PRELIMINARY SURVEY REPORT:

OCCUPATIONAL HAZARD CONTROL OPTIONS FOR CHEMICAL PROCESS UNIT OPERATIONS

AT

Monsanto Company
Pensacola, Florida

REPORT WRITTEN BY:
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NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
Engineering Control Technology Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226

PLANT SURVEYED:	Monsanto Company Site Maleic Anhydride Plant Pensacola, Florida
SIC CODE:	Group No. 281, Industry No. 2815
SURVEY DATE:	November 21, 1983
SURVEY CONDUCTED BY:	Harold D. Van Wagenen Charleston C. K. Wang
EMPLOYER REPRESENTATIVES CONTACTED:	Mr. Richard Monty, Superintendent of Environmental Health and Safety at Pensacola Site (Monsanto Fibers and Intermediates Company) Dr. Lester Bynum, Supervisor of Industrial Hygiene at Pensacola Site (Monsanto Fibers and Intermediates Company) Mr. Will Dunn, Manufacturing Supervisor, Maleic Anhydride Plant (Monsanto Industrial Chemicals Company) Mr. Peter Fodor, Maintenance and Scheduling Supervisor, Maleic Anhydride Plant (Monsanto Industrial Chemicals Company)
EMPLOYEE REPRESENTATIVES CONTACTED:	Not contacted (non-union)
ANALYTICAL WORK PERFORMED BY:	None performed

I. INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is conducting a study titled "Occupational Hazard Control Options for Chemical Process Unit Operations." Objective is to obtain and disseminate information on principles, equipment, and techniques employed in the chemical processing industries to minimize or eliminate worker exposure to hazardous compounds. This project is being conducted by NIOSH personnel on an in-house basis.

Preliminary site visits are made to a number of chemical processing facilities to obtain information on effective control technology. Later, in-depth studies, which may include area and personal monitoring and monitoring of emission sources for specific materials, will be conducted on a minority of these facilities--selected on the basis of the effectiveness of controls observed during preliminary site visits.

The reports from these surveys are then used as a basis for preparing technical reports and journal articles on effective hazard control measures. The information from these research activities builds the data base of publicly available information on hazard control techniques for use in preventing occupational exposure to hazardous chemicals.

This report covers the preliminary visit of November 21, 1983, to the Monsanto Company site at Pensacola, Florida. Two separate Monsanto companies conduct chemical processing at this huge complex; 1) the Monsanto Fibers and Intermediates Company and 2) the Monsanto Industrial Chemicals Company. The Fibers and Intermediates Company, having the preponderance of processing operations and overall site management, approved our site visit to inspect and discuss the control technology employed in minimizing occupational exposure in the recently completed maleic anhydride processing facility. This facility and its personnel are part of the Industrial Chemicals Company. During the visit, it became apparent that personnel from the two Monsanto companies were operating under markedly different interpretations of what constitutes proprietary information. Information on site management and medical, industrial hygiene, and personal protective equipment aspects of control technology were freely forthcoming from the F&I personnel. Unfortunately, because the Industrial Chemicals personnel disclosed only very limited and generalized information about the maleic anhydride facility, this report is sketchy in the control technology areas of work practices, engineering controls, and monitoring.

II. GENERAL FACILITY

This large (approximately 2,000-acre) site is located approximately 11 miles north of the City of Pensacola, abuts the Escambia River, and is reached by U.S. Highway 29. About 500 acres are occupied by processing units, parking lots, tank farms, and various buildings. Originally a Chemstrand site, it is now operated solely by Monsanto. Approximately 4,000 non-union employees comprise the site staff. Of these, about 40 operate the new maleic anhydride facility, with the remainder conducting Fibers and Intermediates operations. Veteran operators from the Fibers and Intermediates Chemical installations were selected by management for training for the maleic anhydride unit prior to its startup.

