkway
Cincinnati, Ohio 45226

HETA 90-198
August 1990
Gencorp Polymer Products
Mogadore, Ohio

NIOSH INVESTIGATORS:
Robert F. Mouradian, Ph.D.
Steven Douglas

Summary

In response to a request for a Health Hazard Evaluation, NIOSH industrial hygienists visited Gencorp Polymer Products in Mogadore Ohio on June 13 and 14, and conducted an on-site evaluation. The investigation included an industrial hygiene walk-through, air sampling for time-weighted average concentrations of styrene and 1,3-butadiene monomer, a semi- quantitative evaluation of exposures with a photo-ionization detector, interviews with employees and management, and a brief review of plant industrial hygiene records.

Information collected during the investigation indicates that there is little chance of continuous or frequent exposure to either monomer. Most exposures are likely to be of short duration and are associated with sampling and unloading of monomer, cleaning of the reactor vessels and repair or maintenance activities.

There was no evidence of styrene exposures that would exceed the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL), the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) or the NIOSH Recommended Exposure Limit (REL).

Short term exposures to 1,3-butadiene were documented during the monomer sampling procedures and probably occur during some other activities. Although 1,3-butadiene exposures are unlikely to exceed either the OSHA PEL or the ACGIH TLV, NIOSH recommends that exposures be limited to the lowest feasible level. This recommendation is based on demonstrated carcinogenic effects in animals and a lack of information that would demonstrate a safe exposure level in humans. Recommendations for minimizing exposures to 1,3-butadiene and styrene were discussed during the closing conference and are presented at the end of this report.

Background and Process Description

In March 1990 the International Chemical Workers Union (ICWU) contacted the National Institute for Occupational Safety and Health (NIOSH) and requested that a Health Hazard Evaluation (HHE) be conducted at Gencorp Polymer Products in Mogadore Ohio. The ICWU asked NIOSH to evaluate the potential for worker exposures to styrene and 1,3-butadiene monomers that are used in the production of styrene-butadiene rubber (SBR) latex.

The SBR production process used at the Gencorp plant is similar to that used in other latex production facilities. Styrene, 1,3- butadiene and an aqueous solution of soaps, inorganic catalysts and other additives is fed into a series of closed reaction vessels. The polymerization reaction is exothermic and is controlled by the feed rate and temperature. Once the reaction is complete, the product flows into a steam stripping vessel where any non-reacted materials are separated from the final product. During the stripping process, samples of the product are collected from the bottom of the stripping tank for quality control analysis. The samples are collected by an automatic valve system which was installed to minimize exposures to the employees who handle quality control samples. The reaction is reported to be over 99% efficient, and by the end of the stripping process there appears to be little chance for exposure to monomer.

At the Mogadore facility, the entire production process is monitored and controlled by an operator who is stationed in an enclosed control room.

Monomer arrives at the Gencorp plant in either tank trucks or rail cars. In either case a small sample of monomer is first collected and sent to the on-site laboratory for quality control analysis. The tank is then unloaded using a positive pressure system that feeds the monomer through a closed system of pipes and into storage tanks. The styrene and 1,3-butadiene are delivered, unloaded and stored in separate areas, all of which are outdoors.

In response to the ICWU request, an industrial hygiene evaluation was conducted. Because the styrene and 1,3-butadiene are the most hazardous materials used in this operation, the NIOSH investigation was focused on operations involving handling of monomer rather than final product. The evaluation included the following five steps:

1. An industrial hygiene walk-through and inspection.

2. Air sampling for 1,3-butadiene and styrene using standard NIOSH methods.

3. A semi-quantitative evaluation of 1,3-butadiene exposure using an HNU Systems photo-ionization detector (PID).

4. A review of industrial hygiene and environmental data collected by GenCorp.

5. Private interviews with employees.

Evaluation Criteria

Health Hazards Associated with 1,3-Butadiene

Historically 1,3-butadiene was considered to be a relatively low toxicity compound with the primary hazards being chemical fires, frostbite from contact with the highly volatile liquid, minor eye irritation and a narcotic effect at several thousand parts per million (ppm). Based on the low acute toxicity and absence of known chronic effects, OSHA originally set a PEL of 1000 parts per million (ppm) as an eight hour time-weighted average.

Recently, carcinogenic and adverse reproductive effects have been documented in laboratory animals exposed to 1,3- butadiene. Although epidemiological studies of exposed workers have been inconclusive, NIOSH believes that the evidence is strong enough to classify 1,3-butadiene as a potential human carcinogen.

