



# **EPA/OSHA JOINT CHEMICAL ACCIDENT INVESTIGATION REPORT**

**BPS, Inc.  
West Helena, Arkansas**

**REPORT**



## **The EPA/OSHA Joint Accident Investigation Program**

EPA and OSHA work together under conditions detailed in a Memorandum of Understanding (MOU) to investigate certain chemical accidents. The fundamental objective of the Joint EPA/OSHA chemical accident investigation program is to determine and report to the public the facts, conditions, circumstances, and causes or likely causes of any chemical accident that results in a fatality, serious injury, substantial property damage, or serious off-site impact, including a large scale evacuation of the general public. The ultimate goal of the accident investigation is to determine the root causes in order to reduce the likelihood of recurrence, minimize the consequences associated with accidental releases, and to make chemical production, processing, handling, and storage safer. This report is a result of a Joint EPA/OSHA investigation to describe the accident, determine root causes and contributing factors, and identify findings and recommendations.

Under section 112(r)(1) of the Clean Air Act Amendments of 1990 (CAA) and under the OSH Act of 1970, industry has a general duty to design and maintain a safe facility taking such steps as are necessary to prevent releases, and to minimize the consequences of accidental releases which do occur, and to provide a safe and healthy workplace for workers. In addition, OSHA has promulgated the Process Safety Management Standard at 29 CFR 1910.119 for the prevention of chemical accidents that impact workers. EPA, under section 112(r)(7) of the CAA, has promulgated regulations for the preparation of risk management programs and plans for the prevention of accidental chemical releases that harm the public and the environment. However, compliance and enforcement with these provisions are not the focus of this report but will be addressed by EPA, OSHA or both as necessary in separate reports or actions.

Prior to releasing an accident investigation report, OSHA and EPA must ensure that the report contains no confidential business information. The Freedom of Information Act (FOIA), the Trade Secrets Act, and Executive Order 12600 require federal agencies to protect confidential business information from public disclosure. To meet these provisions, OSHA and EPA have established a clearance process for accident investigation reports in which the companies who have submitted potentially confidential information used in the report are provided a portion of the draft report. This portion contains only the factual details related to the investigation (not the findings, the conclusions nor the recommendations). Companies are asked to review this factual portion to confirm that the draft report contains no confidential business information. As part of this clearance process, companies often will provide to OSHA and EPA additional factual information. In preparing the final report, OSHA and EPA consider and evaluate any such additional factual information for possible inclusion in the final report.

Chemical accidents investigated by EPA Headquarters are conducted by the Chemical Accident Investigation Team (CAIT) located in the Chemical Emergency Preparedness and Prevention Office (CEPPO) at 401 M Street SW, Washington, DC 20460, 202-260-8600. More information about CEPPO and the CAIT may be found at the CEPPO Homepage on the Internet at <http://www.epa.gov/ceppo>. Copies of this report can be obtained from the CEPPO Homepage

or by calling the National Service Center for Environmental Publications (NSCEP) at 800-490-9198. OSHA Headquarters are located in the US Department of Labor - OSHA, 200 Constitution Ave NW, Washington, DC, 20210, 202-219-8118. More information about OSHA may be found at the OSHA Homepage on the Internet at <http://www.osha.gov>.

### **Chemical Safety and Hazard Investigation Board (CSB)**

In the 1990 Clean Air Act Amendments, Congress created the Chemical Safety and Hazard Investigation Board (CSB). Modeled after the National Transportation Safety Board (NTSB), the CSB was directed by Congress to conduct investigations and report to the public the findings regarding the causes of chemical accidents. Congress authorized funding in November 1997 and the CSB began operations in January 1998. Several investigations by the CSB are underway. More information about CSB may be found at their Homepage on the Internet at <http://www.chemsafety.gov> or <http://www.csb.gov>.

EPA and OSHA plan to complete their work and issue public reports on investigations initiated prior to funding of the CSB. Under their existing authorities, both EPA and OSHA will continue to have roles and responsibilities in responding to, and investigating, chemical accidents. The CSB, EPA, and OSHA (as well as other agencies) will be coordinating their efforts to determine the causes of accidents and to apply lessons learned to prevent future events.

## **Executive Summary**

On May 8, 1997, at approximately 1:15 p.m., Central Daylight Time, a massive explosion and fire occurred at Unit Two of the Bartlo Packaging Incorporated (BPS) facility located in West Helena, Arkansas. As a result of the explosion and fire, three West Helena firefighters were killed. Seventeen firefighters required medical attention due to heat exhaustion and injuries during the response. The Unit Two structure was completely destroyed. Hundreds of residents and patients at a local hospital were either evacuated or sheltered-in-place. The Mississippi river traffic and major roads were closed for approximately twelve hours due to the release of toxic materials from the facility.

Prior to the explosion, BPS employees observed smoke in the Unit Two warehouse. Following established procedures, all employees evacuated the building. The company placed an emergency call to local emergency response groups. Members of the West Helena Fire Department (WHFD) responded to the scene within minutes. A reconnaissance team composed of four firefighters was outside of the Unit Two warehouse when an explosion occurred inside the building. Three firefighters were fatally injured when they were struck by materials blown out of a falling cinder block wall. The fourth firefighter was seriously injured.

EPA and the OSHA conducted a joint investigation of the incident. The Joint Chemical Accident Investigation Team (JCAIT) determined that the incident was most likely caused by the decomposition of a bulk sack containing the pesticide Azinphos methyl (AZM) 50W which had been placed against or close to a hot compressor discharge pipe. Under this scenario, the heat from the discharge pipe would have caused the pesticide material to decompose and give off flammable vapors which resulted in the fatal explosion.

The investigation team could not eliminate the possibility that the AZM 50W arriving at BPS the day of the accident was already decomposing. This alternate scenario could either be an initiating event by itself or a factor influencing the preferred scenario. In other words, a decomposing bag of AZM 50W could have been placed closed to the compressor discharge pipe.

The JCAIT identified the following root causes and contributing factors of the event:

- \$ MicroFlow Company (MFC) and BPS did not have a full understanding of the hazards associated with AZM.
- \$ BPS did not assess the potential hazards of a hot pipe in an area where hazardous chemicals were to be stored when the new warehouse addition was constructed.
- \$ BPS did not have standard operating procedures for material storage and handling.
- \$ On-site information provided to the WHFD was conflicting and incomplete.

The following recommendations were developed by the JCAIT to address the root causes and contributing factors and to prevent recurrence of similar incidents at other facilities:

- \$ Manufacturers should be proactive in testing potentially hazardous materials. Testing for actual conditions and elevated temperatures during storage should be conducted to determine safe storage conditions. Screening tests, such as Differential Scanning Calorimetry (DSC), can be helpful in determining the need for additional testing. However, thermally unstable materials which are intended to be packed and shipped in large volume containers should be tested beyond screening levels.
- \$ Facilities which store, use, handle, manufacture or move hazardous materials should develop and implement a system to review potential hazards of modifications to facilities, equipment, chemicals, technology, or procedures. The system should analyze potential impacts to safety, health, and the environment and take appropriate actions before the modifications are implemented. OSHA's Process Safety Management (PSM), EPA's Risk Management Program (RMP), and the Center for Chemical Process Safety (CCPS) guidelines can help facilities develop such system.
- \$ Facilities that store hazardous chemicals should develop standard operating procedures for material storage and handling that address storage restrictions. Such facilities should adhere to applicable practices outlined by CCPS and the National Fire Protection Association (NFPA). Pesticide facilities are encouraged to also follow NFPA 43D (Code for the Storage of Pesticides), specifically the non-mandatory Appendix B.
- \$ Facilities storing hazardous chemicals should develop an inventory management system with information regarding composition, compatibility, storage, location, and quantity of incoming products. This management system can help the facility comply with storage restrictions and provide emergency responders useful information during a response action.
- \$ EPA and OSHA, in conjunction with interested parties, should facilitate a workshop to make recommendations on how to improve the quality of hazardous materials information available during response actions. The workshop should review appropriate uses of Material Safety Data Sheets by local emergency response groups and how to provide these groups information describing the behavior of hazardous materials when they begin to react or decompose and what responders should look for during a chemical emergency.

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## **1.0 Background**

### **1.1 Introduction**

On May 8, 1997, an explosion and fire occurred at the Bartlo Packaging Incorporated (BPS) facility located in West Helena, Arkansas. As a result of the explosion and fire three firefighters died and seventeen other firefighters required medical attention due to heat exhaustion and minor injuries. Hundreds of residents, including local hospital patients, were evacuated or sheltered in place due to the threat of exposure to toxic chemicals released in the blast. Major roads were closed and the Mississippi river traffic halted. Several emergency response groups participated in the response action. It took approximately two weeks to extinguish the fire.

The Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA) conducted a joint investigation of this event in accordance with a Memorandum of Understanding (MOU) signed in November 1996. The agencies established a joint chemical accident investigation team (JCAIT) made up of personnel from the EPA and OSHA National Offices, OSHA's Health Response Team, and Regional and contractor personnel from both agencies. This report contains a description of the incident and the results of the joint investigation.

### **1.2 Facility Description**

BPS is a corporation with facilities in Helena and West Helena, Arkansas. The West Helena facility is located in an industrial park three miles from the central business district of West Helena, Arkansas. The facility is located in a flat area used primarily for agricultural purposes. The nearest residential area is located less than one mile northeast, and the Mississippi river is located approximately three miles east.

BPS is an agricultural chemical packaging facility. No chemical manufacturing occurs at the facility. BPS receives bulk shipments of agricultural chemicals (pesticides, insecticides, etc.) and repackages them in smaller, water soluble, containers. The operation is conducted for chemical manufacturers using tolling contracts. Under a tolling arrangement a company contracts with another company to perform a specific operation. In this case, chemical manufacturers deliver agricultural chemicals in bulk containers, which BPS repackages according to the manufacturers' specifications. BPS then ships the product back to the specified location.

The West Helena facility employs approximately 130 workers. At the time of the incident 65 employees were on duty. The facility consists of two production buildings (referred as units One and Two), two satellite buildings, and a Agel@ building. The production buildings are constructed of corrugated metal with steel reinforcement. The Unit Two building (Figure 1),

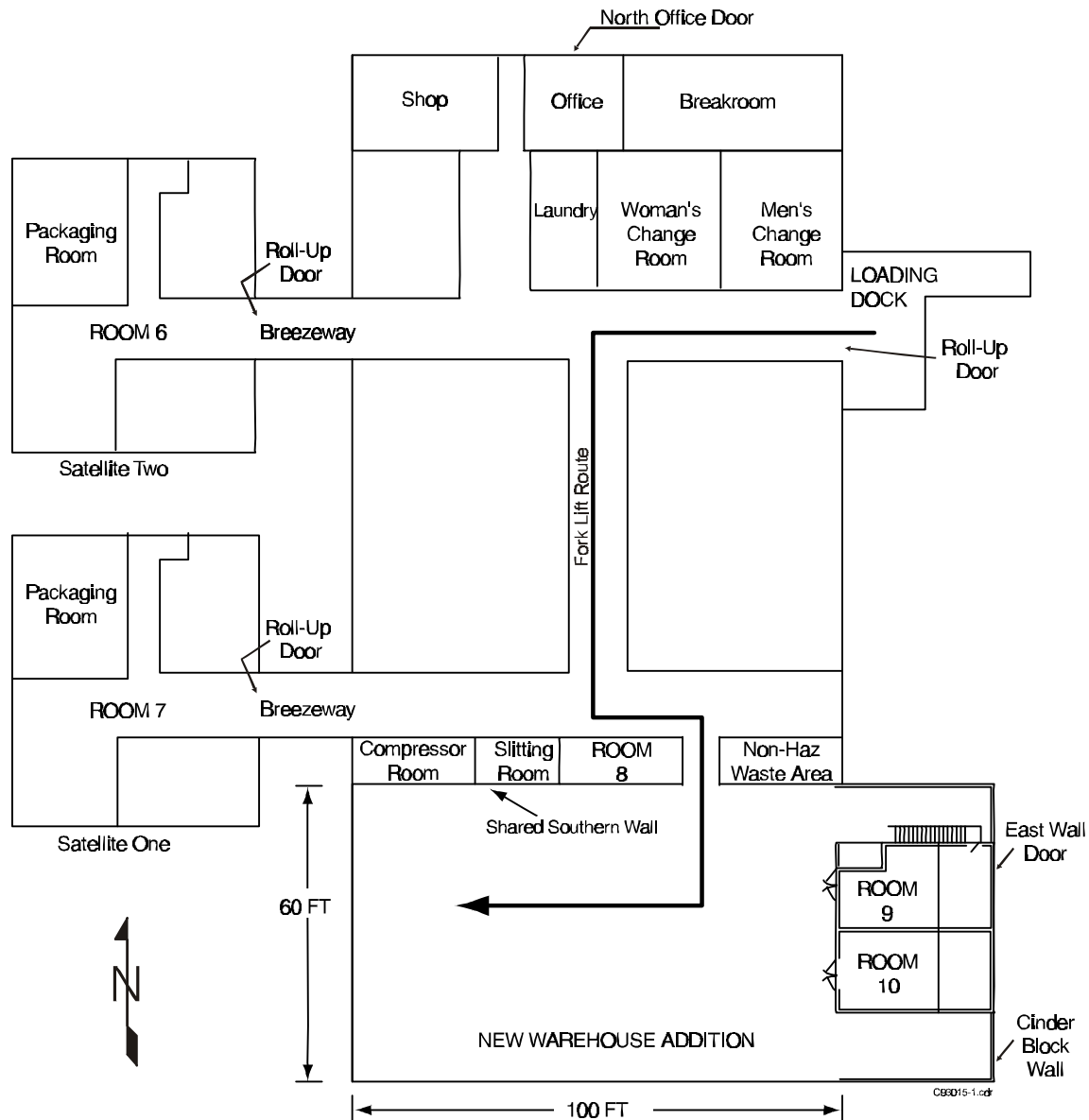


FIGURE 1: FLOOR PLAN - BPS, INC. UNIT #2

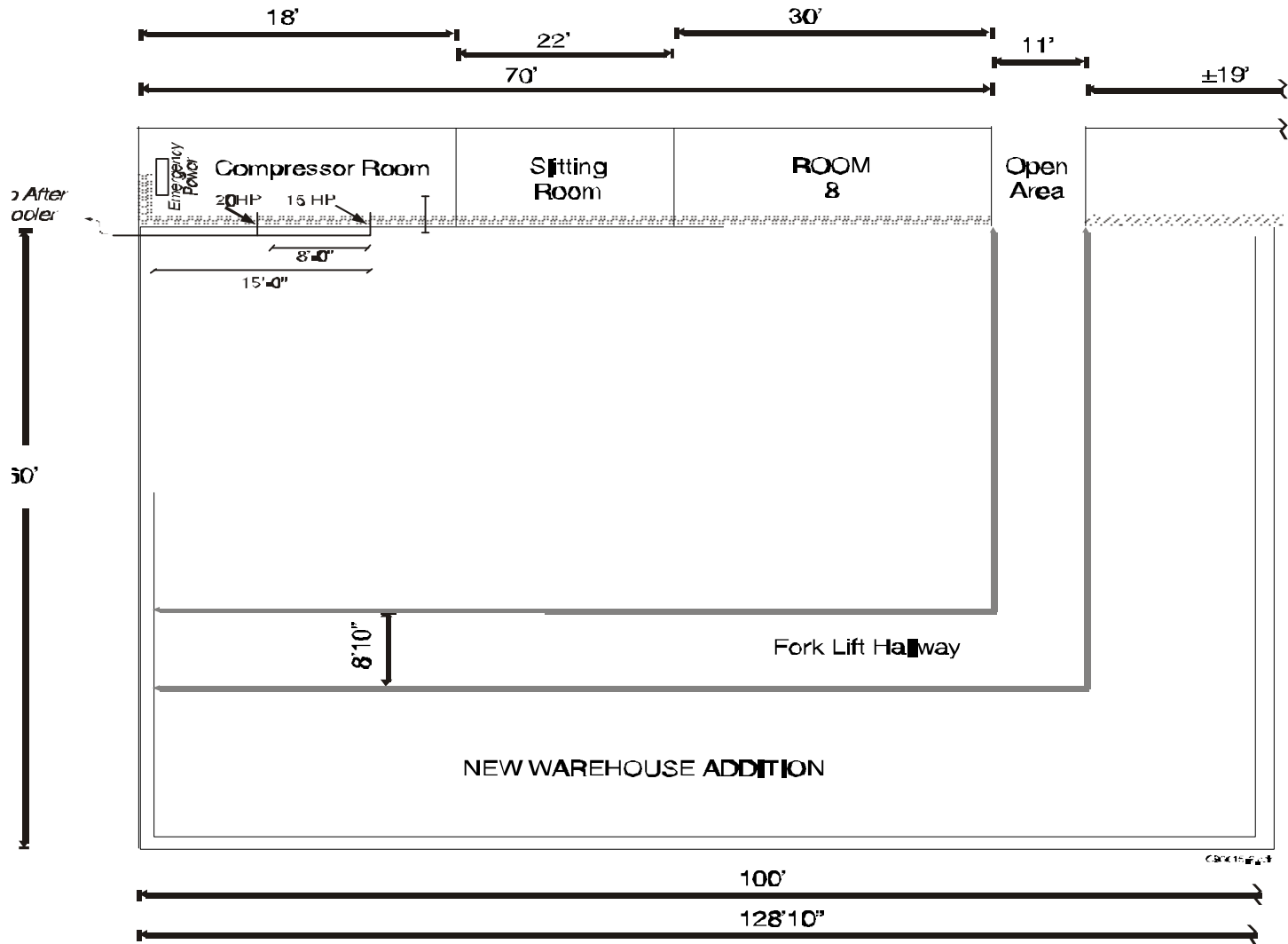


FIGURE 2: NEW WAREHOUSE ADDITION COMPRESSOR SYSTEM

NOT TO SCALE

in which the incident occurred, had a 100' x 150' main area, a 16' x 34' loading dock, and two 50' x 60' satellite buildings connected to the main area by breezeways. In October 1995, a warehouse addition was added to the Unit Two building. It shared the southern wall of the original building (referred to as the new warehouse addition north wall). The addition was approximately 7800 square feet. It was also constructed of corrugated metal with the exception of the outside eastern wall. This particular area had two stories with an exterior (eastern) wall constructed of cinder blocks.

Repackaging operations in the Unit Two building required the use of two reciprocating air compressors. The compressors were located in the southern portion of the original building. The compressors' discharge pipes went through the new warehouse addition's north wall into a common header pipe (Figure 2). This header pipe was fifteen feet long and 5'11" from the concrete pad floor. It ran parallel to the north wall to meet an after-cooler outside the new addition's west wall. The output from the after-cooler was piped back along the same wall 3'7" from the concrete floor carrying the cooled air back to the accumulator tanks under each compressor (Figures 3 and 4).