The principle raw materials for nylon manufacture, cyclohexane and ammonia, come by barge up the Escambia River to the site barge dock. Barge transportation is also anticipated for the main raw material to maleic anhydride processing, n-butane.

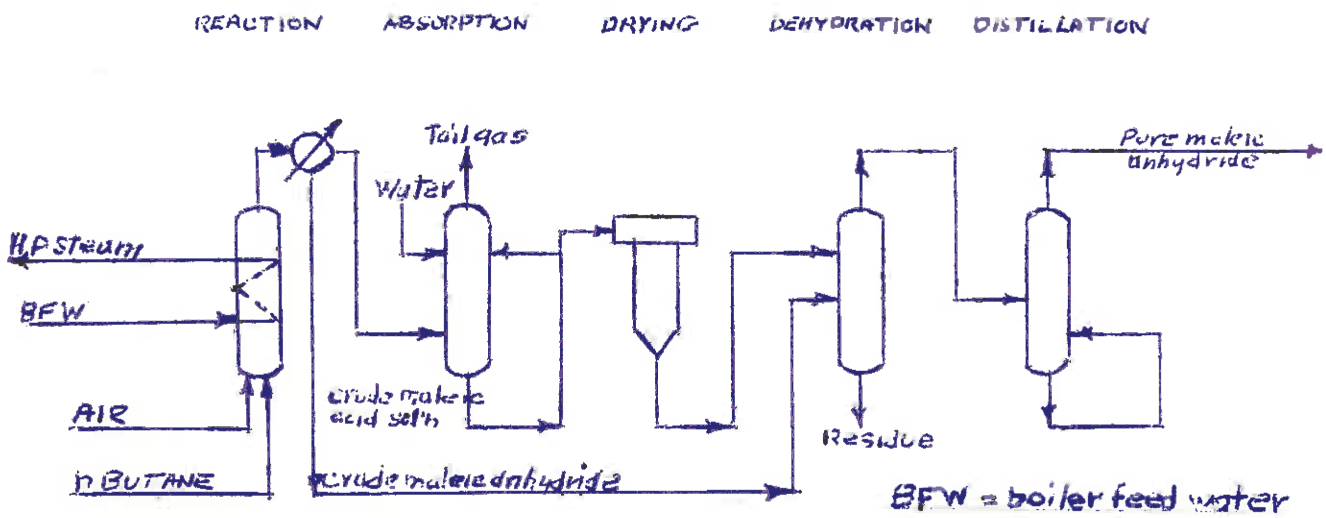
The site organization has five separate occupational protection functions reporting to the Superintendent of Environmental Health and Safety. These are: 1) Safety, 2) Fire Protection, 3) Medical, 4) Environmental Control, and 5) Industrial Hygiene. The site Manager of Industrial Hygiene is in charge of a three-person laboratory as well as two other full-time technicians who make industrial hygiene measurements. The laboratory is fully accredited by the American Industrial Hygiene Association. Site employee medical protection is furnished by a resident physician, two full-time physician assistants, and a full-time audiologist handling noise problems encountered in Fibers and Intermediates operations. Annual physical exams are offered as well as blood and pulmonary function testing. Site fire protection is supported by three fire trucks, and emergency accident cases are handled by a site ambulance. These facilities have operated so well that the City of Pensacola has never been approached for assistance.

The Environmental Control group supervises and monitors all site operations to ensure that U.S. Environmental Protection Agency (EPA) requirements (regulations and limits) are met for hazardous waste handling and disposal, water pollution, and volatile organic compound (VOC) emissions.