In 1984 NIOSH published a Current Intelligence Bulletin summarizing the data that was available at that time, and recommending that worker exposures be limited to the lowest feasible level. This recommendation was based on long-term animal studies that demonstrated carcinogenicity, teratogenicity and adverse effects on the testes and ovaries. Because of the possible link to cancer, most public health agencies have now revised their recommendations concerning worker exposure to 1,3-butadiene. OSHA is currently in the process of revising the PEL and is expected to promulgate a new, lower exposure limit. The ACGIH has set a TLV of 10 ppm and now includes 1,3-butadiene on their list of suspected human carcinogens.

Health Hazards Associated with Styrene

Styrene, or vinylbenzene, is a colorless liquid with a strong odor at room temperature. Like 1,3-butadiene, it is highly flammable and can be a significant fire hazard.

Styrene has been widely used in industry and has been well characterized in terms of acute toxicity. Exposure to styrene vapors at relatively low concentrations can cause immediate irritation of the eyes and respiratory system. At higher concentrations, the vapor is a narcotic and can cause disorientation, confusion and loss of consciousness. Skin contact with styrene liquid causes drying and inflammation and may result in dermatitis or rash.

The health effects associated with long-term exposure are less well known. Long-term exposure at high concentrations may affect the nervous system, respiratory system, liver and skin. Recently, there have been some studies that suggest a link between styrene exposure and cancer. However, the evidence for carcinogenic effects is relatively weak and NIOSH does not currently classify styrene as a human carcinogen.

Based on acute and chronic health effects, OSHA has set a PEL of 50 ppm as an eight hour time-weighted average. OSHA has also issued a Short Term Exposure Limit (STEL) of 100 ppm for an exposure duration of fifteen minutes. The ACGIH TLV is identical to the OSHA PEL, but with a notation that styrene is "identified by other sources as a suspect or confirmed human carcinogen." Current NIOSH policy calls for a REL of 50 ppm as a time-weighted average for a 10 hour day and 40 hour work week. A ceiling limit, or maximum peak exposure, of 100 ppm is also recommended along with a warning to avoid skin contact. NIOSH recommendations are based on nervous system effects, respiratory irritation and suspected adverse reproductive effects.

Air Monitoring Results

As part of the industrial hygiene evaluation, six air samples were collected for 1,3-butadiene analysis and six were collected for analysis of styrene. In each case three of the samples were personal breathing zone samples and three were area samples.

Area samples were collected upstairs at reactor 10 and downstairs near stripper 7 using low flow pumps. Area samples were also collected at the styrene tank farm and near reactor 1 using high flow pumps.

Personal breathing zone samples were collected with the cooperation of a maintenance mechanic, two employees sampling and unloading monomer, and two who were cleaning a reactor vessel.

The data, presented in Table 1, indicates that styrene exposures levels did not exceed any applicable standards. No styrene exposures were detected with personal samplers, and only one area sample contained a detectable level of styrene. 1,3-butadiene was detected in two personal samples with the highest exposure being recorded on the employee who collected the quality control sample and unloaded the tank car. In each case the 1,3-butadiene levels were well below the current OSHA PEL and the ACGIH TLV. As noted elsewhere, NIOSH does not recommend a specific exposure limit and instead recommends that exposures be limited to the lowest feasible level.

The number of samples collected in this evaluation was too small to represent a statistically valid survey, and no generalizations about plant-wide exposures can be made. In addition, it should be noted that these data represent four-hour average exposures and do not provide an accurate representation of any short-term or peak exposures that might have occurred.

Discussion

Based on data collected during the evaluation and on a review of the process, it appears that there is little potential for routine or continuous employee exposures to either styrene or 1,3-butadiene. Most of the production activities are fully automated and occur within closed systems.

Because most handling and storage of monomer occurs outdoors there is little potential for buildup of vapors. However, some activities were identified as possible sources of exposure. Work activities that appear most likely to result in exposure are:

1. Sampling monomer for quality control testing.

2. Unloading styrene or 1,3-butadiene monomer from tank cars or trucks.

3. Opening and cleaning reactor vessels.

4. Repair work on lines that carry monomer.

Each of these possible exposures was evaluated and the findings in each area are presented here.

1. Quality control sampling of monomer.

   When a shipment of monomer arrives at the Gencorp facility, a small sample is collected for quality control analysis. The collection procedure is dependent on which monomer is being sampled and on whether the material was shipped in a rail car or a truck.