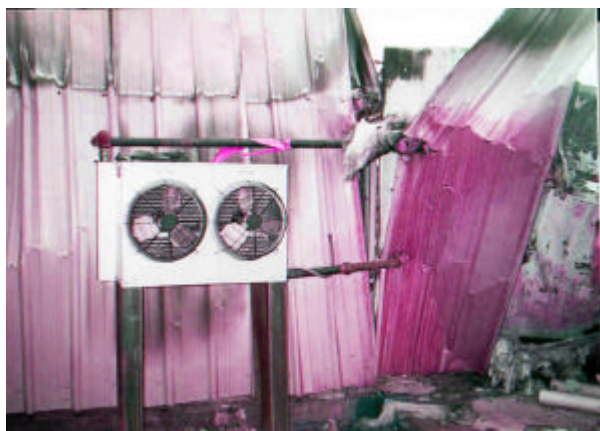


Figure 3. After-cooler



Figure 4. Compressor Discharge Pipe After the Incident

### 1.3 Chemicals in the New Warehouse Addition

The inventory information used by emergency responders during the response action was based mostly on BPS' management recollection. The Agency of Toxic Substances and Disease Registry (ATSDR) developed a table during the response action based on employee interviews (After Action Report, BPS Pesticide Fire, ERSAB, ATSDR, August 4, 1997). Several weeks after the incident, BPS provided to JCAIT information regarding the type and quantities of the chemicals stored in the Unit Two building the day of the incident. Based on the BPS inventory

information and witness statements, the JCAIT determined that the following chemicals were present in the Unit Two new warehouse addition at the time of the incident: Maneb 75DF, Azinphos methyl (AZM) 50W, Alliette Signature WDG, Topsin WSB, Sevin 80 WSP, and Penncozeb 75DF. Material Safety Data Sheets (MSDSs) for Maneb 75DF, Azinphos methyl (AZM) 50W, and Alliette Signature WDG are included in Appendix A.

## **2.0 Description of the Incident**

### **2.1 Sequence of Events**

#### **December 1995- May 7, 1997**

In December 1995, BPS provided MicroFlow Company (MFC) a quotation to repackage bulk AZM 50W into 1 lb. water soluble bags. BPS was to provide warehousing for a two-week supply of materials being repackaged and two weeks prior to and following repackaging. As part of the contract arrangement, BPS requested MFC to do a presentation to BPS workers and managers on safety and health issues related to worker exposure and handling of the AZM 50W. The request was based on AZM's toxicity. The presentation was to be delivered prior to the repackaging operation.

On January 29, 1996, BPS sent a letter to MFC expressing concern about the reactivity/flammability of AZM 50W. Their concern originated through a conversation with a representative of Bayer Agricultural Division. Bayer noted that it had experienced a number of incidents involving thermal decomposition and/or fires involving Guthion (Bayer's AZM formulation). The letter stated that many of Bayer's fires were initiated in ribbon blenders and transfer screws similar to those used at BPS. BPS noted in its letter that the Material Safety Data Sheet (MSDS) provided by MFC did not have information to support a similar situation. BPS questioned why the MSDS provided by MFC did not contain information similar to Bayer's MSDS on Guthion for flammability and reactivity. MFC's MSDS (of January 1995) had a Hazardous Materials Incident System (HMIS) flammability and reactivity rating of 0 compared to Bayer's National Fire Protection Association (NFPA) rating of 2. BPS requested MFC's advice since they have little experience dealing with reactive materials and depend on our customers to inform us of any problems inherent in their materials (letter from BPS to MFC January 29, 1996).

MFC and BPS personnel met on February 8, 1996, to discuss the suitability of the BPS packaging equipment and the apparent inconsistency on the AZM 50W fire and reactivity hazards. As a result, BPS proposed to construct a water deluge system to accommodate a potential smoldering of the product. The parties agreed on a system that would run water lines to the repackaging hopper, with valves located by the packaging room's door. In case of a bad odor while running the equipment, the operator was supposed to flood the hopper with water.

At BPS's request, MFC made a safety presentation on February 12, 1996 to BPS workers

and managers. The presentation included product background, toxicity, safe work practices, and fire/reactivity issues.

On February 13, 1996, MFC sent a follow-up memo by telefax to BPS. It states that A...AZM 50W will begin to smolder and smoke at approximately 170 degrees Fahrenheit. This temperature is consistent with the 167 degrees listed on our MSDS. In the same memo, MFC stated that they were in the process of locating a sample of Guthion 50W to test and that they would update BPS with any new findings. At the time of the incident MFC had not given any additional information to BPS.

The MSDS for AZM 50W provided by MFC to BPS did not reference any 167<sup>0</sup> F (75<sup>0</sup> C) temperature. MFC used a 90% pure AZM technical grade as the AZM 50W active ingredient. The technical grade supplier has a 158<sup>0</sup> F ( 70<sup>0</sup> C) temperature in their MSDS Aconditions to avoid section.

#### **May 7, 1997: Tifton, Georgia, MicroFlow Warehouse**

MFC had made arrangements to ship two truckloads of AZM 50W to BPS from Tifton, Georgia on May 7, 1997 via Milan Express. Each truckload contained 26 bulk bags (supersacks) with approximately 1600 pounds of AZM each. These supersacks are constructed of woven polypropylene coated fabric and have a 45 cubic foot capacity. The supersacks on both trucks had AZM 50W from batches produced from 10/96 to 4/97.

Prior to his arrival to Tifton, the first truck driver picked up the truck in South Bend, Indiana. Then, he picked up plastic lawn mower parts in Elgin, Illinois and delivered them to Macon, Georgia. At 2:45 p.m., MFC personnel started loading AZM 50W onto the first truck. Upon completing the loading, truck driver one left the Tifton warehouse at 3:45 p.m.

At 5:00 p.m. MFC personnel started loading the second AZM 50W truck. Truck driver two had not hauled pesticides before. At 6:30 p.m., the second truck loaded with AZM 50W left Tifton, Georgia bound for BPS.

#### **May 7 - 8, 1997: Road**

Truck driver one pulled over and rested for two hours at Wyona, Missouri. He stated that the AZM 50W odor was making him feel sick. He transported AZM 50W a year earlier from the MFC plant located in Macon, Georgia. He stated that the AZM 50W smell was similar to the previous truck load. The smell had made him feel sick both times, but this particular time it Areally got him.

Truck driver two stopped for an eight-hour rest in route to BPS. He stated that he could smell the cargo from outside the truck. The AZM 50W smelled bad to him but did not make him feel sick.



## **May 8, 1997 : BPS, West Helena, Arkansas**

### **Before the 10:00 a.m. work break**

Truck driver one arrived at BPS, Unit One at 7:20 a.m. He was received by a BPS employee who directed him to Unit Two. Once in Unit Two, truck driver one broke the truck seal at 8:00 a.m. The truck was not unloaded immediately because the fork lift operators were unloading Procure empty drums. The Procure truck was unloaded by 9:55 a.m.

### **From 10:00 a.m. break to lunch break (11:55 a.m.)**

BPS fork lift drivers began unloading the first truck after the 10:00 a.m. break. They had to move other material in the new warehouse addition (empty cardboard and drums) to make space for the incoming AZM. According to BPS forklift drivers the cargo was located along the new warehouse's north wall on a two row/double stack arrangement. They also stated that AZM pallets were spotted approximately six inches from the north wall.

While unloading, fork lift drivers and nearby employees noticed and made comments about the strong odor. They reported that the AZM in the first truck smelled worse than the AZM in the second truck and the AZM repackaged at BPS one year earlier.

A fork lift driver reported a spill in the new warehouse addition right after the 10:00 a.m. break. Twenty to thirty pounds of Alliette Signature had leaked from the top pallet of a previously patched supersack which had reopened. The spill reportedly occurred next to the new warehouse addition north wall, near some empty drums on the west side. The BPS waste monitor began to clean the spill up around 11:30 a.m. He used a forklift to move the top pallet of Alliette and took it to the stretch wrap area. He then took the waste to room seven for disposal.

The second AZM truck arrived at 11:30 a.m., when the first truck had only two pallets left to unload. BPS employees finished unloading the first truck close to lunch time. The first truck pulled away from the loading dock. Another truck, reportedly carrying cardboard, pulled in and stayed at the loading dock for approximately ten minutes. In the meantime, forklift drivers started stacking two rows of Aother@ product to the north wall of the new warehouse addition. After the cardboard truck pulled out, the second truck pulled into the loading dock. Truck driver two broke the truck seal but one of the fork lift operators told him that the unloading would begin after the lunch break.

### **Lunch break (11:55 a.m.-12:25 p.m.)**

All work activities, with the exception of the spill cleanup, stopped during the lunch break. The BPS waste monitor completed the Alliette Signature spill clean-up around 12:20 p.m. He called the shift supervisor to check on the spill clean-up.

Truck driver one was dispatched to Grenada, Missouri and left the site before the explosion.

#### **After lunch break (12:45 p.m.)**

The forklift supervisor returned from lunch, then went back to the slitting room to wrap a pallet. He was the first person to see the smoke. He described it as a yellow powder puffing through the hole around the compressor header pipes. He reported that the smoke (or powder) was coming from the new warehouse addition through the hole and forming in the air, not dropping to the floor. He also stated that the powder had the same smell as the AZM that had been unloaded earlier. He did not see fire but called a fire on the radio at what he thought was approximately 12:50p.m. He grabbed a fire extinguisher and went to rooms eight, nine, and ten to get people out. He then looked back to the compressor area and saw a large cloud of what appeared to be powder. He tried to go into the warehouse area but the powder was too dense. Another employee was in the warehouse with an extinguisher. Neither employee used his fire extinguisher; they left the unused fire extinguishers in the warehouse and evacuated. In the meantime, the shift foreman called a Code Red and the evacuation process continued. Most employees reported seeing yellowish smoke. Others reported the smoke color to be lime green. All the employees reported seeing the smoke coming from the new warehouse addition area where the AZM had just been placed or through the wall holes around the compressor pipes into the slitting room. Employees also reported a rotten egg/skunk odor.

The production manager called 911. The West Helena Fire Department (WHFD) received first notification at 1:02 p.m. According to the 911 call transcription, BPS reported a small smoldering fire with no flames. The production manager stated: Ais where some product was set next to a hot line off an air compressor. It's starting a little bit of a smother, but no fire. But it's a lot of smoke. The caller also referred to a 1,500 pound supersack. A second notification, to the Helena Fire Department, was received at 1:09 p.m.

Three maintenance employees went to Unit Two after the radio fire call. All of them reported seeing smoke coming through the holes around the compressor header pipes. They described it as light yellow close to the roof and thick grey/tan near the floor. One of the employees turned the exhaust fans on. Reportedly, this employee thought that Aone of the supersacks of MicroFlow's was leaning against the pipes. The other employee went to the electrical panels (the electrical panel was adjacent to the compressors room on the way to the breeze way leading to satellite one) and turned the compressors off.

During the evacuation of Unit Two, truck driver two observed yellow Astuff coming out of the back of the building. One of the fork lift operators told him that there was fire close to some pipes. Without having unloaded any product, he closed the doors to the truck and pulled his rig away from the loading dock, taking it across the street.

The shift foreman took a roll call and one employee was missing. A fire truck arrived at

1:15 p.m., just after the first roll call. The firefighters stated they thought yellow product was coming from the building. The WH Fire Chief arrived shortly after the fire truck. One of the firefighters received an MSDS from a BPS employee. He checked the Department of Transportation (DOT) Hazardous Materials Booklet and noted that one of the products on site was water-reactive. The production manager discussed the products' reactivity with the WH Fire Chief. He gave the Fire Chief a binder with the MSDS and a floor plan. The WHFD department called volunteers, other emergency services, and the Helena Fire Department for backup. After consulting with the WH Fire Chief, the maintenance manager closed the three roll-up doors to the loading dock and satellites one and two.

Several BPS employees went to satellite one to locate the missing employee. He was located upstairs in the reclaim area and escorted out. A second roll call took place and all employees were accounted for.

The WH Fire Chief and the maintenance supervisor discussed the smoke location. The Fire Chief observed that the smoke looked more like powder or product and that it was seeping instead of puffing. The maintenance supervisor unlocked and opened a side door on the east side of the new warehouse addition for a firefighter, but the yellow smoke was too thick for the firefighter to enter.

The firefighter reported back to the WH Fire Chief. The WH Fire Chief asked the production manager to show him the building layout to check the location of the smoldering supersack. The WH Fire Chief then asked about the danger of an explosion and the BPS President said there was none.

The four firefighters walked back toward Unit One to get a lifeline. They returned to the Unit Two building close to the room 9 exterior wall (east wall). A bell started to ring inside the building, and the maintenance supervisor explained to the firefighters that the sprinkler system alarm had just gone off. The maintenance supervisor then observed water coming from the sprinkler alarm on the east exterior wall indicating that the sprinkler system had in fact been activated. At 1:34 p.m. the alarm company received a fire notification. (The on-site activation of the sprinkler system sends an electronic notification simultaneously to the alarm company.) The maintenance supervisor asked the firefighters to wait for him to turn the power off before entering the building because the equipment was still energized.

The maintenance supervisor went to the exterior office door by the north side of Unit One to attempt to disconnect the power to the building. The disconnect power box was located in an interior hallway between the office and the maintenance shop. He entered the office and proceeded to the door leading to the hallway. Suspecting fire, he felt the door and found it hot to the touch. He cracked the door and observed that the shop area was full of smoke. He determined that he could not reach the disconnect box safely and retreated. He notified the WH Fire Chief that he was unsuccessful in disconnecting the power to the building.

An electrical company's service man had an appointment with a nearby facility. He saw the police and firemen and went directly to BPS. He tried to get in the building by the office door, but felt heat on the walls and decided to turn the power off from the main power cutouts outside near the transformer. He observed yellowish dust or smoke coming out of the vents. The main power cut consisted of three individual legs. The service man pulled the first leg. As he was getting ready to pull the second leg, an explosion occurred. A firefighter reported seeing a mushroom cloud at the east side of the building. Another firefighter reported hearing a wuff sound like throwing gasoline on a fire, at the same time he saw a massive fireball coming from the building. The explosion caused the cinder block wall to collapse. The four firefighters standing east of room 9 were struck by the collapsing wall. Three of them were killed and the remaining one was seriously injured.

At the time of the explosion, the WHFD received a call from the New Jersey Bartlo Packaging chemist. The fireman reported that the chemist asked whether the sprinkler system had activated and explained to the firefighter that two different types of chemicals were present at the site. According to the firefighter, the chemist said the chemicals would explode if water was put on them.

At 1:39 p.m. the alarm company was notified of the explosion.

## **2.2 Emergency Response Actions**

### **BPS Emergency Preplanning**

BPS was an active member of the Local Emergency Planning Committee (LEPC). BPS had a written Emergency Response and Contingency Plan dated September 1995. They had made arrangements with the WHFD for emergency support and had provided copies of their written plan and MSDSs. BPS had also invited the fire department to tour their facility and to participate in their emergency drills. A West Helena firefighter stated that fire department personnel had toured the facility approximately one month before the incident.

According to BPS employees, the facility had several fire extinguishers but they were to be used only on non-chemical fires. Employees were instructed not to fight chemical fires but to immediately evacuate the building. The Unit Two building reportedly had a fire alarm system which was backed up with radios and intercom. Safety meetings covered evacuation routes. A floor plan showing the evacuation routes was posted on the wall.

### **Initial Response**

Upon being called to the site, the West Helena Fire Chief called in all volunteers and off duty personnel. He also called the Helena Fire Department, the emergency medical services, the State Police, and the Phillips County Office of Emergency Services. This office notified the State Office of Emergency Services, schools and radio stations in accordance with the County and

LEPC Plan.

At the time of the explosion, the Helena Fire department had just arrived. The priority immediately after the explosion was to rescue the injured firefighters and control the fire. Both fire departments retreated from the fire after rescuing the only survivor from the reconnaissance team. Police and emergency medical services also arrived on scene. Several firefighters were treated on-site because of minor injuries and heat exhaustion. The fire chiefs issued an initial evacuation order downwind of the smoke plume, including the Helena Medical Center, and called the West Memphis HazMat team.

At 3:00 p.m. the West Memphis HazMat team arrived at the site to support fire fighting efforts. They provided the first air monitoring equipment. Due to the extreme toxicity of the chemicals involved and changing wind conditions, the evacuation was extended to a three-mile radius area. Most of the Helena Medical Center patients were taken to a community college and others to a hospital in Clarksdale Mississippi. Residents of West Helena and nearby Helena were sheltered in place. A twenty-mile section of the Mississippi river was closed to river traffic due to the prevailing winds at the time of the incident.

### **Response Actions Under the Incident Command System**

At 2:06 p.m. the National Response Center notified EPA Region 6 of the fire and explosion at BPS Inc. The initial notification had no information regarding fatalities, injuries or evacuations. At 5:00 p.m., EPA received a second notification indicating that the incident was out of control and requesting federal assistance. EPA Region 6 dispatched two On-Scene Coordinators (OSC) and activated the Regional Response Team (RRT). Other federal groups joined EPA in the response action. DOD's Pine Bluff Arsenal provided atropine and real time air sampling equipment. The atropine was intended to be used as an antidote for AZM exposure of responders and community members.

The RRT contacted several chemical companies for scientific and technical support. Among other companies, Mobay Chemical, DuPont, Bayer, Rhone Poulenc, and Elf Atochem sent representatives to the site to voluntarily assist in the response action. DuPont also deployed its HazMat team to provide emergency response support.

Response organizations continued air monitoring to determine if the plume contained dangerous levels of toxins. Based on wind conditions and monitoring results the evacuation was downgraded to stand-by status. Local authorities allowed evacuees in the two-mile radius return to their homes.

On May 9, 1997, the Incident Command System (ICS) was officially implemented. Numerous Federal, State, and Local agencies and organizations provided support within the ICS, including US EPA, US ARMY, Arkansas State Police, Office of Emergency Services, West

Helena/Helena/ West Memphis Fire Departments, OSHA, US Alcohol, Tobacco, and Fire Arms (ATF), Center for Disease Control, ATSDR, NFPA, DuPont, BPS, and others.

The EPA On-Scene Coordinator directed the response through the ICS operations. As more information regarding the quantity and nature of the chemicals involved in the fire became available, the fire was allowed to burn with minimal active fire fighting efforts. This decision was made based on the potential water reactivity of the burning chemicals and the concern that incomplete combustion products could be more harmful than those generated by complete combustion.

By May 14, 1997, Maneb was the primary chemical still burning at the facility. Maneb is air reactive and water reactive. After several unsuccessful efforts to extinguish the fire, emergency responders decided to spread the Maneb into thin layers and then to fog it with water. This strategy was chosen based on information provided by Rhone Poulenc on a similar incident in Brazil. All fire zones were extinguished and the site was downgraded from emergency response. After inspection on May 15, 1997, the Arkansas State Police released the site from crime scene status.

The EPA OSC opened the site for the JCAIT to take samples and document the scene before the clean up activities could begin. The JCAIT coordinated site documentation, sample planning, and sample collection with all the on-scene investigative parties. Once the JCAIT completed sample collection, the EPA OSC released the site for cleanup. The BPS contractor began cleanup operations under EPA's oversight on May 22, 1997.

### **2.3 Public Health and Environmental Issues**

Several response organizations, including EPA, Arkansas Department of Health, Mississippi Department of Environmental Quality, and the BPS contractor performed air monitoring. This information was used to determine whether the plume could present a threat to public health or the environment. Chemical companies provided technical assistance on decomposition products and monitoring devices.

The Arkansas Department of Health requested on-site assistance from ATSDR to address the following public health issues: 1) acceptable exposure levels, 2) hospital reoccupation, 3) decontamination of business and residences, and 4) consumption of exposed food products.