The Industrial Chemicals Company started up this new maleic anhydride processing facility in April 1983. The facility, featuring the latest state-of-the-art equipment and technology, is continuous, outdoors, highly automated, and already meeting the 130-million-pound-per-year output rating listed in chemical trade magazines. This processing facility is an entity in itself (being completely separate from Fibers and Intermediates) from raw material unloading through finished product storage and tank car filling. Besides the technology upgrading, the main changed feature of this facility is the shift from employing benzene feed stock to n-butane. Kirk and Othmer's "Encyclopedia of Chemical Technology" states that in 1979, 83 percent of maleic anhydride production was derived from benzene oxidation, 15 percent by n-butane oxidation, and 2 percent as phthalic anhydride by-product. Also, Monsanto is cited as starting the first commercial production by n-butane oxidation in 1974 at their St. Louis, Missouri, site. Trade publications indicate that since 1979, there has been a marked shift toward using n-butane as a substitute feed stock for benzene in maleic anhydride processing; as evidenced by this new Monsanto Pensacola facility, by Monsanto converting most of their St. Louis capacity, and by other chemical manufacturers.

III. PROCESS DESCRIPTION AND EXPOSURE HAZARDS

The predominant commercial route to maleic anhydride is vapor phase oxidation of hydrocarbons (i.e., benzene, n-butane, n-butylene) over a proprietary catalyst. The reaction and recovery of maleic anhydride and its purification is illustrated in the accompanying simplified flow sheet for n-butane oxidation (taken from trade magazine sources).



The reaction step involves oxidation of a relatively low concentration of n-butane in air to form maleic anhydride, oxides of carbon, water, and smaller amounts of partially oxidized by-products. The highly exothermic reaction requires low feed concentrations, expensive heat transfer equipment, and large scale gas handling. This situation can be employed advantageously to produce an important by-product energy source - high-pressure steam. Over 50 molar percent completeness on a once-through basis is claimed for this process when using a proprietary fluid bed catalyst. Advantages cited for a fluid bed reactor over the more conventional fixed bed catalyst system are:

a) Safe operation with a lower air to butane ratio. This reduces air compressor costs, gives better temperature control, and eases catalyst loading, unloading, and maintenance.

b) Longer catalyst life and higher on-stream time.

c) No molten salts or flammable heat transfer fluids employed.

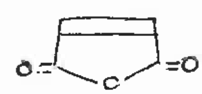
d) Lower capital costs.

The second step is recovery of maleic anhydride from the dilute reactor of gas and purification of the crude product. Maleic anhydride in the reactor off gas is continuously condensed by cooling the gases to a dew point below that of maleic anhydride and above water in a specially designed condenser. Maleic anhydride remaining in the effluent gases is absorbed in water, forming crude maleic acid solution. Next, this is evaporated under vacuum and then thermally converted to anhydride in a specially developed dehydration reactor. Finally, pure maleic anhydride product is achieved by vacuum distillation. The fluid bed reaction and product purification are performed continuously and without use of organic solvents as an entrainer.

This Pensacola maleic anhydride facility operates continuously on a 3-shift, 7-day per week basis with no downtime since initial startup. Operator staff comprises five men per shift. Due to the high degree of automation, three of the five are stationed in the very elaborate control room. To operate on this continuous basis, four separate shift crews are rotated. Currently, the n-butane arrives by rail car and is unloaded into either of two large spherical storage tanks located near the barge unloading area. While exposure to n-butane is not considered a major occupational hazard, it presents major fire and explosion hazards. Hence, the unloading site is located away from the processing unit (approximately one-half mile) and an underground welded line conveys liquid n-butane from the two storage spheres to the initial processing unit, the vaporizer. The n-butane is both shipped and stored as a liquid under 38 psi pressure. A plant project is now underway to receive commercial n-butane by barge. Advantages are lower shipping costs and added ability to take advantage of spot market purchasing. It seems likely the facility started up with a purer grade of n-butane to ensure catalyst performance and later operation demonstrated that lower purity n-butane can be substituted without detrimental effect.

The finished maleic anhydride is stored as a liquid prior to tank car filling for shipment to customers. Dedicated, specially lined, jacketed tank cars are employed. Generally, by the time these tank cars reach customer plants, the maleic anhydride has solidified and remelting will be necessary. Both the Monsanto storage tanks and the dedicated tank cars are blanketed using nitrogen as the inert gas.