   During the NIOSH survey a sample of 1,3-butadiene was collected from a rail car. To collect the quality control sample, an employee places a small flask over the sampling nozzle at the top of the rail car and opens a sampling valve. Because of the high volatility of 1,3-butadiene and the pressure in the tank car, a significant amount of 1,3- butadiene gas escapes. In addition, the liquid collected in the flask immediately starts to boil and can create a significant short-term exposure.

   Once the sample is collected, the flask is returned to the pump-house and heated with steam to drive of the rest of 1,3-butadiene, leaving the polymerization inhibitor as a residue. The evaporation step is performed outdoors, but depending on wind conditions, the 1,3-butadiene vapor can be carried to the operator's station inside the pump-house.

   A real-time measure of exposures during the sampling was made with a PID. The PID, which is only a semi-quantitative instrument, indicated that peak exposures of 50 to 100 ppm might occur during the sampling. During the evaporation step, peak concentrations of 10 to 50 ppm were recorded in the pump-house.

   The procedures used for quality control sampling of the styrene monomer were not observed during the NIOSH visit. Therefore, no specific recommendations can be made. Because styrene is a liquid at normal ambient temperatures, the potential for exposures is probably less than it is for 1,3- butadiene. However, employees should be aware that sampling of monomer can result in exposures, and that appropriate precautions should be taken.

2. Unloading monomer from tank cars and trucks.

   Once the quality control analysis is completed, the monomer is unloaded, or transferred to the tank farm for storage. Again, the procedure used for unloading of the monomer varies somewhat for the two compounds under study and depends on whether the material has been delivered in trucks or rail cars. In all cases, short term exposures are most likely to occur at the start and end of the process when lines are connected and disconnected. There also appears to some potential for exposure to 1,3-butadiene during the actual unloading process. These exposures could occur in the pump-house if the compressor leaked or malfunctioned. No exposures due to compressor leakage were actually documented. However, the risk of exposure could be reduced by having the operator work from the other building.

3. Opening and cleaning of reactor vessels.

During the production process a certain amount of polymerized material tends to collect on the walls and agitator in the reaction vessels. To remove this buildup, the tank is first cleaned with a series of water and/or steam flushes. One or two access ports are then opened by a maintenance team and a flexible exhaust hose is attached to the reactor. The polymer is then blasted off the walls with a high pressure water spray which is controlled by an employee who stands outside the vessel.

If the reactor has two ports, the exhaust hose is attached to one port and the cleaning crew accesses the reactor through the port on the opposite side. If the reactor has only one port, the ventilation and cleaning access are provided through the same opening.

During the HHE, a reactor with the two port design was being cleaned. The ventilation system appeared to be effective and probably reduced exposure to any residual monomer to a minimum. It is reasonable to assume that the single port design is less effective, but no actual evaluation was attempted.

Maintenance workers indicated some concern over short-term exposures that might occur when the reactor vessel is first opened and before the ventilation system is connected. This seems to be a legitimate concern. However, we did not have an opportunity to make any measurements. Some general recommendations on opening and cleaning the reaction vessels are included at the end of the report.

4. Maintenance and repair activities

Although no repairs were in progress during the NIOSH evaluation, some maintenance personnel did indicate concern over possible exposure due to leaks or equipment failures. This type of exposure is common in chemical production facilities and may be difficult to control. The Mogadore plant appeared to be in an excellent state of repair and the employees indicated that any leaks or failures are normally repaired immediately. Exposure during repair activities can best be minimized through the use of proper work practices and with personal protective equipment. Some specific recommendations are included at the end of this report.

Conclusions and Recommendations

In general, the health and safety programs at the Gencorp plant appear to be well developed and effective. Although average exposure levels at the Mogadore plant are probably very low, there are some tasks which are likely to result in short-term exposures to either 1,3 butadiene and/or styrene. As noted earlier, NIOSH considers 1,3-butadiene to be a potential human carcinogen and recommends that exposures to this compound be limited to the lowest feasible level. In addition, although NIOSH does not currently consider styrene monomer to be a known human carcinogen, it would be prudent to limit exposures as much as possible.

The recommendations presented here are intended to minimize short-term exposures that might be associated with specific operations or with unusual circumstances. In some cases these issues may have already been addressed by the company, or alternate approaches may prove to be more feasible.