On-site use of atropine was limited to one firefighter who exhibited exposure symptoms. Reportedly, this firefighter was not wearing respiratory protection. Approximately 400 people reported symptoms consistent with short term exposure to pesticides. Thirteen of those cases were referred for blood tests. These blood tests were reported as normal.

The Arkansas Department of Pollution Control and Ecology collected point of entry water

samples from the community water system wells. The impact was found to be minimal because runoff from fire fighting efforts was contained on-site and no drinking water wells were in the vicinity of the facility.

ATSDR's after action report concluded that no long-term public health effects were expected from the fire and explosion at BPS. This conclusion was based on the toxicology of the chemicals involved and the maximum contaminant levels detected in and around the businesses and residences.

### **3.0 Investigation and Analysis**

#### **3.1 Investigation**

Members of the JCAIT interviewed BPS personnel and other individuals potentially having knowledge about the incident. The JCAIT also requested documents from the facility, documented the scene, and collected samples. Once the initial field activities were completed, the JCAIT identified two distinct problem areas: the existence of a combustible atmosphere in the new warehouse addition and the resulting three firefighter fatalities.

The primary focus of the JCAIT investigation is on the events leading to the creation of the combustible atmosphere. Therefore, most of the initial investigation activities were conducted to support the root cause analysis of this particular problem. The JCAIT acknowledged that other investigation groups, such as the NFPA and the U.S. Fire Administration (USFA), were addressing the three fatalities. It is not the intention of this report to duplicate the work performed by these groups. Instead, this report looks at general areas in the emergency response system that could have contributed to the firefighters' fatalities.

The JCAIT did not attempt to analyze the explosion dynamics. Given the presence of a combustible atmosphere, any source of ignition had the potential to initiate the explosion. However, the most likely source of ignition was the arc(s) created in the facility equipment when the electrical company service man began disconnecting the power to the facility. The JCAIT did attempt to identify the explosion origination point and the source of the combustible material in the air as relevant to the immediate cause. The investigation team used witness statements, photo-documentation of the area, and laboratory analysis in this process. The process required several iterations of analytical work. Some of the laboratory results are not discussed directly in this report because they were either inconclusive (did not confirm or disprove a conjecture) or did not include any detectable contaminants levels. Summary reports on laboratory analyses are included in Appendix B.

## 3.2 Analysis

### 3.2.A Overview of Explosion Scenarios

BPS did not have standard operating procedures (SOPs) for material storage and handling. The general practice at the facility was to store materials in the warehouse as space was made available. There were no established methods to ensure segregation of incompatible materials or protection of stored materials from factors that could cause accidental releases, ignition or reaction of ignitable or reactive materials. According to the BPS Unit Two forklift supervisor, he was not instructed to tell forklift operators where to spot materials in the warehouse. The fork lift operators were supposed to find an empty spot to locate incoming materials. There was no attempt to determine the material's hazard classification and/or incompatibilities.

BPS conducted a hazard review before agreeing to repackage any product. The written procedure required going through a check list before beginning a repackaging operation. The hazard review did not address chemical handling and storage. There was no systematic review of factors that could potentially affect warehousing of hazardous chemicals. For example, in October 1995, BPS added the warehouse area to the Unit Two building. The compressors' discharge pipe was modified to pass through the new warehouse addition's north wall and take a 90-degree elbow turn to meet the outside after-cooler. This modification resulted in a fifteen foot long discharge header pipe running at a height of 6 feet inside the pesticide storage area. No assessment of the potential risks associated with this change was performed.

The incident occurred in early May, which is a peak production month for BPS as the agricultural industry begins to prepare and place orders for various products for their growing season. The morning of the event, forklift operators had to move materials around in the new warehouse to make room for off-loading Procure and AZM. During the investigation, through interviews of forklift operators and supervisors, investigators attempted to identify where materials were spotted in the warehouse. The different accounts regarding what was located in the storage area and where it was located indicated that there was no system in place to manage the storage of the various materials at the facility. This lack of an inventory management system, storage SOPs, and a system to review potential hazards of changes in the facility could have led to a number of warehouse incidents.

All witnesses agree that the smoke originated near the warehouse addition's north wall, close to the compressor header pipe. Witnesses, including the fire fighters, also reported the presence of a product or powder in addition to smoke in this area. This suggests the presence of a hybrid dust/vapor mixture. The JCAIT found no visible crater for the explosion, which is consistent with a dust/vapor explosion. The explosion of an airborne flammable vapor or dust could occur at any location where a flammable concentration has accumulated. This could be at some distance from the source of the dust/vapor mixture. Presumably, the fan located on the southwest side of the building could have drawn the hybrid mixture in that direction, affecting also the direction of the blast. In any case, the explosion origination point is not necessarily the



location of the flammable material source. The source of the flammable material will be discussed in the scenario analysis.

Based on an event and causal factor diagram, analytical results, and professional judgment, the JCAIT identified the following scenarios in the development of the combustible atmosphere that led to the explosion:

- \$ Chemical inside supersack decomposes when placed close to the compressor header pipe
- \$ Decomposition of AZM 50W begins before arriving at BPS
- \$ Incompatible chemicals react
- \$ Malfunctioning compressor overheats a supersack

The JCAIT concluded that a supersack placed close or against the compressor header pipe was the most likely scenario. Several of the chemicals stored in the new warehouse addition at the time of the incident can decompose thermally while in contact with a surface within the temperature range of the compressor header. However, the JCAIT concluded that AZM 50W had a greater probability to initiate the event. It should be noted that most incidents are the result of multiple factors rather than a single cause. The JCAIT did not rule out the possibility that the AZM 50W placed close to the compressor pipe was already decomposing before arriving at the facility. Following an initial decomposition of the AZM 50W, the Maneb adjacent to it could have also been involved in the subsequent explosion. The explosion cause scenarios are discussed below.

#### **Scenario 1: Chemical in Supersack Decomposes when Placed Close to the Compressor Header Pipe**

Critical to the development of this scenario was the need to determine if a supersack was actually placed against the pipe, which chemicals were most likely to have been placed in such proximity, and whether the compressor pipe could reach temperatures high enough to cause the chemical to decompose.

##### **Compressor Discharge Temperature**

At the time of the incident, BPS personnel stated that the surface temperature in the pipe was approximately 145<sup>0</sup> F (63<sup>0</sup> C). In order to confirm this statement and determine the potential involvement of the compressor in the incident, the JCAIT conducted a series of activities. First, the team inspected and documented the compressor system conditions after the event. Observations from this inspection were supplemented with interviews with BPS employees and management and the compressor manufacturer.

Second, the JCAIT conducted a forensic analysis of the compressors and estimated the anticipated temperatures in the discharge pipe's system. The analysis is presented in a report dated August 20, 1997 and referenced as DNV Project No. 232-8384, *Insecticide Warehouse*

*Explosion Investigation.* The summary report is included in Appendix B.

Finally, the JCAIT participated in a simulation conducted by MFC at Tifton Industrial Controls in Tifton, Georgia on May 15, 1998. The simulation intended to measure a range of temperatures in a compressor system re-constructed to simulate BPS operations at the time of the event.

Of particular interest was the surface temperature of the common header pipe at the approximate point where the supersacks could have been spotted. MFC, with the concurrence of OSHA and EPA, developed a testing protocol to provide and connect two compressors to simulate the BPS conditions. The compressors were connected under EPA and OSHA oversight. The JCAIT measured the piping surface temperature at several locations and under different conditions (insulated vs non-insulated).

A summary of the findings is presented below:

- \$ The piping configuration between the compressors and the after-cooler included approximately twenty feet of discharge piping and two short radius turns.
- \$ Discussions held with the manufacturer of the two compressors used at BPS indicated that there are a number of factors which can affect the compressor discharge temperature such as ambient temperature and discharge pressure. However, under normal operating conditions the maximum discharge air temperature of the compressors at the cylinder head would be expected to be in the range of 300<sup>0</sup> to 350<sup>0</sup> F (149<sup>0</sup> - 177<sup>0</sup> C).
- \$ JCAIT estimated that the discharge temperature on a compressor system like the one used at BPS would be approximately 350<sup>0</sup> F (177<sup>0</sup> C). The associated external pipe temperature would be 280<sup>0</sup> F (138<sup>0</sup> C). If the pipe is engulfed by an insulating type material, such as a supersack, the pipe would be expected to attain the same temperature as the discharge air. See DNV Project No. 232-8384 in Appendix B.
- \$ During the MFC's Tifton simulation, the team measured the non-insulated pipe temperature at the distance where the supersack could have been in contact with the header pipe. Once equilibrium was reached, the surface temperature at that point was approximately 255<sup>0</sup> F (124<sup>0</sup> C). The group then wrapped a two foot section of the pipe with a fibrous glass insulation to roughly simulate the effect of a supersack against the pipe. The temperature increased from 255<sup>0</sup> to 301<sup>0</sup> F (124<sup>0</sup> to 149<sup>0</sup> C) in less than 30 minutes. The maximum insulated header temperature in the simulation was 336<sup>0</sup> F (169<sup>0</sup> C).

The JCAIT also reviewed technical literature, including the compressor operator's manual, to determine how the BPS compressor system compares with industry practices:

- \$ The *Operator's Manual* for the Model 460 Compressor, Overheating Section, states that the piping to the after-cooler location should be as short as possible, preferably no more than three feet. For runs over three feet, the pipe size should be increased by one pipe size for each eight foot run.
- \$ The *Compressed Air and Gas Handbook*, published by the Compressed Air and Gas Institute, states that the discharge piping, i.e., the piping between the compressor and the after-cooler, the after-cooler separator, and the air receiver, should be as short and direct as possible and should use Along-radius elbows where bends are necessary.
- \$ The American Society of Mechanical Engineers (ASME B19.1 - 1995) *Safety Standards for Air Compressor Systems*, Section 2.1.8. High Temperature states, External surfaces subject to temperatures in excess of 175° F (80° C) which personnel may have contact, shall be guarded or insulated.

The JCAIT concluded that the common header pipe connected to the two-compressor discharges was in fact substantially higher than the 145° F (63° C) estimated by BPS employees and management. From the above results, the JCAIT estimates that the discharge header in the warehouse could have been in excess of 300° F (149° C).

### **Chemical Location**

Shortly after the incident, BPS employees and management identified the decomposing material as an AZM supersack placed against or close to the hot compressor discharge pipe. The JCAIT confirmed that supersacks of materials were being spotted in close proximity or against walls at BPS. After the incident, JCAIT observed supersacks spotted along the wall in the Unit One warehouse. In this case, the supersacks were stacked two-high. The edge of the bottom supersack was within inches of the wall. The top supersack was listing so that it was in contact with the wall (Figure 5).



Figure 5. Supersack set-up at BPS Unit One

Several of the chemicals stored in the new warehouse addition at the time of the incident had the potential to decompose thermally while in contact with the hot compressor pipe. The JCAIT collected bulk samples of the combusted residue where the explosion occurred, attempting to determine the exact location of each chemical pallet. The analysis of these samples was of limited use due to the total destruction of the area and combustion of the sampled material (Figure 6). The collection and analysis of samples was supplemented with the analysis of other physical evidence and witnesses' statements.



Figure 6. Aerial Photo BPS Unit Two

Based on witness interviews, the JCAIT identified the approximate location of the chemicals in the warehouse area (Figure 7). Even though witness accounts are somewhat conflicting regarding the quantity and approximate location of the stored chemicals, most statements agree that AZM supersacks had just been placed next to the compressor piping. Witnesses also agree that the yellow smoke or powder was coming from this location. Forklift operators recollect placing Maneb pallets by the compressor pipe in an attempt to make room for the incoming AZM. In addition to the witness statements the JCAIT:

- \$ Screened the bulk residue samples for various pesticides including AZM, Maneb, Topsin, and Sevin. Only semi-quantitative values of AZM and Maneb were reported.
- \$ Secured and analyzed the remains of the new warehouse addition ventilation fans which had visible yellow residue (Figure 8). AZM and its major decomposition products were confirmed.

The JCAIT concluded that it was highly probable that pallets of both AZM and Maneb were placed along the compressor pipe the day of the event.





Figure 8. Ventilation Fan with Yellow Residue

### **AZM and Maneb Thermal Decomposition**

Both AZM and Maneb can decompose thermally if they are exposed to elevated temperatures during a period of time.

Maneb is classified by the Department of Transportation (DOT) for transportation purposes as an ASpontaneously Combustible Material@ unless it is stabilized. If it is stabilized, Maneb is classified as a ADangerous When Wet Material.@ This classification includes materials that evolve flammable gas when in contact with water. Maneb presumably falls in this category because of formation of carbon disulfide. According to the MSDS, the Maneb at BPS was stabilized.

Data related to AZM decomposition temperature is rather conflicting. MSDS do not identify AZM as flammable and most literature provides a decomposition temperature of 320<sup>0</sup> F (160<sup>0</sup> C).

The JCAIT requested representative samples from the manufacturers of AZM 50W and Maneb 75DF to conduct several thermal stability tests including decomposition temperature and color changes associated with temperature. The JCAIT also conducted Differential Scanning Calorimetry (DSC) tests on other AZM formulations, including the 90% pure technical formulation used as the active ingredient in AZM 50W. A summary of the tests findings and literature search are presented below:

## AZM 50W

- \$ AZM 50W showed visible color change to dark tan at 217<sup>0</sup> F (103<sup>0</sup> C). The sample showed visible smoke at 340<sup>0</sup> F (171<sup>0</sup> C).
- \$ The DSC analysis showed the 90% AZM technical formulation decomposing exothermally (1100 J/g) at approximately 320<sup>0</sup> F (160<sup>0</sup> C). Other formulations, including AZM 50W, decomposed exothermally (600 J/g) at approximately 338<sup>0</sup> F (170<sup>0</sup> C). The smaller amount of heat released by the 50% formulations compared to the 90% pure technical grade is consistent with the addition of inert ingredients.
- \$ A basket test to determine safe storage temperatures for bulk AZM 50W showed decomposition of the sample beginning between 158<sup>0</sup>-176<sup>0</sup> F (70<sup>0</sup>-80<sup>0</sup> C). The decomposition temperature corresponds to an estimated safe storage temperature of 79<sup>0</sup> F (26<sup>0</sup> C), using a 10% safety factor, based on volume and surface area specifications for supersacks provided by MFC. It should be noted that the test does not predict a safe time interval corresponding to this temperature.
- \$ MFC conducted a twelve month storage stability study in support of registration of its product. The procedure included the use of two 2.5 pound samples. For this test the product was stored at 68<sup>0</sup> F  $\pm$  36<sup>0</sup> F (20<sup>0</sup> C  $\pm$  2<sup>0</sup> C) for twelve months.
- \$ The *EPA Office of Pesticides: Product Properties Test Guidelines* (OPPTS 830.6317) for pesticide registration requires storage stability tests to be conducted under either of the following conditions: A) At 68<sup>0</sup> or 77<sup>0</sup> F (20<sup>0</sup> C or 25<sup>0</sup> C); B) Under warehouse conditions which reflect the expected storage conditions of the commercial product; C) The test parameters may be expanded to include accelerated conditions, such as elevated temperatures (104<sup>0</sup>-129<sup>0</sup> F) (or 40<sup>0</sup>-54<sup>0</sup> C) or cold temperature (-20<sup>0</sup>-0<sup>0</sup> C).
- \$ In a test to determine whether it would melt, decompose, or the vapor given off would ignite, the AZM sample turned yellowish brown, then black, gave off yellow smoke, and the vapors ignited. A second test confirmed these results.

A study conducted by G. Bertoni and Co-workers; *Lazioni Commerciali in Ambienti Refrigerata*., Annali di Chimica, 1985, states that accidental overheating of an AZM mixture may occur during the mixing process and since the active principle melts at low temperatures (m.p. 162<sup>0</sup> -165<sup>0</sup> F) (m.p. 72<sup>0</sup>-74<sup>0</sup> C) and decomposition begins at a temperature of about 212<sup>0</sup> F (100<sup>0</sup> C), gases and vapors are set free. The study concluded that:

- \$ The product begins decomposition around 100<sup>0</sup> C. As temperature increases an intense exothermic reaction occurs between 338<sup>0</sup> and 356<sup>0</sup> F (170<sup>0</sup> and 180<sup>0</sup> C) with a loss of volatile products of about 40% of the initial weight.

- \$ AZM is a thermally unstable material; a slow process of degradation of the compound occurs below 122<sup>0</sup> F (50<sup>0</sup> C).
- \$ The spontaneous degradation of AZM is noticeably accelerated by any increase of temperature so that attention has to be paid to storage of this product and its commercial forms.
- \$ It is recommended to keep AZM away from any heating. If the temperature rises above 100<sup>0</sup> C decomposition is very fast and at 170<sup>0</sup>-180<sup>0</sup> C the product decomposes almost instantaneously.

### **MANEB 75DF**

- The sample of Maneb 75DF showed a black spot beginning at 320<sup>0</sup> F. Visible smoke was observed at 340<sup>0</sup> F (171<sup>0</sup> C).
- \$ Under nitrogen atmosphere, Maneb 75DF did not release a significant amount of energy when heated during the DSC. In the temperature range of 338<sup>0</sup>-410<sup>0</sup> F (170<sup>0</sup>-210<sup>0</sup> C) the samples heated in nitrogen showed an exothermic reaction followed by an endothermic reaction. The net result under these conditions was a slight absorption of heat with decomposition occurring at approximately 338<sup>0</sup> F (170<sup>0</sup> C).
- \$ Zi-Ru Liu, et al. published a study in *Thermochimica Acta* 220 (1003) 229-235 entitled *Heat Changes Associated with the Thermal Decomposition of Maneb and Zineb*. This study focuses on the heat changes on thermal decomposition of Maneb and Zineb using DSC. It acknowledges that both endothermic and exothermic processes are present in their initial decomposition. The study concludes that the initial decomposition temperature in air is greatly decreased compared with that in nitrogen. The study indicates that the thermal decomposition of Maneb is accelerated and is an exothermic process accelerated in air or oxygen gas.
- \$ The basket test results for Maneb 75DF showed an onset temperature between 221<sup>0</sup>-239<sup>0</sup> F (105<sup>0</sup>-115<sup>0</sup> C). Using similar procedures as described for AZM, an estimated maximum safe storage temperature of 181<sup>0</sup> F (83<sup>0</sup> C) was calculated for a supersack of Maneb. The test does not predict a safe time interval corresponding to this temperature.
- When tested for melting, decomposition, and evolution of ignitable vapor, Maneb 75DF decomposed into a black material, white vapors evolved from the decomposing sample, the vapors ignited into a yellow/orange flame, and the vapor flame self-sustained several seconds after the removal of the ignition source. In a second test Maneb produced vapors that ignited as a yellow flame; at full decomposition the sample produced white smoke.
- As mentioned before, both AZM 50W and Maneb 75DF could have been placed close or



against the compressor header pipe. The test on both substances indicate that decomposition could have occurred at the temperature likely reached by the compressor exhaust pipe, but AZM begins to decompose at a lower temperature than Maneb. Statements provided by most witnesses of the incident describe a yellow smoke or gas which is consistent with what was observed during experimental tests.