Whereas benzene is considered particularly toxic (a carcinogen) with long-term exposure causing anemia and leukopenia at concentrations too low for detection by odor or simple instruments, n-butane (CH_3-CH_2-CH_2-CH_3) is a colorless simple asphyxiant, irritant, and anesthetic at high concentrations. OSHA has no PEL listing for n-butane, but ACGIH (1983-84) recommends an 8-hour threshold limit value (TLV) of 800 ppm (1,900 mg/m^3). n-Butane has a boiling point of -0.5^{o}C, a closed cup flash point of -76^{o}F, and a disagreeable odor which can be detected at low concentrations. Lower and upper explosive limits (lel and uel) are 1.9 and 8.5 percent by volume, respectively. Large quantities of n-butane are sold as a petrochemical feed stock at between 95 and 99.5 mal percent purity under contract specification standards.

Maleic anhydride is represented structurally as  . It occurs either as a colorless liquid or a white solid with an acrid, irritating odor detectable by the average person at 1 ppm or under. Both OSHA PEL and ACGIH 8-hour TLV is 0.25 ppm (1 mg/m^3). Based on this data, maleic anhydride is considered to have good warning properties. It has a melting point of 127°F (53°C), vapor pressure of 0.16 mm Hg at 20°C, flash point (closed cup) of 215°F, and lower and upper explosive limits (lel and uel) of 1.4 and 7.1 percent by volume, respectively. Dust and vapors of maleic anhydride must be kept away from flames or sparks because it is both flammable and explosive. Because of its corrosivity to both skin and eyes, extreme care must be exercised in handling or sampling this product to avoid eye or skin contact. It is a severe irritant of the eyes and is both an irritant and sensitizer of the skin and the respiratory tract. Asthma may result from repeated overexposure. Subacute inhalation can cause severe headaches, nosebleeds, nausea, and temporary impairment of vision.

IV. CONTROLS

Summary

Occupational exposures can be controlled by the application of a number of well-known principles, including engineering controls, work practices, personal protective equipment, and monitoring. These means may be applied at or near the hazard source, to the general workplace environment, or at the point of occupational exposure to individuals. Controls applied at the source of the hazard, including engineering controls (material substitution, process/equipment modification, isolation or automation, local ventilation) and work practices, are generally the preferred and most effective means of control for both occupational and environmental problems. Controls which may be applied to hazardous emissions dispersed in the workplace environment include general dilution ventilation, dust suppresssion, and housekeeping. Control measures which are applied near or by individual workers, include the use of remote control rooms, isolation booths, work practices, and personal protective equipment.

In general, a system comprised of the above control means is required to provide worker protection under normal operating conditions as well as under conditions of process upset, failure, and/or maintenance. Process and workplace monitoring devices, personal exposure monitoring, and medical monitoring are important mechanisms for providing feedback concerning the effectiveness of the controls in use. Ongoing monitoring and maintenance of controls to ensure the proper use and operating conditions, and the education and commitment of both workers and management to occupational health are also important ingredients of a complete, effective, and durable control system.

These principles of control apply to all situations, but their optimum application varies from case-to-case. A great deal of preplanning and situation analysis was performed prior to the erection of this Monsanto maleic anhydride processing facility. From the standpoint of preventing and/or minimizing worker occupational exposure, planning, design, and layout of this facility concentrated on four fundamental factors according to Mr. Monty (Site Superintendent of Environmental Health and Safety). These factors are:

a) Switching from benzene to n-butane as feed stock.

b) Buttoning up the facility so there were as few emission sources as possible.

c) Selecting and using customary and also special personal protective equipment.

d) Automation of processing equipment so that workers would not have to be in contact with chemicals.