1. The collection procedure used in quality control sampling of the 1,3-butadiene tanks appears to be the single most important source of exposure. The exposure level should be reduced by using a closed sampling system, possibly with a vent line that would carry the vapor away from the employee who does the sampling. An alternate approach would require the use of personal protective equipment including a full- face respirator, gloves and apron. Because personal protective equipment is often uncomfortable and requires employee participation, redesigning the sampling system is the preferred approach. The respirator program that is currently in use at Gencorp was not reviewed as part of the NIOSH evaluation. As always, a program that meets OSHA standards is recommended.

2. The evaporation of 1,3-butadiene during the quality control measurement should be conducted in a more controlled environment. It is recommended that the evaporation be done in a laboratory-type hood or that a vented evaporation device be installed near the unloading area. This could be a simple device with a steam heated base and an exhaust stack that would carry the vapor above, and away from, the breathing zone.

3. Controls and monitors should be installed in the new operator's shelter at the 1,3-butadiene unloading area. This would allow the operator to stay in the shelter and away from the compressor.

4. Employees who unload or sample either styrene or 1,3- butadiene should be required to wear chemical protective clothing including gloves and eye protection.

5. In response to employee complaints about odors while loading tank trucks, ventilation should be extended to the loading area.

6. In several areas, the pipes carrying monomer or other raw materials did not appear to be clearly marked. Failure to identify content and flow direction can present a hazard to maintenance and repair workers. All pipes should be clearly labelled and the flow direction should be marked to minimize the chance of exposure during repair and maintenance activities.

7. Although NIOSH investigators did not witness the procedures used in opening reactors for cleaning, there was some concern expressed over possible exposures at that time. The most effective control would be a negative pressure system that would insure that air flows into the vessel as it is opened. This type of system would require careful design to prevent formation of a vacuum that would hold the hatch shut. However, it should be possible to develop such a system. A simpler, but probably less effective, alternative would be to provide portable fans which the maintenance workers could use to direct vapors away from the breathing zone. Once the reactor ventilation system is connected the fans would then be removed to prevent interference with normal operation of the ventilation system.

8. The ventilation system used during reactor cleaning appeared adequate, but should be tested at the start of each cleaning operation. A simple qualitative test would be conducted by using smoke tubes which are available from most safety suppliers. The efficiency of the single port systems is likely to be less than that of the dual port systems. It is therefore especially important that the single port system be evaluated.

9. The current practice of having personal protective equipment, including a self contained breathing apparatus (SCBA), available for maintenance workers during incidents such as spills should be continued. As noted earlier, the current respirator program was not reviewed, but should meet OSHA requirements.

10. 1,3-butadiene was detected in the air sampler worn by a mechanic who was repairing a pump. This may indicate a need for improved ventilation during pump repair and similar activities. The possibility of improved general ventilation and/or installation of local exhaust should be considered.

Table I
Results of Styrene & 1,3-Butadiene Monitoring
HETA 90-198
Gencorp Polymer Products Inc.
June 14, 1990

Employee / Location	Average Vapor Concentration (mg/m^3) Styrene	1,3-Butadiene
REACTOR 7, BLOW-DOWN (AREA)	ND	ND
REACTOR 10, TOP LEVEL (AREA)	ND	ND
STYRENE TANK FARM (AREA)	0.1	NA
REACTOR 1, STRIPPER (AREA)	NA	0.2
REACTOR CLEANER	ND	ND
PUMP REPAIR MECHANIC	ND	1.4
STYRENE SAMPLING & UNLOADING	ND	NA
BUTADIENE SAMPLING & UNLOADING	NA	6.3

All data represents 4 hour average concentration
Limit of detection for Styrene = 0.01 mg/sample
Limit of detection for 1,3 Butadiene = .01 mg/sample

Evaluation Criteria

Exposure Standard (mg/m^3)	Styrene	1,3-Butadiene
OSHA PEL	215	2200
OSHA STEL	425	NA
ACGIH TLV	213	22
ACGIH STEL	425	NA
NIOSH REL TWA AVERAGE	213	LFL
NIOSH REL CEILING	426	NA

Abbreviations

mg/m^3 : milligrams of contaminant per cubic meter of air
OSHA : Occupational Safety and Health Administration
PEL : Permissible Exposure Limit (8-hour exposure)
STEL : Short Term Exposure Limit (15-minute exposure)
ACGIH : American Conference of Governmental Industrial Hygienists
TLV : Threshold Limit Value (8-hour exposure)
ND : Not Detected
NA : Not Available