The JCAIT concluded that AZM 50W was the material responsible for the initial evolution of the combustible atmosphere. If a supersack of AZM 50W was placed in contact with or in close proximity to the hot compressor pipe, the heat could have initiated its thermal decomposition. The decomposing material would propagate away from the pipe in the direction of the center of the supersack. The contact of the decomposing material with the pipe in this instance would not necessarily be prolonged. The decomposition would be accompanied by the evolution of gas and smoke (the products of decomposition).

AZM's volatile decomposition products, as all organic compounds, evolve flammable constituents upon decomposition. In particular, a literature reference (*Combustion Products from Pesticides and Other Chemical Substances Determine by Use of DIN 53 436*, L. Smith-Hansen and K. Haahr-Jorgensen, *Fire Safety Journal* 23(1994), 51-66), lists six organic combustion products from the decomposition of AZM. The article further states that generally, large numbers of different organic species are formed during decomposition due to incomplete decomposition and partial oxidation. As mentioned before, the flammable gases from decomposition would not have been confined to the immediate area above the supersacks and could have ignited/explored at some distance from the origination point.

## **Scenario 2. AZM decomposition begins before arriving to BPS:**

The JCAIT postulated as a possible scenario that a thermal decomposition was occurring inside a supersack of AZM 50W before it arrived at BPS. This decomposition could have generated the airborne flammable substances that exploded in the warehouse. The scenario is supported mostly by witness statements concerning the smell of the supersacks that were unloaded the morning of the event. The truck driver reported that the AZM 50W smell had made him feel sick and that he had to stop and rest for that reason. On separate interviews, BPS employees stated that he had made the same remarks to them the morning of the incident. Other BPS employees reported the unusual smell as well.

Chemical powders can undergo smoldering combustion. Hot temperature spots can become entrapped in bulk containers (e.g. a supersack). Smoldering can also occur as a result of self heating when the temperature of a bulk material is raised to a level at which the rate of heat production exceeds the rate of heat loss. In either case, the container and contents can thermally insulate, allowing exothermic reactions to continue at a very slow rate. When the container is disturbed, the reaction can spread and the reaction rate can increase until the self heating reaction reaches the surface. The hot material or its decomposition products may reach temperatures sufficient to burst into flames, especially when disturbed.

Less: *Loss Prevention in the Process Industry*, volume 2; 17.5 explains as follows: AA dust deposit can undergo smoldering for a long period. It is not unknown for large piles to smoulder for a matter of years. Both air access and heat loss are restricted so that combustion is very slow, but is sustained. Such smoldering may give no readily detectable effects. In particular, there may be no smoke or smell from the burning. This delay between ignition and outbreak of flaming can create hazards. Fire may break out unexpectedly in a factory shut down overnight or at a weekend, or the cargo of a ship may be discovered to be on fire when it is unloaded. Hazards of dust fires include those of a dust explosion resulting from the formation and ignition of a dust suspension, of the ignition of other flammable materials and of the evolution of toxic combustion products.®

The AZM unloaded at BPS the day of the incident was contained in supersacks approximately 1600 pounds of material each. The product had been stored in Tifton, Georgia. NOAA reported a daily average temperature of 76° F (24° C) for Tifton, GA during the month of April. The maximum temperature reported by NOAA for Helena, Arkansas on May 8, 1997 was 82° F (28° C).

MFC files show eight minor incidents from 1987-1996. These incidents were associated with AZM 50W smoldering as a result of the material coming in contact with hot surfaces (mostly hot bearings) during production. In those instances, MFC flooded the smoldering product with water. A manufacturer of another AZM formulation reported twelve incidents in the 1960's, five in the 1970's, and seven in the 1980's. All of them involved excessive heating during processing or storage. As stated in previous sections, MFC had discussed with BPS the product's potential for smoldering while in contact with hot bearings. Reportedly, MFC advised BPS to flood production hoppers in the presence of a bad odor during the repackaging operation.

In theory, one of the AZM 50W supersacks could have had a smoldering hot spot as a result of the mixing operations. A smoldering spot in a bulk container could have been in storage without being detected. Sensors normally used in automatic fire protection systems cannot usually detect this kind of condition. This hot spot could have initiated a self heating reaction which accelerated during the unloading at BPS. The smoke or powder was discovered right after the lunch break. There is an approximate 15 minute time span from the time the waste monitor left the new warehouse addition, and the smoke was discovered. After the discovery, the reaction seemed to have continued at an increasingly accelerated rate. An accelerated reaction rate after being disturbed is consistent with industry's experience of smoldering spots insulated by the bulk container.

The scenario, however, is based solely on witness statements. These statements are not consistent. Thermally stable AZM has a very strong and persistent odor. The truck driver and BPS employees were not familiar with AZM. Their statements concerning whether or not this load had a different odor from a previous one are at times contradictory.

The JCAIT inspected the truck several days after the incident looking for evidence of AZM 50W decomposition. Prior to the incident, the truck had transported plastic lawn mower parts. Therefore, there was no potential for the AZM 50W to react with a compound previously transported in the truck. Wipe samples conducted in the truck confirmed only the presence of AZM. Early AZM decomposition products would be in the form of volatile gases and vapors. Since several days had passed since the incident, it was not reasonable to expect positive sampling of volatile compounds.

The JCAIT requested MFC split control samples from the production batches offloaded at BPS. Laboratory analysis showed no signs of thermal decomposition. The fact that the control samples showed no signs of decomposition, however, does not rule out the possibility of a hot spot entrapped in a supersack. In addition, these control samples have been in a controlled environment that could be substantially different from actual storage conditions. Similarly, there is no evidence that the AZM supersacks delivered at BPS were exposed to factors that could induce its thermal decomposition.

The JCAIT concluded that this is a possible scenario but the available evidence is uncertain and cannot substantiate it. However, the team acknowledges that a self heating process could have either initiated the event or accelerated the thermal decomposition of a supersack placed close to a heat source.

### **Scenario 3. Incompatible Chemicals React**

The following pesticides were present in the Unit Two new warehouse addition at the time of the incident: Azinphos methyl 50W, Maneb 75DF, Alliette Signature WDG, Topsin WSB, Sevin 80 WSP, and Penncozeb 75DF. In addition, a spill of twenty to thirty pounds of Alliette Signature was reported next to the new warehouse addition north wall shortly before the incident.

The team reviewed the chemical properties and reactivity of these pesticides to estimate potential hazardous reactions that could have initiated the explosion and subsequent fire. This review is discussed below and summarized in the table at the end of this section. The pesticides present represent the following types of chemicals:

- Carbamate - Topsin and Sevin;
- Dithiocarbamate - Maneb and Penncozeb; and
- Organophosphorus - Azinphos methyl and Alliette.

The analysis showed that none of the pesticides would be expected to be highly reactive with each other under normal conditions. Based on their chemical structures, there would be no reason to expect any of these substances to react with each other if they were accidentally mixed together. The form in which these substances were stored (i.e., solid formulations) and the presence of inert ingredients would make reactions particularly unlikely.

The carbamates and Dithiocarbamate are chemically similar; chemical reactions would not be expected to take place between such similar chemicals. Maneb and Penncozeb (Mancozeb), in particular, are compounds of the same base chemical and are very similar; Maneb is the manganese salt of dithiocarbamic acid, and Penncozeb is a compound of dithiocarbamic acid and both manganese and zinc. Topsin (Thiophanate methyl), a carbamate, is combined in formulations with both Maneb and Mancozeb (*Farm Chemicals Handbook*, 1994), indicating that no reaction takes place when these substances are mixed. There appears to be no reason to expect a reaction between the carbamates Topsin and Sevin (carbaryl), because of their chemical similarity, or between Sevin (carbaryl) and Maneb or Penncozeb, by analogy with Topsin.

Alliette (Fosetyl-aluminum) and Azinphos methyl are Organophosphorus compounds, not carbamates or Dithiocarbamate, but no reaction would be expected upon mixing with carbamates or Dithiocarbamate, based on the chemical structures of these substances. Fosetyl-aluminum is combined in formulations with Mancozeb (*Farm Chemicals Handbook*, 1994), indicating that no reaction would take place between these substances. This type of formulation also provides evidence that Fosetyl-aluminum likely would not react with Maneb, because Maneb is very similar to Mancozeb, and would be expected to react similarly.

Several of the pesticides are reported to be incompatible with strong oxidizers, and it is likely that all of them would react with strong oxidizers under some conditions. No oxidizers were reported to be present, however. Based on this analysis, the JCAIT concluded that the event was not initiated by the Alliette Signature spill or the reaction of incompatible chemicals placed in proximity.

### Reactivity and Flammability of Pesticides Present in New Warehouse Addition at BPS

| Name               | Common Name/Chemical Name/Formula of Active Ingredient                                                                       | Reactivity and Flammability Data                                                                                                                                                                                                                                                       | Potential Reactions with Other Pesticides Present                                                                                       |
|--------------------|------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| Azinphos methyl    | Azinphos methyl<br>O,O-(Dimethyl S[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate<br>$C_{10}H_{12}N_3O_3PS_2$ | Decomposes at elevated temperatures.<br>Hydrolyzed in alkaline and acidic media. Contact with strong oxidizers may cause fires and explosions.<br>Combustible (conflicting data).                                                                                                      | None expected.                                                                                                                          |
| Topsin             | Thiophanate-methyl<br>Dimethyl[(1,2-phenylene)bis(iminocarbonothionyl)]bis(carbamate)<br>$C_{12}H_{14}N_4O_4S_2$             | Compatible with other agricultural chemicals that are neither highly alkaline nor contain copper.<br>No data on flammability (probably combustible).                                                                                                                                   | None expected. May be combined in formulations with Maneb and Mancozeb (Penncozeb), indicating no reaction.                             |
| Alliette Signature | Fosetyl-aluminum<br>Aluminum tris(O-ethyl phosphonate)<br>$C_6H_{18}AlO_9P_3$                                                | Stable under storage conditions.<br>Incompatible with strong bases, mineral acids, strong oxidizers, strong reducing agents.<br>Non-flammable.                                                                                                                                         | None expected. May be combined in formulations with Mancozeb (Penncozeb), indicating no reaction.                                       |
| Sevin              | Carbaryl<br>1-Naphthyl <b>B</b> methyl carbamate<br>$C_{12}H_{11}NO_2$                                                       | Stable under storage conditions.<br>Incompatible with alkalis and strong acids.<br>Combustible.                                                                                                                                                                                        | None expected.                                                                                                                          |
| Maneb              | Maneb<br>Manganese ethylenebis(dithiocarbamate)<br>$(C_4H_6MnN_2S_4)_x$                                                      | Decomposes on prolonged exposure to air or water.<br>Incompatible with strong acids and strong oxidizers.<br>Classified by DOT as spontaneously combustible or dangerous when wet.                                                                                                     | None expected. May be combined in formulations with Thiphanate-methyl (Topsin) and Mancozeb (Penncozeb), indicating no reaction.        |
| Penncozeb          | Mancozeb<br>Manganese ethylenebis(dithiocarbamate) complex with zinc ion<br>$(C_4H_6MnN_2S_4)_x(Zn)_y$                       | Stable under storage conditions.<br>Decomposed in acid and alkaline conditions, by heat, and when exposed to moisture and air. Incompatible with strong acids and strong oxidizers.<br>Compatible with most common pesticides.<br>No data on flammability - probably similar to Maneb. | May be combined in formulations with Thiphanate-methyl (Topsin) and Maneb, and with Fosetyl-aluminum (Alliette) indicating no reaction. |

Sources:

*Farm Chemicals Handbook* 94. Hazardous Substances Databank (HSDB), National Library of Medicine, for Azinphos methyl, Fosetyl-aluminum, Maneb, Mancozeb. MSDS for Azinphos methyl 50W, Alliette Signature, Sevin, Maneb 75DF, Penncozeb 75DF. TOMES for carbaryl. Worthing, ed., *The Pesticides Manual* (1987).]

#### **Scenario 4. Malfunctioning Compressor Overheats Supersacks Near the After-cooler Piping**

Two multistage reciprocating air compressors were used in the Unit Two building. As stated previously, these compressors discharged into a common header pipe that was located on the warehouse side of the wall, approximately five feet above the deck. This header was 15 feet long and led to an after-cooler outside the building. The 15-hp unit suffered substantial damage during the incident. After the explosion, this unit was found lying on its side with no lubricating oil in the crankcase. The concrete foundation by the compressor had substantial heat damage and spalling in a configuration that suggested a liquid had burned on the surface. The 20-hp unit had only moderate damage, remained in its upright position after the event, and had a substantial amount of oil in the crankcase.

The JCAIT dismantled the 20-hp compressor. The 20-hp compressor did not show any observable internal damage. The JCAIT also performed a forensic analysis of the 15-hp unit to determine whether or not the unit was working properly at the time of the event (DNV Project No. 232-8384). The forensic analysis conducted on the 15-hp compressor showed that:

- The aluminum bell housing for the electric motor and the aluminum header for the first stage had melted away. The melted residue had been deposited on the engine and compressor mount platform immediately below the motor when it was still in the upright position. This indicates that the compressor was exposed to heat before falling on its side.
- The pulley side of the compressor had sustained direct flame impingement heat, but little was observed on the opposite side. The damage areas indicate that an intense fire had been burning on the deck next to the pulley side while the compressor was still upright.
- The connecting rod and journal bearings had not been scored. This indicates that the unit had sufficient lubrication when last run.
- A coke-like residue was inside the crankcase. This indicates that a lubricating oil fire had developed inside. Presumably, it was ignited by a liquid fire on the deck after the compressor fell over. It is also likely that the oil leaked out through the pulley side bearing.

Based on these findings, JCAIT concluded that the 15-hp compressor was not malfunctioning before the event. Therefore, this scenario was discarded by the investigation team.

### **3. 2. B Overview of Early Emergency Response**

There are many factors that could be root causes or could have contributed to the three firefighter fatalities. A formal analysis requires a thorough review of operational parameters and human performance influencing factors including training, competency, pre-planning, policies and procedures, etc. A critique of these factors and the local emergency response activities is outside the scope of this investigation. However, the JCAIT evaluated some general aspects of the emergency response system (related to the BPS explosion) which can foster unsafe situations. By doing this, the JCAIT attempts to promote efforts to provide local emergency response groups with information critical to their safety when responding to chemical incidents.

BPS personnel believed and informed the WHFD that a smoldering bag of AZM had initiated the incident. This fact is indicated in witness accounts, the BPS 911 call transcript, and an early press release from the facility management. As a repackaging tolling operator, BPS did not have in-house expertise to test and identify the hazards associated with the chemicals they were handling. Instead, BPS was relying on the chemical manufacturer's information (in this case MFC) to address the chemical hazards. On the other hand, the WHFD relied on BPS to provide them with chemical hazard information.

### **On-site information**

BPS management told the WH Fire Chief that AZM would not explode. Neither the facility personnel nor the documents handed to the fire department conveyed the danger of explosion. The MSDS for AZM used by the BPS personnel and firefighters was provided to BPS by MFC. The MSDS includes the following information concerning the thermal stability and reactivity and flammability hazards of AZM 50W:

- \$ HMIS flammability rating of 0 (non-combustible).
- \$ HMIS reactivity rating of 0.
- \$ Stable under normal conditions.
- \$ High temperatures may cause hazardous vapors.
- \$ Store in cool, dry, well ventilated place. Do not place near heat or open flame.

There is no data on the AZM 50W indicating the possibility of an explosion hazard. It does not include a safe storage temperature or a decomposition temperature. It does, however, warn against placing AZM near heat. The JCAIT reviewed several other MSDS for different AZM formulations, in particular, the MSDS for Bayer's Guthion, which BPS had discussed with MFC. This MSDS includes the following information:

- \$ NFPA flammability rating of 2. (JCAIT Note: An NFPA flammability rating of 2 applies to materials that must be moderately heated or exposed to relatively high ambient conditions before ignition can occur. These materials would not under normal conditions form hazardous atmospheres with air, but under high ambient temperatures or under moderate heating might release vapor in sufficient quantities to produce hazardous atmospheres with air.)
- \$ NFPA reactivity rating of 2. (JCAIT Note: An NFPA reactivity rating of 2 applies to materials that are normally unstable and readily undergo violent chemical change, but are not capable of detonation. It applies to materials that can undergo chemical change with rapid release of energy at normal temperatures and pressures and materials that can undergo violent chemical changes at elevated temperatures and pressures.)
- \$ During routine handling of this material, there should be little risk of dust explosion.

- \$ Stable material. Unstable in sustained temperature above 100 °F (38° C).
- \$ Storage temperature: 30-day average not to exceed 100 °F.
- \$ Store in cool, dry area away from heat source.

It should be noted that NFPA 472 *Standard on Professional Competency of Responders to Hazardous Material Incidents*, 1997 edition, Non mandatory Appendix A-21.4 explains that: ASome materials have products of combustion or decomposition that present a significant greater degree of hazard than the inherent physical and toxic properties of the original material. The degree of hazard is dependent on the conditions at the time of the incident@.

In addition to the AZM 50W, the WHFD had the DOT's *Emergency Response Guidebook*. In the 1993 edition, Guide Number 55 applies to AZM. In the Fire and Explosion Section, Guide 55 indicates A Some of these materials may burn, but none of them ignites readily. Container may explode violently in heat of fire.@

The WH Fire Chief reported during an interview that fire personnel received the following HazMat training; two career firemen (both killed during the event) had 80 hours of technician level training; all fire personnel had training through the awareness level; and other firemen were trained through the technical and operational level. As part of the emergency preparedness program, the WHFD received MSDSs from BPS and had been invited to tour the facility and participate in their emergency response drills. As mentioned before, the fire department had toured the facility one month before the incident.

Training and pre-planning are critical to emergency response groups. Additionally, adequate information is essential for incident-specific risk management. Chemical emergency situations are among the worst work environments for human performance. It is in emergency situations where the human information processing system is burdened with multiple and critical tasks. The information provided to local emergency responders has to be structured and prioritized for this specific use to maximize human performance.

MSDSs are developed to comply with OSHA's Hazard Communication Standard to communicate the hazards posed by chemicals to employees. Additionally, they are extensively used by emergency response groups during chemical releases. The JCAIT looked at the MSDSs present at BPS at the time of the incident from a local emergency response standpoint. The number of MSDSs at BPS do not constitute a statistical representation of the MSDSs developed by the chemical industry. Evaluating the MSDSs present at BPS, the JCAIT found the following:

- \$ MSDSs did not have a standard format. Information relevant or critical during an emergency response operation may not be readily available or may be presented in a confusing format.



- \$ Some MSDSs had a check-box format. In the case of the Maneb MSDS, information was incomplete or conflicting. For example, hazard information stated the chemical was Awater reactive. However, the information on firefighting stated Ause water. No further explanation on how the firefighting water will interact with the Maneb was provided (e.g. should the firefighters use fog vs a large stream). Similarly, no information was provided related to Maneb being stored in the presence of a water-based sprinkler system.
- \$ Some terms were not clearly explained. In the case of the AZM 50W MSDS, information included in the section AUnusual Fire and Explosion Hazards stated that the Avapors and fumes from fire are hazardous. The term hazardous does not convey whether the vapors and fumes are toxic, combustible or both.