Engineering Controls

As already mentioned, engineering controls include material substitution, process/equipment modification, and isolation and/or automation. All of these have been applied in this Monsanto processing unit as follows:

1) Material Substitution - The shift to n-butane feed stock from benzene is based on a number of factors:

   a) Commercial n-butane is cheaper than benzene. In 1979, the differential was 8 cents per pound.

   b) Theoretically, a pound of n-butane can yield 1.69 pounds of maleic anhydride versus 1.26 pounds from a pound of benzene. The lower cost of n-butane and the higher theoretical yield provide a substantial economic basis for the shift.

   c) The carcinogenic nature of benzene and the resultant proposed OSHA PEL of 1 ppm is a major negative from the standpoint of worker occupational exposure. The fire and explosive nature of n-butane is partially counterbalancing.

   d) The EPA National Emission Standard for Hazardous Air Pollutants - "Benzene Emissions from Maleic Anhydride Plants" (40 CFR Part 61) called for no detectable benzene emissions from any new benzene-based maleic anhydride production units. This provides a powerful incentive even though EPA emission standards for volatile organic emissions (VOC) cover n-butane.

2) Process/Equipment Modification - Monsanto made a concerted effort to minimize the number of potential emission sources; e.g., replacing flanged with welded lines wherever possible. Unavoidable potential emission sources (such as pumps, relief valves, etc.) were reduced to approximately 60. To monitor these potential emission points, an elaborate automated warning system was installed (see monitoring). The advantages from minimizing potential emission sources has been partially counterbalanced by increased maintenance problems; i.e., in clearing lines where maleic anhydride has solidified. Maintenance personnel and operators involved in such situations employ personal protective equipment to safeguard themselves from contact with solid maleic anhydride and inhalation of maleic anhydride vapors.

   In n-butane unloading, storage, chemical processing, and finished maleic anhydride tank storage and tank car filling, vapor recovery systems are employed. These are designed to function as closed loops to prevent emissions to the atmosphere and to remove vapors where possible. In those cases where vapors cannot be economically recovered, they are collected and destroyed by incineration. These vapor-handling systems permit compliance with strict EPA volatile organic compound (VOC) emission limits and minimize occupational exposure.

3) Isolation and/or Automation - Both of these engineering control principles have been applied. Several specific means of automation, which function to prevent worker contact with chemicals, are in place and appear to be operating effectively. They were classified as proprietary and therefore can be described only in very general terms. One is a complicated system within the chemical processing unit for taking internal samples and transmitting them to a centrally located vapor phase gas chromatography analytical setup. By this means, completeness of reaction and other process composition information are obtained without the need for facility operators to manually withdraw processing samples and convey them to a laboratory. GC results generated in this central analytical setup are electronically transmitted to the central control room. In a similar manner, operating condition information is obtained at locations throughout the facility and transmitted to panel boards in the same control room. Another proprietary process control mechanism acts to prevent abnormal occupational exposure. Monsanto has installed two different means for accurately accounting for total usage of n-butane in the unit (a carbon material balance). Under normal, controlled reaction operation, the two schemes show similar consumption of n-butane. However, if the results of the two schemes vary beyond an acceptable parameter, the entire unit is automatically shut down, thus stopping unknown diversion of n-butane until the situation is corrected.

Monitoring

From the standpoint of direct prevention of occupational exposure, the multipoint emission sensing system already mentioned, provides excellent and straightforward monitoring. A separate large board in the central control room contains warning lights and horns connected directly to all 60 possible unit emission sources. Details of the sensing elements and the actuating levels causing central control room warning were not disclosed.

Industrial hygiene area sampling and measurements conducted during the maleic anhydride facility startup were reported to have shown that the OSHA 0.25 ppm PEL limit for maleic anhydride was being met. Personal sampling has not been performed because of the lack of a suitable sampling method and equipment.

Work Practices

Little information was elicited relative to the training programs conducted for the personnel of the maleic anhydride facility. Since we were told that only veteran chemical operators from the Fibers and Intermediates Company Pensacola staff (not new hires) were selected by management for this new unit, it appears that general training had already been assimilated and that only details of the individual job classifications for this specific facility were included.

