United States
Environmental Protection
Agency

United States
Occupational Safety and
Health Administration

EPA 550-R-97-002
October 1997

EPA
CEPP
OSHA

EPA/OSHA JOINT CHEMICAL ACCIDENT INVESTIGATION REPORT

Napp Technologies, Inc.
Lodi, New Jersey

REPORT

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The EPA/OSHA Accident Investigation Program

Under a Memorandum of Understanding, EPA and OSHA have jointly assumed the responsibilities to conduct chemical accident investigations. The fundamental objective of the EPA/OSHA chemical accident investigation program is to determine and report to the public the facts, conditions, circumstances, and cause or probable cause 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 cause 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 an outgrowth of a joint EPA/OSHA investigation to describe the accident, determine root causes and contributing factors, and identify findings and recommendations.

Basis of Decision to Investigate and for Involvement of EPA

An explosion and fire took place at the Napp Technologies facility at Lodi, New Jersey, on April 21, 1995, resulting in deaths, injuries, public evacuations, and serious damage both on and off site. The accident involved a commercial chemical mixture, a gold precipitating agent identified as ACR 9031 GPA, owned by Technic Inc. (Technic) of Cranston, Rhode Island and comprised of sodium hydrosulfite, aluminum powder, potassium carbonate and benzaldehyde (hereinafter "GPA"). EPA and OSHA undertook an investigation of this accident because of the serious consequences and the characteristics of the substances involved. This investigation was conducted in conjunction with OSHA's enforcement investigation.

At the time of the accident at the Napp facility, Napp was performing a toll blending operation. Under a toll arrangement, a company performs chemical manufacturing, blending, or other operations for other companies. Those other companies may not have the equipment or capacity for these operations or may have other reasons for outsourcing these tasks. One of the purposes of this investigation was to identify hazards specific to the toll manufacturing industry that might lead to chemical accidents, and develop recommendations to prevent accidents and improve safety in the toll manufacturing industry.

Executive Summary/Overview

On April 21, 1995, at approximately 7:45 a.m., a violent explosion and fire occurred at the Napp Technologies, Inc. (Napp) specialty chemical plant in Lodi, New Jersey. Five employees of Napp ultimately died (four employees were fatally injured at the site, the fifth employee died several days later due to injuries related to the event). A majority of the facility was destroyed as a result of the fire, and other businesses near the facility were destroyed or significantly damaged. Approximately 300 residents in the area were evacuated from their homes and a school. Additionally, firefighting efforts generated chemically contaminated water that ran off into the streets and nearby Saddle River.

At the time of the explosion and fire, Napp was conducting a blending operation involving water-reactive chemicals. The chemical mixing portion of the operation, which should have been completed in less than an hour, continued for nearly 24 hours. Operators noticed an unexpected reaction taking place in the blender, producing increasing heat and release of foul-smelling gas over time.

The joint chemical accident investigation team (JCAIT) formed by OSHA and EPA determined that the most likely cause of the accident was the inadvertent introduction of water/heat into water-reactive materials (aluminum powder and sodium hydrosulfite) during the mixing operation. The water caused sodium hydrosulfite in the blender to decompose, generating heat, sulfur dioxide, and additional water. The decomposition process, once started, was self-sustaining. The reaction generated sufficient heat to cause the aluminum powder to rapidly react with the other ingredients and generate more heat. During an emergency operation to off-load the blender of its reacting contents, the material ignited and a deflagration occurred which resulted in the deaths of the Napp employees and destruction of the facility.

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

- <u>An inadequate process hazards analysis was conducted and appropriate preventive actions were not taken.</u>. Napp's process hazard analysis identified the water reactivity of the substances involved, but was inadequate to identify and address other factors, including sources of water/heat, mitigation measures, recognition of deviations, consequences of failures of controls, and steps necessary to stop a reaction inside the blender. Consequently, appropriate prevention actions were not taken.