The JCAIT concluded that the on-site hazard information was conflicting and incomplete. It is critical that fire departments collect as much hazard information as possible within the time, resources, and training limitations. In addition to MSDS, NFPA 472 *Standard on Professional Competency of Responders to Hazardous Material Incidents*, 1997 edition, Appendix A Explanatory Material, identifies other sources of information for hazard identification such as the *North American Emergency Response Guidebook*, hazardous material databases, technical information centers (CHEMTREC/CANUTEC/SETIQ), shipper/manufacturer contacts, and monitoring equipment.

### **Risk Perception/Risk Management**

The WHFD was reviewing MSDSs when the explosion occurred. The firemen that died were close to the building getting ready to enter the building. From witness interviews they were trying to locate the smoldering Abag in the warehouse.

BPS employees were not aware of any explosion hazards. The employees did not show extreme concerns to the WHFD. The facility personnel conveyed more the need of air-packs due to the toxicity of the chemicals rather than any fire and explosion hazards. The production manager had entered the building several times just before the explosion. He actually closed the building doors (with the fire chief approval) which in effect confined the combustible atmosphere.

The lack of awareness of the potential explosion hazard played an important role in the tactics used by the WHFD. With a better understanding of the potential hazards, the WHFD would presumably have been more cautious. NFPA 1561, *Standard on Fire Department Incident Command System*, Explanatory Appendix A-4-1.2, explains that the risk to fire department personnel is the most important factor to be considered by the incident commander in determining the strategy to be employed in each situation. One of the factors involved in the management of risks levels is the pessimistic evaluation of changing conditions.

NFPA 1561, 4-1.2 states that AThe concept of risk management shall be utilized on the basis of the following principles: (a) Activities that represent a significant risk to the safety of personnel shall be limited to situations where there is a potential to save endangered lives; (b) Activities that are routinely employed to protect property shall be recognized as inherent risks to the safety of personnel, and actions shall be taken to avoid these risks; (c) No risk to the safety of personnel shall be acceptable where there is no possibility to save lives or property.

NFPA 1561, A-4-1.3, further explains: "The acceptable level of risk is directly related to the potential to save lives, the risk to fire department personnel must be evaluated in proportion to the ability to save lives, the risk to fire department personnel must be evaluated in proportion to the ability to save property of value. Where there is no ability to save lives or property, there is no justification to expose fire personnel to any avoidable risk, and defensive fire suppression operations are the appropriate strategy."

As stated in the previous section, the on-site information available to the WHFD was conflicting. The AZM 50W MSDS did not state the potential for an explosion hazard. In addition, BPS management may have given the WHFD a false sense of risk when asked about the danger of an explosion. However, chemical warehouses may present unique and unexpected hazards to emergency responders because of unknown combustion products and chemical interactions. In the BPS incident, the building had been evacuated and no lives were threatened. Factoring conflicting information and the unexpected hazards presented in a chemical storing area into the risk management decision process could have helped the emergency responders to develop a safer response strategy.

## **4.0 Root Causes and Recommendations**

### **4.1 Root Causes and Contributing Factors**

Root causes are the underlying prime reasons, such as failure of particular management systems, that allow the faulty design, inadequate training, or deficiencies in maintenance to exist. These, in turn, lead to unsafe acts or conditions which can result in an accident. Contributing factors are reasons that, by themselves, do not lead to the conditions that ultimately caused the event; however, these factors facilitate the occurrence of the event or increase its severity. Although the JCAIT cannot precisely determine the exact cause of this event, there is sufficient information to support several root and contributing causes. The root causes and contributing factors of this event have broad application to a variety of situations and should be considered lessons for industries that conduct similar operations. The JCAIT identified the following root causes and contributing factors of the event:

#### **\$ MFC and BPS did not have a full understanding of the hazards associated with AZM.**

EPA's Office of Pesticides requires manufacturers to conduct storage stability tests under one of the following conditions: A) At 20° C or 25° C; B) Under warehouse conditions which reflect the expected storage conditions of the commercial product; C) The test parameters may be expanded to include accelerated conditions, such as elevated temperatures (or 40° C-54° C) or cold temperature (-20° C-0° C). MFC conducted the study at 20°C ± 2° C for twelve months and a two pound bag. In order to comply with the Office of Pesticides requirements, MFC should have tested for the actual container size (1,600 pounds) and expected storage and transportation temperatures which can be considerably higher than the 20°C used by MFC in their test.

In addition, the Office of Pesticide Programs requires the use of DSC to test pesticides for explosiveness. DSC is a screening test. For thermally unstable materials, the DSC test does not provide specific enough information to predict safe storage temperatures of large storage or shipping containers.

MFC failed to provide BPS with adequate information on the hazards associated with the chemical. As MFC did not perform adequate testing, hazard information relative to the thermal stability and explosiveness of AZM was not included in the MSDS.

**\$ BPS did not assess the potential hazards of a hot pipe in an area where hazardous chemicals were to be stored when the new warehouse addition was constructed.**

In October of 1995 BPS added the warehouse area to the Unit Two building. The compressors' discharge pipe was modified to go through the area where hazardous chemicals were stored. A review of the impact of the change should have identified the risks associated with this configuration to workers and/or heat sensitive chemicals.

**\$ BPS did not have standard operating procedures for material storage and handling**

Standard operating procedures could have prevented BPS from placing a thermally unstable substance next to a heat source, in this case, the compressor header pipe.

**\$ On-site information provided to the WHFD was conflicting and incomplete.**

The AZM 50W MSDS did not specifically identify an explosion hazard. Generally, chemical hazard information on MSDS is not structured and prioritized for local emergency response use. MSDSs may not have enough information to help emergency responders conduct safe operations and should not be relied upon as the sole source of information during an emergency response. In fact, DOT's *Emergency Response Guidebook* on-site had a warning related to containers exploding violently in the heat of fire. Additional sources of information can help local responders to conduct safer operations.

## **4.2 Recommendations**

The following recommendations were developed by the JCAIT that address the root causes and contributing factors to prevent recurrence or similar incidents at other facilities:

**\$** Manufacturers should be proactive in testing potentially hazardous materials. Testing for actual conditions and elevated temperatures during storage should be conducted to determine safe storage conditions. Screening tests, such as DSC, can be helpful in determining the need for additional testing. However, thermally unstable materials which are intended to be packed and shipped in large volume containers should be tested beyond screening levels.

**\$** Facilities which store, use, handle, manufacture, or move hazardous materials should develop and implement a system to review potential hazards of modifications to facilities, equipment, chemicals, technology, or procedures. The system should analyze potential impacts to safety, health, and the environment and take appropriate actions before the modifications are implemented. OSHA's Process Safety Management (PSM), EPA's Risk Management Program (RMP), and the Center for Chemical Process Safety (CCPS) guidelines can help facilities develop such system.

- \$ Facilities that store hazardous chemicals should develop standard operating procedures for material storage and handling that address storage restrictions. Such facilities should adhere to applicable practices outlined by CCPS and NFPA. Pesticide facilities are encouraged to also follow NFPA 43D (Code for the Storage of Pesticides), specifically the non-mandatory Appendix B.
- \$ Facilities storing hazardous chemicals should develop an inventory management system with information regarding composition, compatibility, storage, location, and quantity of incoming products. This management system can help the facility comply with storage restrictions and provide emergency responders useful information during a response action.
- \$ EPA and OSHA, in conjunction with interested parties, should facilitate a workshop to make recommendations on how to improve the quality of hazardous materials information available during response actions. The workshop should review appropriate uses of MSDS by local emergency response groups and how to provide these groups information describing the behavior of hazardous materials when they begin to react or decompose and what responders should look for during a chemical emergency.

## **Appendix A**

AZM 50W, Maneb 75DF and Alliette Signature MSDSs

# MATERIAL SAFETY DATA SHEET

## SECTION 1 - MANUFACTURER INFORMATION

MANUF/DIST: MICRO FLO CO.  
P. O. Box 5948  
Lakeland, FL 33807

EMERGENCY PHONE: (800) 424-9300

TRADE NAME/SYNONYMS : AZINPHOS METHYL 50W SOLUBLE  
CHEMICAL NAME/SYNONYMS: See Hazardous Ingredients Below  
CHEMICAL FAMILY : Organophosphorus Insecticide  
FORMULA :  $C_{10}H_{14}N_3O_3PS_2$   
PRODUCT CODE : Reg. # 51036-164

## HAZARDOUS MATERIAL IDENTIFICATION SYSTEM (HMIS)

|   |                    |    |   |
|---|--------------------|----|---|
| * | HEALTH . . . . .   | .2 | * |
| * | FLAMMABILITY . . . | .0 | * |
| * | REACTIVITY . . .   | .0 | * |
| * | PROTECTION . . .   | .2 | * |

## SECTION 2 - HAZARDOUS INGREDIENTS

THIS PRODUCT CONTAINS HAZARDOUS INGREDIENTS: Yes

| <u>CHEMICAL NAME</u> | <u>CAS NUMBER</u> | <u>%</u> | <u>PEL-OSHA</u> | <u>TLV-ACGIH</u> |
|----------------------|-------------------|----------|-----------------|------------------|
| Azinphos methyl      | 86-50-0           | 50.0     | (skin)          | 0.2mg/m3         |
| Inert ingredients    |                   | 50.0     |                 |                  |
| Total:               |                   | 100.0%   |                 |                  |

THIS PRODUCT CONTAINS CARCINOGENS (NTP, IARC, or OSHA): NO

## SECTION 3 - HEALTH HAZARD DATA

HEALTH EFFECTS (Acute and Chronic):  
(LD50 Values for azinphos methyl technical)  
Acute Oral LD50 (rat) = 13-16 mg/kg  
Acute Dermal LD50 (rat) = > 220 mg/kg  
Acute Inhalation = 0.03 mg/l

MAY BE LETHAL IF INHALED, SWALLOWED OR ABSORBED THROUGH SKIN

### PRIMARY ROUTES OF ENTRY:

Poisonous if swallowed, inhaled, or absorbed through skin. Rapidly absorbed through skin surfaces & eyes. Contaminated clothing must be removed immediately. Exposed persons must receive prompt medical treatment.

Physician Note: This product is a strong cholinesterase inhibitor.

### MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

Low cholinesterase levels.

### SIGNS & SYMPTOMS OF POISONING:

Headaches, nausea, vomiting, cramps, weakness, blurred vision, pin-

point pupils, tightness in chest, labored breathing, nervousness, sweating, watering of eyes, drooling or frothing of mouth & nose, muscle spasms, and coma.

#### EMERGENCY FIRST AID PROCEDURES:

Call a doctor (physician), clinic, or hospital immediately. Explain that the victim has been exposed to azinphos methyl & describe his condition. If the doctor cannot come, take the victim to a hospital or clinic at once.

#### IF INHALED:

Remove victim to fresh air. If not breathing, give artificial respiration, preferably mouth to mouth, & maintain until doctor sees victim. If breathing is difficult, give oxygen.

#### IF IN EYES OR ON SKIN:

Immediately flush with plenty of water for 15 mins. while removing contaminated personal clothing & shoes to avoid continued possible exposure.

#### IF SWALLOWED:

Induce vomiting immediately by giving 2 glasses of water & touching back of throat with finger. Do Not Induce Vomiting Or Give Anything By Mouth To An Unconscious Person. Have victim lie down & keep quiet.

NOTE TO PHYSICIAN: Antidote - give atropine sulfate in large doses. TWO to FOUR mg. intravenously or intramuscularly as soon as cyanosis is overcome. Repeat at 5-10 min. intervals until atropinization signs appear. 2-PAM chloride may be administered as an adjunct to, but not substitute for atropine. DO NOT GIVE MORPHINE OR TRANQUILIZERS BECAUSE THESE MAY ACCENTUATE PHARMACOLOGIC EFFECT OF THIS PRODUCT.

### SECTION 4 - CHEMICAL DATA

|                                    |        |
|------------------------------------|--------|
| BOILING POINT (°F)                 | : N/A  |
| SPECIFIC GRAVITY (WATER=1)         | : See* |
| VAPOR PRESSURE (mmHg)              | : N/A  |
| PERCENT VOLATILE BY VOLUME         | : N/A  |
| VAPOR DENSITY (AIR=1)              | : N/A  |
| EVAPORATION RATE (butyl acetate=1) | : N/A  |

\*Packed Bulk Density 30-35 lbs/ft<sup>3</sup>

SOLUBILITY IN WATER:  
Wets & suspends

APPEARANCE AND ODOR INFORMATION:  
Fine, light yellowish powder with a "rotten cabbage" odor.

### SECTION 5 - PHYSICAL HAZARD DATA

FLASH POINT (Method Used): N/A  
FLAMMABLE LIMITS: Lel - N/A UEL - N/A

#### EXTINGUISHING MEDIA:

Small Fires: Dry chemicals, CO<sub>2</sub>, Halon, water spray or foam.  
Large Fires: Water spray, fog or standard foam is recommended.

#### SPECIAL FIRE FIGHTING PROCEDURES:

NIOSH self contained breathing apparatus (SCBA). Fight fire

upwind. Stay away from tank ends. For LARGE fires: Dike area to prevent runoff. Fight fire from maximum distance. Wear chemical protective clothing.

**UNUSUAL FIRE AND EXPLOSION HAZARDS:**  
Vapors and fumes from fire are hazardous. Use mist if possible to avoid dispersing powder. Evacuate people located downwind from fire.

**INCOMPATIBILITY (Materials to avoid):**  
Alkaline materials.

**HAZARDOUS DECOMPOSITION PRODUCTS:**  
Toxic gases and vapors such as sulfur dioxide, oxides of nitrogen, phosphoric acid mist, and carbon monoxide, may be released in a fire involving this product.

**WILL HAZARDOUS POLYMERIZATION OCCUR:**  
Has not been known to occur under normal conditions.

**IS THE PRODUCT STABLE:**  
Under normal conditions.

**CONDITIONS TO AVOID FOR STABILITY:**  
High temperatures may cause hazardous vapors. Avoid contact with strong oxidizers or alkaline substances.

#### SECTION 6 - SPILL OR LEAK PROCEDURES

**STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED:**  
Use self contained breathing apparatus & full protective clothing.  
Large Spill: Dike far ahead of material in case of rain. Keep out of bodies of water.  
Small Spill: can be taken up and placed in properly labeled containers for later disposal.

**WASTE DISPOSAL METHODS:**  
Azinphos is an acutely hazardous waste. Dispose in accordance with State and Federal authorities in compliance with RCRA regulations.

**CONTAINER DISPOSAL:**  
Completely empty bag into application equipment. Then dispose of empty bag in a sanitary landfill or incinerate, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

#### SECTION 7 - EXPOSURE CONTROL INFORMATION

**VENTILATION:**  
Required for handling indoors with localized exhaust recommended

**RESPIRATORY PROTECTION:**  
For exposure in enclosed areas, use a respirator with either an organic vapor removing cartridge with a prefilter approved for pesticides (MSHA/NIOSH approval number prefix TC-23C), or a canister approved for pesticides (MSHA/NIOSH approval number prefix TC-24G).  
For outdoor exposure, use a dust/mist filtering respirator.



(MSHA/NIOSH approval number prefix TC-21C)

PROTECTIVE GLOVES:  
Waterproof

OTHER PROTECTIVE EQUIPMENT:  
Chemical-resistant footwear plus socks  
Protective eyewear such as safety goggles or a face shield  
Chemical-resistant headgear for overhead exposure  
Chemical resistant apron when cleaning equipment, mixing, or loading  
Coveralls over short-sleeved shirt and short pants

Discard clothing and other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them. Follow manufacturer's instructions for cleaning and maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

#### USER SAFETY RECOMENDATIONS

1. Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet
2. Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing
3. Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing

#### WORK PRACTICES:

REPEATED EXPOSURES TO CHOLINESTERASE INHIBITORS SUCH AS AZINPHOS METHYL MAY WITHOUT WARNING, CAUSE PROLONGED SUSCEPTIBILITY TO VERY SMALL DOSES OF ANY CHOLINESTERASE INHIBITOR. Persons working with this product should have frequent blood tests of their cholinesterase levels. If it falls below a critical point, no further exposure should be allowed until it has been determined by blood tests that it has returned to a normal level. Keep all unprotected persons & animals away from treated area or where there is a danger of drift. Do Not rub eyes or mouth with hands. If you feel sick in any way, STOP work and get help right away.

### SECTION 8 - SPECIAL PRECAUTIONS

#### PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE:

Store in a cool, dry well-ventilated place. Do not store near heat or open flame. Keep out of reach of children. STORE IN ORIGINAL CONTAINERS ONLY. DO NOT USE OR STORE IN OR AROUND HOME. Empty container retains product residue. Observe all labeled safeguards until container is disposed in accordance with state and local laws.

#### MAINTENANCE PRECAUTIONS:

Wear full protective clothing when working on equipment that has been used to apply or package this product. Residues left in equipment are extremely hazardous.

#### OTHER PRECAUTIONS:

Respirators should be cleaned & cartridges replaced according to

instructions included with respirators. Replace gloves frequently. Refer to product label for further precautions regarding reentry and worker warnings

**ADDITIONAL COMMENTS:**

To the best of our knowledge, the information contained herein is accurate. However, Micro-Flo does not assume any liability for the accuracy or completeness of the information. Final determination is the sole responsibility of the user.

SEGREGATE FROM FOOD, FEEDSTUFFS, & CLOTHING (49CFR 177.841)

**SECTION 9 TRANSPORT INFORMATION**

D.O.T. Proper Shipping Name (49CFR 172.101): Organophosphorus Pesticides, Solid, Toxic, N.O.S. (Contains Azinphos Methyl)

D.O.T. Hazards Class: 6.1

UN/NA Number: UN2783

Packing Group: PG II

Label(s) Required: Primary - Poison

Subsidiary - NA

Placard(s) Required: Primary - Poison

Subsidiary - NA

Emergency Response Guide: #55

**SECTION 10 REGULATORY INFORMATION**

CERCLA Reportable Quantity: #1

RCRA Status: Not Regulated

SARA TITLE III:

Section 302 Extremely Hazardous Substance: YES

Section 311 Hazard Categories: Immediate

Section 313 Toxic Chemicals: NO

Revision: 1/95

# MANEB 75DF

## FUNGICIDE

elf atochem

ATO

FORM 4627  
REV. 5/96

## MATERIAL SAFETY DATA SHEET

**EMERGENCY  
TELEPHONE NUMBERS:**  
♦ (215) 419-5054 (9 a.m.-5 p.m. EST) (PRIMARY)  
(800) 424-9300 (CHEMTREC)

**ADDRESS:**  
ELF ATOCHEM NORTH AMERICA, INC.  
AGCHEM DIVISION  
2000 MARKET ST., 21st FLOOR  
PHILADELPHIA, PA 19103-3222

### PRODUCT IDENTIFICATION

**PRODUCT  
NAME**  
MANEB 75DF FUNGICIDE

**EPA REG. NO.**  
4581-371

**ELF ATOCHEM NORTH AMERICA, INC.  
CODE NUMBER**  
326

**CHEMICAL NAME AND  
MOLECULAR FORMULA**  
MANGANESE ETHYLENE BIS  
(DITHIOCARBAMATE) (POLYMERIC)  
(C<sub>4</sub>H<sub>4</sub>MnN<sub>2</sub>S<sub>2</sub>)<sub>x</sub>

**SYNONYMS**  
MANEB, TRIMANGOL

**CAS NUMBER  
OF ACTIVE INGREDIENT**  
12427-38-2

**CHEMICAL FAMILY**  
DITHIOCARBAMATE

### HAZARDOUS INGREDIENTS

| MATERIALS<br>OR COMPONENTS        | % WW  |
|-----------------------------------|-------|
| MANEB <sup>1</sup>                | 75.0  |
| ETU <sup>2</sup><br>(CAS 96-45-7) | trace |

<sup>1</sup> This ingredient has been listed as toxic under SARA 313.