An important aspect of work practices is area cleanup and general housekeeping. Generally, there is a correlation between how well the job is conducted and the level of general housekeeping. On this basis, the Pensacola maleic anhydride facility measured up well.

Personal Protective Equipment

All the requisite personal protective equipment necessary for safe job performance is supplied by the company. Personal protective equipment is a necessity in a number of hazardous situations; 1) maintenance operations on various pieces of processing equipment and/or auxiliaries, 2) cleaning up spills or product disposal, 3) taking finished product samples for chemical analysis, and 4) emptying and filling storage tanks and tank car or tank truck shipment lots.

Having the overall site management responsibility, the Monsanto Fibers and Intermediates Company has developed a very thorough program and a detailed written summary of all site wide aspects of personal protective equipment. Successive steps taken in this program are:

A) Individual facility supervision provides a list of personnel whose jobs will require the use of personal protective equipment, including respiratory protection.

B) The Medical Department evaluates these employees as to their physical/medical capabilities in relationship to the hazardous chemicals they encounter in their specific jobs.

C) The Industrial Hygiene Department is responsible for providing information on specific chemicals and hazards, and for making decisions as to the need for, and suitability of, various protective equipment items. For the job categories determined to require respirators, the Department selects the types to be used, and provides training aids, demonstrations, and qualitative fit tests for the involved facility personnel.

D) The facility supervision must ensure that appropriate training is conducted and that the use and maintenance of the personal protective equipment is carried out in accordance with the guidelines established by the site management. The workers have the responsibility for cleaning and maintaining the respirators issued to them.

   In the maleic anhydride facility, the extent of the personal protective equipment required, depends directly on the possibility and/or probability of body contact with liquid or solid maleic anhydride and/or inhalation of the vapors. The plant safety manual sheet for maleic anhydride issued by the site manager of industrial hygiene states:

   1) Employees are required to use splashproof safety goggles and rubber gloves if there is even a remote possibility of solid or liquid maleic anhydride or liquids containing maleic anhydride contacting the eyes.

2) If greater possibility of such bodily contact is likely, then use of a face shield, full protective clothing, and/or apron, boots, and respirators are required.

3) Where the job requires respiratory protection, the guidelines are:

   a) If job or task exposures have been determined to exceed 0.25 ppm (1 mg/m^3), but less than 12.5 ppm (50 mg/m^3), the use of a full-face respirator with organic vapor/acid gas cartridges is required. A Scott air Pak can also be employed.

   b) If exposure is greater than 0.25 (1 mg/m^3) (approximately the threshold of smell), but concentration is unknown and judged hazardous, the only acceptable respirator is the Scott air Pak.

4) An eye wash fountain should be available within the immediate work area for emergency use.

5) Both impervious and non-impervious clothing, which has been contaminated or soaked with maleic anhydride, should be promptly removed and placed in a closed container for storage. It should either be thoroughly cleaned of this hazardous chemical before rewearing or discarded.

6) As a general safeguard, all employees should thoroughly wash their hands and other exposed body parts before eating, smoking, or using toilet facilities.

V. CONCLUSIONS AND RECOMMENDATIONS

This Monsanto Industrial Chemicals Division maleic anhydride facility is a very impressive highly automated, continuous, outdoor production operation. A relatively small number of skilled operators man this high output facility. Based on the information gathered during this limited inspection, we believe that this facility warrants further investigation to document what appears to be a good worker hazard protection program.

As noted in the introduction, it was apparent that personnel from the Fibers and Intermediates Company had a markedly different interpretation of what constitutes proprietary information than the Industrial Chemicals Company maleic anhydride facility production managers. An in-depth survey of this very modern maleic anhydride production facility seems neither possible, nor warranted, in view of the restricted inspection and discussion which was permitted. This is unfortunate as it was apparent that a good health and safety program was in effect, and a substantial amount of effective non-proprietary (our opinion) control technology was being employed.