<sup>2</sup> Ethylenethiourea (ETU), a trace contaminant and break-down product of Maneb 75DF, has been categorized as a probable human carcinogen by IARC, and as a group b carcinogen by NTP. ETU has also caused birth defects in laboratory animals.

#### ♦ WARNING:

This product contains chemicals known to the state of California to cause cancer. (See ingredient 1 listed above.)

This product contains chemicals known to the state of California to cause cancer and birth defects or other reproductive harm. (See ingredient 2 listed above.)

### SARA TITLE III

Hazards Classification (40 CFR 370):

Immediate Health: YES  
Delayed Health: YES  
Fire: YES  
Sudden Pressure: NO  
Reactivity: YES

Section 313 (40 CFR 372): This product contains the following chemicals subject to SARA Section 313 reporting requirements: Maneb.

### NFPA RATINGS

Flammability: 1  
Reactivity: 1  
Health: 2

### SHIPPING INFORMATION

**PROPER SHIPPING  
DESCRIPTION**  
MANEB PREPARATIONS,  
STABILIZED,  
4.3, UN2968, PGIII

**PLACARD**  
DANGEROUS WHEN WET  
IMO: MARINE POLLUTANT  
MANEB 75DF, when shipped  
domestically in the U.S.A. can be shipped  
as AGRICULTURAL FUNGICIDE,  
SOLID, NOT REGULATED BY D.O.T.  
(according to 49 CFR)

### PHYSICAL PROPERTIES

#### PHYSICAL STATE

**BOILING POINT/RANGE**  
NA

**MELTING POINT**  
DECOMPOSES BEFORE MELTING

**FREEZING POINT**  
NA

**MOLECULAR WEIGHT (CALCULATED)**  
(265.3)

**BULK DENSITY**  
0.65 g/ml at 20°C

**VAPOR PRESSURE (mm Hg)**  
NEGLECTIBLE AT  
ROOM TEMPERATURE

**VAPOR DENSITY (AIR=1)**  
NA

**SOLUBILITY IN H<sub>2</sub>O**  
DISPERSIBLE

**% VOLATILES BY VOLUME**  
NA

**EVAPORATION RATE**  
NA

**APPEARANCE AND ODOR**  
GREENISH TO GRAYISH YELLOW  
SOLID MICRO-GRANULE.  
NO SPECIFIC ODOR.

### FIRE AND EXPLOSION DATA

**FLASH POINT (TEST METHOD)**  
NE

**FLAMMABLE LIMITS**  
NA

**AUTOIGNITION TEMPERATURE/  
FIRE POINT**  
NE

#### EXTINGUISHING MEDIA

☒ WATER SPRAY ☒ DRY  
CHEMICAL  
☒ WATER FOG ☐ ALCOHOL  
FOAM  
☐ WATER STREAM ☒ FOAM  
☒ CO<sub>2</sub> ☐ EARTH OR  
SAND

#### SPECIAL FIRE FIGHTING PROCEDURES

☐ DO NOT ENTER BUILDING  
☐ ALLOW FIRE TO BURN  
☐ WATER MAY CAUSE FROTHING  
☐ DO NOT USE WATER  
☒ OTHER:  
WEAR SELF CONTAINED  
BREATHING APPARATUS AND  
PROTECTIVE CLOTHING.

#### UNUSUAL FIRE AND EXPLOSION HAZARDS

☐ DUST EXPLOSION HAZARD  
☐ SENSITIVE TO SHOCK  
☐ CONTAMINATION  
☐ TEMPERATURE  
☒ OTHER:  
TOXIC AND FLAMMABLE FUMES.

### REACTIVITY DATA

#### STABILITY

☒ STABLE ☐ UNSTABLE

#### CONDITIONS CONTRIBUTING TO INSTABILITY

☒ THERMAL DECOMPOSITION  
☐ PHOTO DEGRADATION  
☐ POLYMERIZATION  
☐ CONTAMINATION

#### INCOMPATIBILITY — AVOID CONTACT WITH

☒ STRONG ACIDS  
☐ STRONG ALKALIS  
☒ STRONG OXIDIZERS  
☒ OTHER:  
MATERIALS THAT REACT  
WITH WATER

### REACTIVITY DATA, CONTINUED

#### HAZARDOUS DECOMPOSITION PRODUCTS, THERMAL AND OTHER:

THERMAL — CARBON DISULFIDE  
OTHER — ETHYLENE THIOUREA

#### CONDITIONS TO AVOID

☒ HEAT  
☒ OPEN FLAMES  
☒ SPARKS  
☒ IGNITION SOURCES  
☒ OTHER:  
DAMPNESS OR WET

### SPILL OR LEAK

#### STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

☒ FLUSH WITH WATER  
☐ ABSORB WITH SAND  
OR INERT MATERIAL  
☐ NEUTRALIZE  
☒ SWEEP OR SCOOP UP AND  
REMOVE  
☐ KEEP UPWIND. EVACUATE  
ENCLOSED SPACES  
☐ PREVENT SPREAD OR SPILL  
☐ DISPOSE OF IMMEDIATELY

#### WASTE DISPOSAL METHOD:

Waste resulting from the use of this  
product may be disposed of on site or at  
an approved waste disposal facility.

NA = NOT APPLICABLE  
NE = NOT ESTABLISHED  
DNA = DATA NOT AVAILABLE  
♦ = SECTION REVISED

CONTINUED ON OTHER SIDE

**MATERIAL  
SAFETY  
DATA SHEET**

ELF ATOCHEM NORTH AMERICA, INC.  
PRODUCT NAME:  
MANEB 75DF FUNGICIDE  
CODE NUMBER:  
326

BEFORE USING PRODUCT, READ AND FOLLOW DIRECTIONS AND PRECAUTIONS ON PRODUCT LABEL AND BULLETINS.

### **TOXICITY**

#### **ORAL (ACUTE)**

LD<sub>50</sub> (RAT) > 5,000 mg/kg

#### **DERMAL (ACUTE)**

LD<sub>50</sub> > 2,000 mg/kg

#### **INHALATION (ACUTE)**

LC<sub>50</sub> (RAT) > 2.0 mg/L (4 hr.)

#### **CHRONIC, SUBCHRONIC, ETC.**

Rats fed 2 years on a diet containing 250 ppm suffered no ill effects. In long term feeding studies on rodents, some dithiocarbamates have induced carcinogenicity and birth defects at high dietary intake levels.

### **HEALTH HAZARD INFORMATION**

#### **EFFECTS OF EXPOSURE TO CONCENTRATE**

#### **PERMISSIBLE EXPOSURE LIMIT (TLV/TWA OR CEILING (C))**

|       |                         |        |
|-------|-------------------------|--------|
| ACGIH | TLV/TWA                 | 5 mg/m |
| OSHA  | (C) 5 mg/m <sup>3</sup> |        |

#### **IRRITATION**

|   |                                          |
|---|------------------------------------------|
| — | <input checked="" type="checkbox"/> EYE  |
| — | <input type="checkbox"/> SEVERE          |
| — | <input type="checkbox"/> MODERATE        |
| — | <input checked="" type="checkbox"/> MILD |
|   | (TRANSIENT)                              |

#### **CORROSIVITY**

NA

#### **SENSITIZATION**

NOT A SKIN SENSITIZER

#### **INHALATION EFFECTS**

NA

#### **LUNG EFFECTS**

COUGHING, IRRITATION  
UPON OVEREXPOSURE

### **HEALTH HAZARD INFORMATION, CONTINUED**

#### **EMERGENCY FIRST AID**

##### **INGESTION**

- ☒ GET MEDICAL ATTENTION
- ☒ INDUCE VOMITING
- ☐ DO NOT INDUCE VOMITING
- ☒ GIVE TWO GLASSES OF WATER

##### **DERMAL**

- ☒ GET MEDICAL ATTENTION IF IRRITATION PERSISTS
- ☒ FLUSH WITH SOAP AND WATER
- ☒ CONTAMINATED CLOTHING — REMOVE AND LAUNDER
- ☐ CONTAMINATED SHOES — DESTROY

##### **EYE CONTACT**

- ☐ GET MEDICAL ATTENTION
- ☒ FLUSH WITH PLENTY OF WATER FOR AT LEAST 15 MINUTES
- ☒ OTHER:  
GET MEDICAL ATTENTION IF IRRITATION PERSISTS

##### **INHALATION**

- ☒ GET MEDICAL ATTENTION
- ☒ REMOVE TO FRESH AIR
- ☒ IF NOT BREATHING, GIVE ARTIFICIAL RESPIRATION, PREFERABLY MOUTH-TO-MOUTH
- ☐ GIVE OXYGEN

### **SPECIAL PROTECTION INFORMATION**

#### **VENTILATION REQUIREMENTS —**

ALWAYS MAINTAIN EXPOSURE BELOW PERMISSIBLE EXPOSURE LIMITS

- ☐ CONSULT AN INDUSTRIAL HYGIENIST OR ENVIRONMENTAL HEALTH SPECIALIST
- ☐ LOCAL EXHAUST
- ☒ USE WITH ADEQUATE VENTILATION
- ☐ CHECK FOR AIR CONTAMINANT AND OXYGEN DEFICIENCY

#### **EYE**

WEAR PROTECTIVE EYEWEAR WHEN MIXING OR LOADING

#### **HAND (GLOVE TYPE)**

WEAR WATERPROOF GLOVES WHEN APPLYING OR HANDLING

#### **RESPIRATOR TYPE —**

NOT REQUIRED—USE NORMAL SAFETY PRECAUTIONS

#### **OTHER PROTECTIVE EQUIPMENT**

Applicators and other handlers must wear:

- coveralls over long-sleeved shirt and long pants,
- waterproof gloves,
- shoes plus socks,
- protective eyewear when mixing or loading,
- chemical-resistant apron when cleaning equipment, mixing, or loading.

### **SPECIAL PRECAUTIONS**

#### **PRECAUTIONARY LABELING**

- ☒ WASH THOROUGHLY AFTER HANDLING
- ☒ DO NOT GET IN EYES, ON SKIN OR CLOTHING
- ☒ DO NOT BREATHE DUST, VAPOR, MIST, GAS
- ☒ KEEP CONTAINER CLOSED
- ☒ KEEP AWAY FROM HEAT, SPARKS AND OPEN FLAMES
- ☐ STORE IN TIGHTLY CLOSED CONTAINERS
- ☐ DO NOT STORE NEAR COMBUSTIBLES
- ☐ KEEP FROM CONTACT WITH CLOTHING AND OTHER COMBUSTIBLE MATERIALS
- ☒ EMPTY CONTAINER MAY CONTAIN HAZARDOUS RESIDUES
- ☐ USE EXPLOSION-PROOF EQUIPMENT

#### **OTHER HANDLING AND STORAGE CONDITIONS**

Store in the original container in a dry area. If allowed to become wet the product will deteriorate and represent a fire hazard. Keep away from sources of ignition (e.g. sparks and open flame). Close bag when not in use. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur.

### **PLEASE NOTE**

Elf Atochem North America, Inc. believes that the information and recommendations contained herein (including data and statements) are accurate as of the date hereof. NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, WARRANTY OF MERCHANTABILITY, OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED, IS MADE CONCERNING THE INFORMATION PROVIDED HEREIN. The information provided herein relates only to the specific product designated and may not be valid where such product is used in combination with any other materials or in any process. Further, since the conditions and methods of use of the product and of the information referred to herein are beyond the control of Elf Atochem, Elf Atochem expressly disclaims any and all liability as to any results obtained or arising from any use of the product or reliance on such information.

DATE: 5/96

ADDRESS:  
ELF ATOCHEM NORTH AMERICA, INC.  
AGCHEM DIVISION  
2000 MARKET ST., 21st FLOOR  
PHILADELPHIA, PA 19103-3222



CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE

Material Safety Data Sheet

Date Prepared:

2/05/96 Supersedes Date: 0/00/00

## 1. CHEMICAL PRODUCT AND COMPANY DESCRIPTION

RHONE-POULENC AG COMPANY  
AGRICULTURAL CHEMICALS  
2 T.W. Alexander Drive  
Research Triangle Pk NC 27709

Emergency Phone Numbers:  
FOR EMERGENCIES INVOLVING A SPILL, LEAK, FIRE, EXPOSURE OR ACCIDENT  
CONTACT: CHEMTREC (800-424-9300) OR RHONE-POULENC (800-334-7577).

For Product Information:  
(800) 334-9745

Product Status:  
FIFRA regulated use only.

EPA FIFRA Registration Number:  
264-515

Chemical Name or Synonym:  
ETHYL HYDROGEN PHOSPHONATE, FOSETYL-AL

Molecular Formula:  
 $C_6H_{18}AlO_9P_3$

## 2. COMPOSITION/INFORMATION ON INGREDIENTS

| Component                        | CAS Reg Number | OSHA<br>Hazard | Percentage |
|----------------------------------|----------------|----------------|------------|
| FOSETYL-AL                       | 39148-24-8     | Y              | 90.0       |
| CRYSTALLINE SILICA AS QUARTZ     | 14808-60-7     | Y              | < 0.25     |
| OTHER INGREDIENTS (TRADE SECRET) | *****          | N              | BALANCE    |

## 3. HAZARDS IDENTIFICATION

### A. EMERGENCY OVERVIEW:

End of Page 1

Continued on Next Page



CHIPCO(R) ALLETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE

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### 3. HAZARDS IDENTIFICATION (Continued)

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**Physical Appearance and Odor:**  
green granules solid, acidic odor.

**Warning Statements:**  
CAUTION! HARMFUL IF INHALED, SWALLOWED OR ABSORBED THROUGH SKIN. CAUSES MODERATE EYE INJURY.

#### B. POTENTIAL HEALTH EFFECTS:

**Acute Eye:**  
Irritant. Causes redness, tearing.

**Acute Skin:**  
Harmful if absorbed through skin. Irritant. Causes redness, swelling.

**Acute Inhalation:**  
Harmful if inhaled. May cause upper respiratory tract irritation.

**Acute Ingestion:**  
Harmful if ingested.

**Chronic Effects:**  
This product contains ingredients that are considered by OSHA, NTP, IARC or ACGIH to be probable or suspected human carcinogens (see Section 11 - Chronic).

---

### 4. FIRST AID MEASURES

---

#### FIRST AID MEASURES FOR ACCIDENTAL:

**Eye Exposure:**  
Hold eyelids open and flush with a steady, gentle stream of water for at least 15 minutes. Seek medical attention.

**Skin Exposure:**  
In case of contact, immediately wash with plenty of soap and water for at least 15 minutes. Seek medical attention. Remove contaminated clothing and shoes while washing. Clean contaminated clothing and shoes before re-use or discard if they cannot be thoroughly cleaned.

**Inhalation:**  
Remove victim from immediate source of exposure and assure that the

End of Page 2

Continued on Next Page



**CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE**

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**4. FIRST AID MEASURES ( Continued )**

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victim is breathing. If breathing is difficult, administer oxygen, if available. If victim is not breathing, administer CPR (cardio-pulmonary resuscitation). Seek medical attention.

**Ingestion:**

If victim is conscious and alert, give 2-3 glasses of water to drink and induce vomiting by touching back of throat with a finger. Do not induce vomiting or give anything by mouth to an unconscious person. Seek immediate medical attention. Do not leave victim unattended. Vomiting may occur spontaneously. To prevent aspiration of swallowed product, lay victim on side with head lower than waist. If vomiting occurs and the victim is conscious, give water to further dilute the chemical.

**MEDICAL CONDITIONS POSSIBLY AGGRAVATED BY EXPOSURE:**

Inhalation of product may aggravate existing chronic respiratory problems such as asthma, emphysema or bronchitis. Skin contact may aggravate existing skin disease.

**NOTES TO PHYSICIAN:**

All treatments should be based on observed signs and symptoms of distress in the patient. Consideration should be given to the possibility that overexposure to materials other than this product may have occurred.

Treat symptomatically. No specific antidote available.

---

**5. FIRE FIGHTING MEASURES**

---

**FIRE HAZARD DATA:**

**Flash Point:**

Not Applicable

**Extinguishing Media:**

Recommended (small fires): dry chemical, carbon dioxide, Recommended (large fire): water spray, alcohol foam, polymer foam, ordinary foam.

**Special Fire Fighting Procedures:**

Firefighters should wear NIOSH/MSHA approved self-contained breathing apparatus and full protective clothing. Dike area to prevent runoff and

End of Page 3 Continued on Next Page



CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE

Material Safety Data Sheet

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### 5. FIRE FIGHTING MEASURES (Continued)

---

contamination of water sources. Dispose of fire control water later.

#### Unusual Fire and Explosion Hazards:

Under fire conditions, toxic, corrosive fumes are emitted.

#### Hazardous Decomposition Materials (Under Fire Conditions):

oxides of phosphorus

oxides of carbon

phosphine gas

---

### 6. ACCIDENTAL RELEASE MEASURES

---

#### Evacuation Procedures and Safety:

Wear appropriate protective gear for the situation. See Personal Protection information in Section 8. Ventilate closed spaces before entering. Stay upwind if possible.

#### Containment of Spill:

Follow procedure described below under Cleanup and Disposal of Spill.

#### Cleanup and Disposal of Spill:

Avoid creation of dusty conditions. Scrape up and place in appropriate closed container (see Section 7: Handling and Storage). Decontaminate tools and equipment following cleanup.

#### Environmental and Regulatory Reporting:

If spilled on the ground, the affected area should be scraped clean and placed in a appropriate container for disposal. Do not flush to drain. Prevent material from entering public sewer system or any waterways.

---

### 7. HANDLING AND STORAGE

---

#### Minimum/Maximum Storage Temperatures:

No Data Available

#### Handling:

Avoid direct or prolonged contact with skin and eyes. Do not breathe

End of Page 4

Continued on Next Page





**CHIPCO(R) ALLETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE**

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**7. HANDLING AND STORAGE ( Continued )**

---

dusts. Do not breathe vapors and mists. Do not ingest.

**Storage:**

Store in an area that is away from foodstuffs or animal feed.

---

**8. EXPOSURE CONTROLS/PERSONAL PROTECTION**

---

**Introductory Remarks:**

These recommendations provide general guidance for handling this product. Because specific work environments and material handling practices vary, safety procedures should be developed for each intended application. While developing safe handling procedures, do not overlook the need to clean equipment and piping systems for maintenance and repairs. Waste resulting from these procedures should be handled in accordance with Section 13: Disposal Considerations.

Assistance with selection, use and maintenance of worker protection equipment is generally available from equipment manufacturers.

**Exposure Guidelines:**

Exposure limits represent regulated or recommended worker breathing zone concentrations measured by validated sampling and analytical methods, meeting OSHA requirements. The following limits (ACGIH, OSHA and other) apply to this material, where, if indicated, S-skin and C-ceiling limit:

**CRYSTALLINE SILICA AS QUARTZ**

|       | Notes | TWA         | STEL |
|-------|-------|-------------|------|
| ACGIH |       | 0.1 mg/cu m |      |
| OSHA  |       | 0.1 mg/cu m |      |

**Engineering Controls:**

Where engineering controls are indicated by use conditions or a potential for excessive exposure exists, the following traditional exposure control techniques may be used to effectively minimize employee exposures.

**Respiratory Protection:**

End of Page 5 Continued on Next Page



**CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE**

**Material Safety Data Sheet**

**Date Prepared:**

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**8. EXPOSURE CONTROLS/PERSONAL PROTECTION (Continued)**

---

When respirators are required, select NIOSH/MSHA approved equipment based on actual or potential airborne concentrations and in accordance with the latest OSHA standard (29 CFR 1910.134) and/or ANSI Z88.2 recommendations.

Under normal conditions, in the absence of other airborne contaminants, the following devices should provide protection from this material up to the conditions specified by OSHA/ANSI: Air-purifying (half-mask/full-face) respirator with cartridges/canister approved for use against dusts, mists and fumes, pesticides. Under conditions immediately dangerous to life or health, or emergency conditions with unknown concentrations, use a full-face positive pressure air-supplied respirator equipped with an emergency escape air supply unit or use a self-contained breathing apparatus unit.

**Eye/Face Protection:**

Eye and face protection requirements will vary dependent upon work environment conditions and material handling practices. Appropriate ANSI Z87 approved equipment should be selected for the particular use intended for this material.

It is generally regarded as good practice to wear a minimum of safety glasses with side shields when working in industrial environments.

**Skin Protection:**

Skin contact should be minimized through use of gloves and suitable long-sleeved clothing (i.e., shirts and pants). Consideration must be given both to durability as well as permeation resistance.

**Work Practice Controls:**

Personal hygiene is an important work practice exposure control measure and the following general measures should be taken when working with or handling this material:

- (1) Do not store, use, and/or consume foods, beverages, tobacco products, or cosmetics in areas where this material is stored.
- (2) Wash hands and face carefully before eating, drinking, using tobacco, applying cosmetics, or using the toilet.
- (3) Wash exposed skin promptly to remove accidental splashes of contact with this material.

**End of Page 6**

**Continued on Next Page**



**CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE**

Material Safety Data Sheet

Date Prepared:

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**9. PHYSICAL AND CHEMICAL PROPERTIES**

---

Physical and Chemical properties here represent typical properties of this product. Contact the business area using the Product Information phone number in Section 1 for its exact specifications.

**Physical Appearance:**  
green granules solid.

**Odor:**  
acidic odor.

**pH:**  
3.5 to 4 at 5 wt/wt%.

**Specific Gravity:**  
No Data Available

**Water Solubility:**  
dispersible

**Melting Point Range:**  
No Data Available

**Boiling Point Range:**  
No Data Available

**Vapor Pressure:**  
No Data Available

**Vapor Density:**  
No Data Available

**Molecular Weight:**  
354.1

---

**10. STABILITY AND REACTIVITY**

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**Chemical Stability:**  
This material is stable under normal handling and storage conditions described in Section 7.

End of Page 7

Continued on Next Page



**CHIPCO(R) ALIETTE(R) SIGNATURE(TM) BRAND WDG FUNGICIDE**

**Material Safety Data Sheet**

**Date Prepared:**

**2/05/96 Supersedes Date: 0/00/00**

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**10. STABILITY AND REACTIVITY ( Continued )**

---

**Conditions To Be Avoided:**  
moisture

**Materials/Chemicals To Be Avoided:**  
strong bases  
strong oxidizing agents  
strong reducing agents  
mineral acids

**The Following Hazardous Decomposition Products Might Be Expected:**  
**Decomposition Type:** thermal  
oxides of phosphorus  
oxides of carbon  
phosphine gas

**Hazardous Polymerization Will Not Occur.**  
**Avoid The Following To Inhibit Hazardous Polymerization:**  
not applicable

---

**11. TOXICOLOGICAL INFORMATION**

---

**Acute Eye Irritation:**  
**Toxicological Information and Interpretation**  
eye - eye irritation, rabbit.  
Under test conditions, material caused mild irritation effects  
in rabbit eyes.

**Acute Skin Irritation:**  
**Toxicological Information and Interpretation**  
skin - skin irritation, rabbit.  
Under test conditions, material caused slight irritation effects  
to rabbit skin.

**Acute Dermal Toxicity:**  
**Toxicological Information and Interpretation**  
LD50 - lethal dose 50% of test species, > 2000 mg/kg, rabbit.

**Acute Respiratory Irritation:**  
No test data found for product.

**Acute Inhalation Toxicity:**

**End of Page 8 Continued on Next Page**

## 16. OTHER INFORMATION

National Fire Protection Association Hazard Ratings--NFPA(R):

2 Health Hazard Rating--Moderate

0 Flammability Rating--Minimal

1 Instability Rating--Slight

National Paint & Coating Hazardous Materials Identification

2 Health Hazard Rating--Moderate

0 Flammability Rating--Minimal

1 Reactivity Rating--Slight

Reason for Revisions:

Conversion to ANSI MSDS format.

Key Legend Information:

ACGIH - American Conference of Governmental Industrial Hygienists

OSHA - Occupational Safety and Health Administration

TLV - Threshold Limit Value

PEL - Permissible Exposure Limit

TWA - Time Weighted Average

STEL - Short Term Exposure Limit

NTP - National Toxicology Program

IARC - International Agency for Research on Cancer

ND - Not determined

RPI - Rhone-Poulenc Established Exposure Limits

Disclaimer:

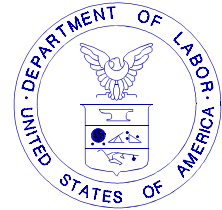
The information herein is given in good faith but no warranty, expressed or implied, is made.

## **Appendix B**

### Summary of Laboratory Results

U.S. DEPARTMENT OF LABOR  
OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION  
SALT LAKE TECHNICAL CENTER  
PHYSICAL MEASUREMENT AND ANALYSIS BRANCH  
1781 SOUTH 300 WEST  
SALT LAKE CITY, UTAH 84165-0200

(801)-487-0073 ext. 272  
FAX (801)-487-1190



12 December 1997

Report of analysis of samples for BPS, INC.

For smoldering point analysis, a volume of approximately 2mL of material was introduced into a modified Setaflash© flashpoint tester. The tester was modified by having removed the cup cover so that the test could be carried out as an "open cup" procedure. The material was heated up from room temperature until smoking was observed and then until a visible change occurred to the material.

Sample J56676 (Azinphos) showed a color change to dark tan at 217°F. A further change to a dark red-brown color occurred as the temperature was increased. The sample showed visible smoke at approximately 340°F.

Sample R68650 (Maneb) showed a small black spot beginning at about 320°F. The sample changed to black increasingly as the temperature increased. Visible smoke was observed at 415°F.

The smoldering temperature results reported are given for sample test results performed under laboratory conditions, and may not be representative of smoldering temperature value(s) resulting under differing conditions.

Report of analysis of Samples V30707, V30708, V30709 from inspection of explosion at BPS, Inc.

Three samples were submitted for materials analysis on 6/4/97. They were assigned sample numbers as shown below:

V30707 - Fiberglass exhaust north (hanging from the compressor line)

V30708 - Fiberglass Enclosure (burned remnant of fiberglass paneling).

V30709 - New, unused "Supersack"

V30707 showed continuous fiber fiberglass of diameter approximately 12 micrometers embedded in white, brittle ash, consistent with a partially burned structural fiberglass panel. It was unclear as to whether there was any latent supersack material left. The majority (80%) of the material remaining was continuous fiber fiberglass

V30708 was continuous fiber fiberglass. The diameter of this fiberglass was nominally the same as for V30707 at 12 micrometers. However, the index of refraction was different reflecting a different source

for the fiberglass by the manufacturer. Little other material was present other than a small amount of powder adherent to the fibers.

V30709 appeared to be a way, fibrous synthetic material and was confirmed to be polypropylene by a telephone call to Dorothy Hullett, an employee of Rexam Mulox, the bag manufacturer. Ashing of the sack material at 500 °C produced a black residue in an aluminum pan. No such residue was noted on V30707.





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## Memo

DATE: November 4, 1997

MEMORANDUM FOR: Al Heins

THRU: Lois Moncrief, Jerry Schultz, and Mike Shulsky

FROM: Wayne Potter, David Armitage, Richard Lawrence, Pat Hearty, and Joanna Shulsky

SUBJECT: Organic Division Analytical Results for BPS, Inc. and Microflow, Inspection # 6-009401

### Analytical Screening

Samples J56742 through J56752 and J56755 through J56760 (field numbers 521-01 through 04, 521-06 through 11, Oil 1, 522-Fan SW, 522-Fan SE and 522-01 through 04) were screened by HPLC for various pesticides including: azinphos-methyl, maneb, topsin (thiophanate-methyl) and carbaryl (Sevin). Only azinphos-methyl and maneb were reported, and their values should be considered as semi-quantitative only. Gas Chromatography-Mass Spectroscopy (GCMS) on J56742 (field number 521-01) confirmed the presence of azinphos-methyl as well as some of its decomposition products, the major one being O,O,S-trimethyl ester of phosphorodithioic acid. However, GCMS is unable to determine if the decomposition products were present before analysis or created during the sample analysis. J56742, as well as J56744, J56745 and J56758 (field numbers 521-01, 521-03, 521-04 and 522-02 respectively) were also run by GC-FPD. Both azinphos-methyl and the major decomposition product mentioned above were observed. The samples reported as <QL for azinphos-methyl should be considered as maximum values, the actual value would be less than the percentage reported. The values reported for maneb on samples J56747 and J56760 (field numbers 521-07 and 522-04) are minimum values, the actual value is greater than the reported value. Note: these samples were not analyzed for fosetyl-aluminum (Aliette Signature).

## **1) Mass Spectroscopy**

Azinphos-methyl was identified in sample J56755 (field number 522-Fan SW) by HPLC. Azinphos-methyl could not be confirmed by GCMS, but the major decomposition product, O,O,S-trimethyl ester of phosphorodithioic acid, was identified. However, azinphos-methyl was confirmed in sample J56755 by GC-FPD. The material analyzed was primarily the yellow stuff off of the fan. The other fan (sample J56756, field number 522-Fan SE) had very little material on it, and was only screened for pesticides (not including maneb).

## **2) Atomic Absorption**

An initial screening for soluble aluminum compounds was performed by atomic absorption analysis on samples J56700 through J56721 (bulk field numbers 1A, 2A, 2B, 3A, 3B, 4A, 4B, 5A, 5B, 6A, A1, AR, and also wipe field numbers BPS-1 through BPS-10). The compound, fosetyl-aluminum (Aliette Signature) is a soluble aluminum. Preliminary tests with a standard indicated that this procedure could be used to detect the presence of fosetyl-aluminum. Unfortunately the samples all contained high background levels of soluble aluminum and the results of this procedure was inconclusive. Fosetyl-aluminum is used as a premix with mancozeb.

## **3) HPLC**

### **A) Bulks**

These same bulk samples (bulk field numbers 1A, 2A, 2B, 3A, 3B, 4A, 4B, 5A, 5B, and 6A) were given new lab numbers (J56637-46) and analyzed by HPLC-UV for azinphos-methyl (0300), maneb (M177), thiophanate-methyl (D347) and carbaryl (sevin, 0525). No detectable amounts of these compounds were found in any of these bulk samples except 2B and 4B. Maneb was found on 2B and 4B.

### **B) Wipes**

Similarly, the wipe samples mentioned in the paragraph above (wipe field numbers BPS-1 through BPS-10) were also given new lab numbers (J56649-58 ) and analyzed by HPLC-UV for azinphos-methyl (0300). Detectable amounts of azinphos-methyl were found on samples J56649, J56650 and J56652 (field numbers BPS-2, BPS-3 and BPS-1 respectively). These samples were each confirmed by peak wavelength ratioing.

### **C) Air Samples**

J57349-53 (Field numbers A-1, A-2, A-4, B-1 and BLANK) were air samples that were analyzed by HPLC-UV for azinphos-methyl and also a qualitative HPLC analysis. No detectable amounts of analytes were found on these air samples.

## **4) Fosetyl-Aluminum Samples**

These samples (bulk field numbers 1A, 2A, 2B, 3A, 3B, 4A, 4B, 5A, 5B, 6A, A1, AR, and also wipe field numbers BPS-1 through BPS-10) have not yet been analyzed for fosetyl-aluminum. Fosetyl-Aluminum is not compatible with the HPLC or ion chromatography (IC) analysis. A method in the literature analyzed fosetyl-aluminum by GC-FPD using a process of methylation. Several attempts were made to methylate fosetyl-aluminum but our attempts were unsuccessful. So currently our laboratory does not have a method for the analysis of fosetyl-aluminum.

## **5) HPLC and GC**

### **A) Repirator Mask Samples**

A respirator used in the BPS Explosion was examined for contamination of the organophosphorus insecticide Azinphos Methyl 50W, the fungicide Maneb and their decomposition products. The respirator used during the evacuation by John Fernirola was analyzed for any decomposition products. It was reported that John Fernirola went into the smoke in effort to extinguish the source of the smoke. This respirator worn by John Fernirola (E62546) appeared to be coated with smoke and looked like a likely candidate to find the decomposition products. When Maneb is heated, the major decomposition products are carbon disulfide and ethylene thiourea. Carbon disulfide is collected with charcoal and ethylene thiourea is collected with a glass fiber filter. The respirator used by John Fernirola was a 3M-5300 using a 501 organic vapor cartridge. The cartridge has a glass fiber filter on the outside and charcoal on the inside. The glass fiber filter was analyzed for ethylene thiourea and the charcoal was analyzed for carbon disulfide. A portion of the charcoal was desorbed with toluene and analyzed by gas chromatography using a flame photometric detector. Carbon disulfide was not detected. A portion of the glass fiber filter was extracted with water and analyzed by HPLC using a UV detector. Ethylene thiourea was not detected. The outside of the mask was wiped with several glass fiber filters soaked with methanol, toluene and water. These wipes were analyzed by GCMS for analyte identification. GCMS identified 2-naphthalenol, phthalate ester, and approximately C<sub>14</sub>-C<sub>18</sub> acids.

A portion of the glass fiber filter covering the charcoal on the organic vapor cartridge was extracted with acetonitrile and analyzed by HPLC using a UV detector. Azinphos-methyl was not detected on the glass fiber filter or the charcoal portion of the cartridge. Mass spectroscopy also analyzed samples from the cartridge of the mask. GCMS identified limonene, ethanol, isopropanol, methyl chloroform, ethylfluralin, aliphatic C<sub>9</sub>-C<sub>10</sub> (approximately), terpene, C<sub>3</sub>-C<sub>4</sub> benzenes, dichlorobenzene, and siloxane on the charcoal from the cartridge. GCMS identified naphthalenol, dursban, O,S-dimethyltetrachlorothiophthalate, an ethyl ester of a long chain acid, phthalate esters, and a couple of unidentified compounds, including an unknown amine, on the glass fiber filter portion of the cartridge.

## Results

### Air Samples

|        | Azinphos-methyl | Qualitative HPLC for other Compounds |
|--------|-----------------|--------------------------------------|
| J57349 | ND              | ND                                   |
| J57350 | ND              | ND                                   |
| J57351 | ND              | ND                                   |
| J57352 | ND              | ND                                   |
| J57353 | BLANK           | BLANK                                |

### Bulk Samples

|        | Field# | Azinphos-methyl | Maneb | Topsin | Carbaryl |    |
|--------|--------|-----------------|-------|--------|----------|----|
| J56637 | 1A     | ND              | ND    | ND     | ND       | ND |
| J56638 | 2A     | ND              | ND    | ND     | ND       | ND |
| J56639 | 2B     | ND              | ND    | .03%   | ND       | ND |
| J56640 | 3A     | ND              | ND    | ND     | ND       | ND |
| J56641 | 3B     | ND              | ND    | ND     | ND       | ND |
| J56642 | 4A     | ND              | ND    | ND     | ND       | ND |
| J56643 | 4B     | ND              | ND    | .6%    | ND       | ND |
| J56644 | 5A     | ND              | ND    | ND     | ND       | ND |
| J56645 | 5B     | ND              | ND    | ND     | ND       | ND |
| J56646 | 6A     | ND              | ND    | ND     | ND       | ND |

|        | Field #   | Azinphos-methyl | Maneb |
|--------|-----------|-----------------|-------|
| J56742 | 521-01    | 9.0%            | 4.0%  |
| J56743 | 521-02    | .06%            | .06%  |
| J56744 | 521-03    | .3%             | .08%  |
| J56745 | 521-04    | .2%             | .08%  |
| J56746 | 521-06    | ND              | ND    |
| J56747 | 521-07    | .003%           | 2.0%  |
| J56748 | 521-08    | .002%           | ND    |
| J56749 | 521-09    | .01%            | .1%   |
| J56750 | 521-10    | ND              | ND    |
| J56751 | 521-11    | .004%           | ND    |
| J56752 | OIL 1     | NA              | NA    |
| J56753 | FGLAS EXN | NA              | NA    |
| J56754 | FGLAS END | NA              | NA    |

|        |            |      |       |       |
|--------|------------|------|-------|-------|
| J56755 | 522-FAN SW | 1.3% | ND    |       |
| J56756 | 522-FAN SE |      | ND    | NA    |
| J56757 | 522-01     |      | .006% | .06%  |
| J56758 | 522-02     |      | .02%  | .001% |
| J56759 | 522-03     |      | .01%  | .03%  |
| J56760 | 522-04     |      | .02%  | 5.0%  |

| Field # |    | Aluminum (as Al), Soluble Salts |
|---------|----|---------------------------------|
| J56700  | 1A | 5.0%                            |
| J56701  | 2A | 9.0%                            |
| J56702  | 2B | 8.0%                            |
| J56703  | 3A | 7.0%                            |
| J56704  | 3B | 6.0%                            |
| J56705  | 4A | 9.0%                            |
| J56706  | 4B | 9.0%                            |
| J56707  | 5A | 6.0%                            |
| J56708  | 5B | 8.0%                            |
| J56709  | 6A | 9.0%                            |
| J56710  | A1 | .2%                             |
| J56711  | AR | .8%                             |

## Wipes

| Field # |        | Azinphos-Methyl |
|---------|--------|-----------------|
| J56649  | BPS-2  | 46.0 $\mu$ g    |
| J56650  | BPS-3  | 43.0 $\mu$ g    |
| J56651  | BPS-7  | <QL             |
| J56652  | BPS-1  | 110.0 $\mu$ g   |
| J56653  | BPS-5  | ND              |
| J56654  | BPS-6  | ND              |
| J56655  | BPS-4  | ND              |
| J56656  | BPS-8  | <QL             |
| J56657  | BPS-9  | ND              |
| J56658  | BPS-41 | BLANK           |

| Field # |        | Aluminum (as Al), Soluble Salts |
|---------|--------|---------------------------------|
| J56712  | BPS-2  | NA                              |
| J56713  | BPS-3  | NA                              |
| J56714  | BPS-7  | NA                              |
| J56715  | BPS-1  | NA                              |
| J56716  | BPS-5  | NA                              |
| J56717  | BPS-6  | NA                              |
| J56718  | BPS-4  | NA                              |
| J56719  | BPS-8  | NA                              |
| J56720  | BPS-9  | NA                              |
| J56721  | BPS-10 | BLANK                           |

## Respirators

| Field # | CS <sub>2</sub> | Ethylene Thiourea | Azinphos-methyl | Maneb |    |
|---------|-----------------|-------------------|-----------------|-------|----|
| E62546  | EPA001          | ND                | ND              | ND    | NA |

HPLC and GC analysis by Dave Armitage and Wayne Potter

AA analysis by Richard Lawrence

GC-Mass Spec. analysis by Pat Hearty and Joanna Shulsky

Compiled and written by Wayne Potter

DET NORSKE VERITAS (U.S.A.), INC.  
Materials Engineering Section



## MEMORANDUM REPORT

DATE: August 20, 1997

FROM: A. C. (Del) Underwood, PE  
CWI, API-510, NDE Level III

SUBJECT: Insecticide Warehouse Explosion Investigation  
DNV Project No. 232-8384

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Suite 100  
Houston, Texas 77064 USA  
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### Introduction

On Wednesday and Thursday, June 11th and 12th, 1997, I accompanied Awilda Fuentes from EPA, Michael Marshall and Jay Falls, both from OSHA, to the examination of the site and compressor equipment involved in the explosion of the BPS Insecticide Warehouse in West Helena, Arkansas. This was an incident that occurred approximately one month earlier. The primary interest in this effort was to determine the condition of the 15-hp air compressor prior to the incident, and to evaluate its involvement in the cause.

Conclusions, site observations with photographs, and subsequent tests and calculations follow.

### Conclusions

Based on the evaluation of the following information and observations, I concluded that the compressor of interest was not the source of ignition. The range of temperature in the discharge header, however, could have been sufficient to decompose the packaged insecticide stacked against the discharge header, resulting in the production of combustible gas. The expanding cloud of combustible gas, if it continued to be fed by the decomposition, would be anticipated to have eventually found a spark or other source of ignition.

#### The following observations were made at the site:

1. Two multistage reciprocating air compressors were involved in the fire. One was a 15-hp unit, that had encountered substantial damage, while the other one was a 20-hp unit, that had more moderate damage. The smaller damaged compressor is shown in Figure 1.
2. The location on the concrete foundation where the compressors were operating, shown in Figure 2, had sustained heat damage and spalling in a configuration suggesting that a liquid had burned on the surface in that area. This was typified by the concentration of spalling in the joint in the concrete.
3. The compressor room was separated from the warehouse area by a corrugated metal wall.

4. The two compressor discharges fed a common header pipe that was located on the warehouse side of the wall approximately five feet above the deck. This header led to an aftercooler outside the building. The output from the aftercooler was then piped back along the same wall closer to the deck carrying the cooled air back to the accumulator tanks under each compressor.
5. The 15-hp compressor, found on its side after the fire, was reported to have contained no lubricating oil in the crankcase after the fire.
6. The 20-hp compressor remained upright in its operating position, and sufficient oil was found in the crankcase.
7. The aluminum bell housings for the electric motor and the aluminum inlet header for the first stage on the 15-hp compressor had melted away. The melted residue had been deposited on the engine and compressor mount platform immediately below the motor when it was still in the upright position. The motor and compressor crankcases are shown in Figures 3 and 4, respectively.
8. The condition described in item 7 indicates that the compressor was exposed to heat (likely radiant from above) before falling on its side.
9. The pulley side of the compressor had sustained direct flame impingement heat, but little was observed on the opposite side. Figures 5 and 6 depict this condition. The damage areas indicate that an intense fire had been burning on the deck next to the pulley side while the compressor was still upright.
10. An accumulation of solidified resin was deposited on the side and end cap of the accumulator tank (Figure 7), that appears to have come from a pool of melted plastic when the compressor fell over on its side.
11. Upon dismantling of the compressor to examine the bearings, it was observed that the connecting rod and journal bearings had not been scored. This indicated that the unit had sufficient lubrication when last run.
12. The babbit in the cap half of the connecting rod bearing nearest the pulley (Figure 9) had partially melted away, and showed some fresh, bright scoring in the rod half. The brightness indicates that this scoring resulted subsequent to the fire, and was likely caused by manual rotation of the pulley during investigation. Otherwise, it showed no damage.
13. The two journal bearings are shown in Figures 10 and 11. It is possible that some of the crank case oil could have leaked out of the bearing next to the pulley while the compressor was on its side.
14. The first stage aluminum piston had melted away leaving only part of the skirt along the cylinder wall. Figure 12 is a photograph taken after the head had been removed. Note that the wrist pin had slipped to the left (toward the pulley side of the compressor). Sufficient heat had to be present inside the crankcase after it tipped over to expand the aluminum alloy connecting rod sufficiently for it to release the pin.
15. Re-solidified aluminum had accumulated on the pulley side of the inside of the crankcase. Figure 13 is a view looking from the opposite side of the pulley.



16. An accumulation of coke-like residue was found inside the crankcase indicating that a lubricating oil fire had developed inside. This is assumed to have been ignited by the liquid fire on the deck after the compressor fell over. It is also probable that some of the oil leaked out through the pulley side journal bearing and contributed to the plastic fire.
17. Disassembly of the 20-hp compressor indicated no observable internal damage to the bearings or other components.



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August 31, 1998

**To:** Mr. David Goldbloom-Helzner, ICF, 9300 Lee Highway, Fairfax, VA 22031-1207  
Ms. Awilda Fuentes, EPA, Mail Code 5104, 401 M Street SW, Washington DC

20460 *GM* *WJ*  
**From:** Arthur Miller, William Fenlon, SHE Technologies, 1050 Gravel Rd. Webster  
N.Y. 14580, Tel: (716)-671-1080, FAX: (716)-671-1343

**Subject:** BPS Warehouse Decomposition Incident - Final Report of Test Results and  
Conclusions

**INTRODUCTION**

In our earlier memorandum of 1/27/98, we recommended that Chilworth Technology Inc. perform "Basket Tests" to determine safe storage temperatures for bulk materials. The purpose of the testing was twofold: to obtain basic thermal stability data for key materials known to be in the BPS warehouse, and to prove or disprove, if possible, any of the three postulated root cause decomposition scenarios. The key materials in the warehouse were AZM (Azinphos Methyl 50W Soluble) and Maneb 75DF. The scenarios were: decomposition of AZM prior to being stored in the warehouse, decomposition of AZM caused by exposure to the compressor exhaust line, or decomposition of Maneb caused by exposure to the compressor exhaust line.

**TEST RESULTS**

**1. AZM**

Screening DSC tests were performed on AZM by the EPA's NEIC; results reported on 12/30/97 indicated an average (extrapolated) onset temperature of approximately 167 C. The basket tests performed by Chilworth Technology on AZM are summarized in their report "Process Safety Test Results and Interpretation for AZM (Azinphos Methyl 50W Soluble), Report No. R/1669A/0698/DC (Revised June 30, 1998)", a copy of which has been sent to ICF Kaiser International, Inc. The test methodology is outlined in their report and will not be repeated in this report.

The results of the 100 mm basket test in the Chilworth study showed an onset temperature between 70-80 C; larger samples (and longer time intervals) would be predicted to show even lower temperatures. For example, using the procedure outlined in Chilworth's report, and the ratio of the volume of the chemical container to the surface area of the container, an extrapolated maximum safe storage temperature of 29.6 C was

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obtained when using the volume and surface area specifications for the AZM container, as specified by Ms. Awilda Fuentes. Note that this procedure does not predict a safe time interval corresponding to this temperature. The extrapolation for AZM, not found in Chilworth's original report referenced above, is summarized in attachment 1 (plot of onset temperature vs. vessel size). This attachment should be appended to Chilworth's AZM report.

Preliminary tests were also performed by Chilworth on AZM to determine if the material could be safely subjected to dust explosion hazard testing. These tests, consisting of an ignition tube and flat plate heating tests, both heated by an open flame, showed decomposition of the sample accompanied by the evolution of yellowish smoke and flammable vapors. In an EPA draft summary (Pages 12 and 13) prepared by Ms. Fuentes, several BPS employees were reported to have observed yellowish smoke prior to the explosion, consistent with Chilworth's observations. These observations are different from that reported by the Southwest Research Institute's report 01-6666-039a (August 1997), in which brownish-white smoke was reported. However, these tests were performed on a hot plate surface vs. Chilworth's open flame heating method, most likely accounting for the difference in observed smoke color.

### **2. MANEB**

Screening DSC screening tests performed on Maneb by EPA's NEIC showed an average (extrapolated) onset temperature of approximately 183 C. The basket tests performed by Chilworth on Maneb are summarized in their report "Process Safety Test Results and Interpretation for Maneb 75DF Fungicide, Report No. R/1669B/0798/DC (July 10, 1998)". A copy of this report has been sent to ICF Kaiser International, Inc.

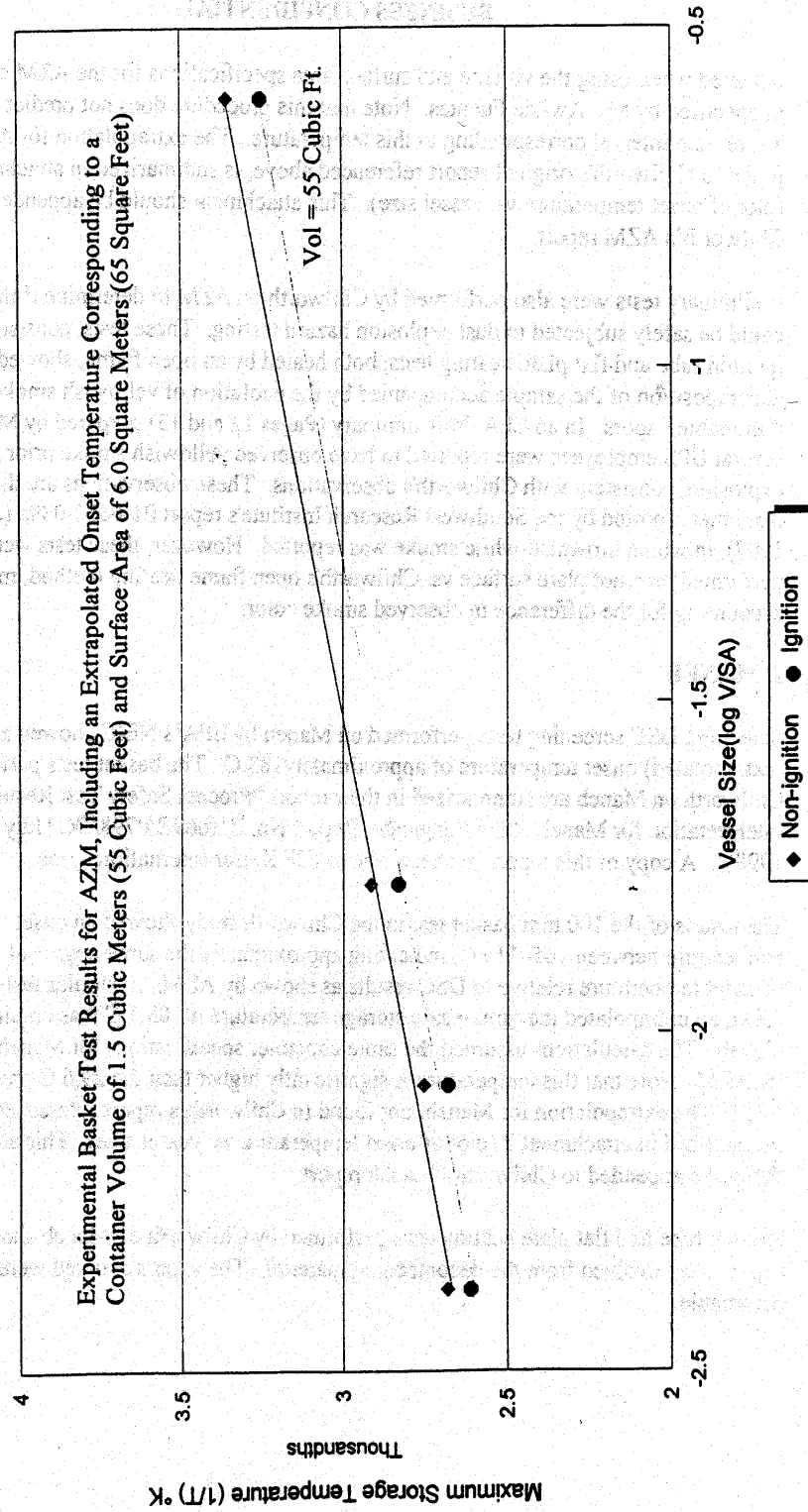
The results of the 100 mm basket test in the Chilworth study showed an onset temperature between 105–115 C, indicating approximately the same degree of lowering of onset temperature relative to DSC results as shown by AZM. In similar fashion to AZM, an extrapolated maximum safe storage temperature of 83.1 C was obtained for Maneb. The calculations assumed the same container specifications for Maneb as used for AZM. Note that this temperature is significantly higher than the 29.6 C predicted for AZM. The extrapolation for Maneb, not found in Chilworth's report referenced above, is summarized in attachment 2 (plot of onset temperature vs. vessel size). This attachment should be appended to Chilworth's Maneb report.

Ignition tube and flat plate heating tests performed by Chilworth on Maneb showed white vapors were evolved from the decomposing material. The vapors evolved were flammable.

# Attachment 1

## Basket Test ICF Kaiser - AZM

Experimental Basket Test Results for AZM, Including an Extrapolated Onset Temperature Corresponding to a Container Volume of 1.5 Cubic Meters (55 Cubic Feet) and Surface Area of 6.0 Square Meters (65 Square Feet)



Differential Scanning Calorimetry Results  
Root Cause Investigation of Explosion at Bartlo Packaging South, Inc.  
NEIC Project SPOO30

## INTRODUCTION

On May 8, 1997, an explosion took place at the Bartlo Packaging South, Inc. facility in West Helena, Arkansas. NEIC is assisting the joint EPA and OSHA investigation by providing information obtained by differential scanning calorimetry (DSC) on the decomposition of two pesticides. The DSC results give the amount of energy released by decomposition and the temperature at which decomposition occurs.

## BACKGROUND

The two pesticides analyzed by NF-IC are Azinphos-methyl (AZM) and Maneb. Eight samples of AZM were received from the OSHA lab. Two samples of AZM were sent directly to NEIC by the Agriculture Division of Bayer Corporation in Kansas City, Missouri. These are labeled Guthion, which is Bayer's name for A.ZM. One is Guthion Technical, which is 93.6% AZM, and the other is Guthion 50% Wettable Powder (WP), which is 50% AZM. The Guthion Technical is from Batch No. 7030105, and the Guthion WP is from Batch No. 7030063, according to the information supplied by Bayer. A sample of Maneb 75DF was received from the OSHA laboratory in Salt Lake City. It was packaged in 23 separate bottles for shipping purposes. Three of the bottles were analyzed by DSC.

When a material undergoes a chemical change such as a decomposition, heat is either absorbed or released. Often decompositions are initiated simply by raising the temperature of the materials. Differential scanning calorimetry is a method for measuring the heat released or absorbed during a decomposition or other reaction. The differential scanning calorimeter gradually increases the temperature of a reference cell and a sample cell. If a reaction of the material in the sample cell takes place which either releases or absorbs heat, the DSC measures the amount of heat involved and the temperature at which the reaction starts, called the onset

temperature. The heat released or absorbed is measured in Joules per gram (J/g). In order to put the reported values in perspective, decomposition energies for a number of common explosives and other compounds are given below:

TABLE 1 Decomposition of Common Materials

| Material              | Decomposition energy (J/g) |
|-----------------------|----------------------------|
| Trinitrotoluene (TNT) | 1690                       |
| Ammonium nitrate      | 1600                       |
| Dibenzoyl peroxide    | 1400                       |
| Cellulose             | 330                        |

Reference: Theodor Grewer, "The Influence of Chemical Structure on Exothermic Decomposition," *Thermochimica Acta*, **187** (1991) 133.

## RESULTS AND DISCUSSION

The results of the DSC analyses are shown in Table 2. DSC scans for all four of the formulations are shown in the attached figures. The two types of AZM received from Bayer were each analyzed in triplicate. The agreement between the triplicates was good, as shown by the standard errors of the means in Table 2. Relatively pure AZM (93.6%) decomposes exothermically (1100 J/g) at 164 degrees Celsius. The Bayer Guthion 50% wettable powder decomposes exothermically (600 J/g) at 168 degrees Celsius. The smaller amount of heat released by the 50% powder compared to the technical grade AZM is consistent with dilution by an inert ingredient. The eight samples of AZM received from the OSHA lab were each scanned two times. Since no differences were observed between the different samples, the results were averaged. The included figure for the AZM from OSHA shows two scans of the sample labeled J56673. One scan shows a well shaped Gaussian curve and the other shows a poorly shaped exothermic curve due to heat and mass transfer effects. Only well shaped curves were averaged together for the results in Table 2 (6 scans in all). All sixteen of the scans show a considerable release of energy of about 600 Joules per gram.

In contrast to AZM, Maneb 75 DF does not release a significant amount of energy when it decomposes. In the temperature range of 170 to 210 °C two processes occur; one is exothermic and the other endothermic. This is evident in the three scans for Maneb which are shown in two figures. Treating these scans in the standard manner with the instrument software gives the onset temperature and heat released shown in table 2. On average, there is a net absorption of heat, not a release. As shown in the figures, the differential scanning calorimeter data for Maneb 75DF is not as reproducible as it is for AZM. Nevertheless, it is clear that little or no energy is released by the decomposition of Maneb 75DF, which starts slightly over 170 °C.

TABLE 2 Decomposition Temperatures and Heat Released

| Sample                                 | Temperature (° Celsius)<br>(a) | Heat Released (Joules/gram)<br>(a) |
|----------------------------------------|--------------------------------|------------------------------------|
| Bayer Guthion Technical<br>(93.6% AZM) | 163.6 (0.3)                    | 1096 (40)                          |
| Bayer Guthion 50% Wettable<br>Powder   | 168.0 (0.9)                    | 596 (50)                           |
| AZM from OSHA                          | 166.6 (2)                      | 519 (6)                            |
| Maneb 75 DF                            | 183 (5)                        | -22 (30)                           |

a: Standard error of the mean in parenthesis

## EXPERIMENTAL

A Perkin Elmer DSC 7 calorimeter was used for the measurements. Samples were placed in screw top stainless steel capsules sealed with a gold plated copper seal. Sample sizes ranged from 1 to 6 mg, with most in the middle of that range. Samples were scanned from 50°C to 200°C at a scan rate of 10 degrees per minute. The instrument was purged with nitrogen during all measurements. The instrument was calibrated with indium, both for the onset temperature and for the energy released. Results were plotted so that an exothermic reaction gave a downward peak, and an endothermic reaction (such as the melting of indium) gave an upright peak. Instrument software was used to calculate the onset temperature and the heat released.





Uncertainty in determining the baseline contributed to imprecision in the heat release data. The DSC data for AZM and Maneb were not as reproducible or accurate as the data for the standard, which is the melting of metallic indium. There are several reasons why this occurs. Organic substances do not conduct heat as well as metals. Decompositions which produce gaseous or volatile products, such as those of AZM and Maneb, show more variation.

## **Appendix C**

### References

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