- <u>Standard operating procedures and training were less than adequate.</u> Napp's standard operating procedures (SOPs) and related training did not adequately address emergency shutdown, including conditions requiring shutdown and assignment of shutdown responsibility, and operating limits, including the consequences of deviations, abnormal situations, and corrective steps required.

- <u>The decision to re-enter the facility and off-load the blender was based on inadequate information</u>. Although Napp was aware of, and concerned for, the strong possibility of a fire,

there was a lack of knowledge or understanding whether off-loading the blender would have made the situation worse or the potential for violent deflagration.

- The equipment selected for the GPA blending process was inappropriate. The blender used by Napp for the process was inappropriate for the materials blended.

- Communications Between Napp and Technic were inadequate. Napp was carrying out a blending operation for another company. Inadequate communication of hazard information between the companies led to an inadequate process hazard review.

- The training of fire brigade members and emergency responders was inadequate. Napp fire brigade members were not trained to respond to the type of emergency that occurred.

The JCAIT developed recommendations that address the root causes and contributing factors to prevent a reoccurrence or similar event at other facilities:

- Facilities need to fully understand chemical and process hazards, failure modes and safeguards, deviations from normal and their consequences, and ensure that all relevant personnel know the proper actions to take to operate the process safely, recognize and address deviations, return to normal operations, or safely shutdown. This is best achieved though process hazards analyses, standard operating procedures, and training;

- Guidance is needed to address the unique circumstances surrounding tolling arrangements and the responsibilities for hazards assessments and communication of process safety information;

- Facilities should ensure that equipment manufacturers' recommendations for proper use of equipment are followed;

- OSHA and EPA should review the lists of substances subject to the Process Safety Management standard and Risk Management Program regulations to determine whether reactive substances should be added;

- OSHA needs to review the role of MSDSs in conjunction with HazCom, HazWoper, and PSM Standards to clarify that MSDSs should not be used beyond their intended design. Industry should consider additional consensus standards or guidelines to address MSDS consistency and use; and

- OSHA and EPA should consider whether additional guidance or outreach is needed for users to understand the limitations of MSDSs and industry awareness that more than the MSDS is needed to conduct full process hazards analyses.

Table of Contents

Page

1.0 Background 1

1.1 Facility Information 1

1.2 Process Information 3

1.3 Chemical Information 5

2.0 Description of the Accident 9

2.1 Events Preceding the Blending Operation 9

2.2 Preparations for Blending 9

2.3 Blending Operation 12

2.4 The Explosion and Fire 15

2.5 Emergency Response 16

2.6 Napp Fire Brigade Members and Emergency Responders 17

3.0 Analyses and Significant Facts 18

3.1 Analyses 18

3.2 Significant Facts 18

4.0 Causes of the Accident 21

4.1 Possible Causes of Chemical Reaction 21

4.2 Most Likely Causes of Chemical Reaction 24

4.3 Root Causes and Contributing Factors 26

5.0 Recommendations 29

6.0 Outcomes of OSHA/Napp Technologies Settlement 32

Appendices

A Results of Analysis of the Accident 34

B Chemical Reactions 37

C Accidents Involving Sodium Hydrosulfite and Aluminum 41

D References 45

E Photographs of Napp Technologies (Figures 4-24) 47

List of Figures and Exhibits

Figure 1 Napp Layout 2

Figure 2 P-K Blender 4

Figure 3 Intensifier Bar 6

Exhibit 1 Timeline of Events 11

Figure 3A Vacuum System 14

1.0 Background

1.1 Facility Information

The Napp Technologies, Inc. (Napp) facility in Lodi, New Jersey, was located on Main Street in a mixed industrial/residential section of Lodi. Napp shared a block with other businesses and was directly across the street from homes and retail businesses (see Figure 24).

Operations

Napp's primary business is pharmaceutical manufacturing. However, in limited cases, it also performs toll blending operations. In a tolling arrangement a company contracts with another company to perform a specific operation. Typically, the company letting the toll contract lacks the equipment or capacity to manufacture the chemical product. The raw material is delivered to the toll manufacturer, who processes it according to customer specifications, and delivers it to the original company for a fee or toll.

At the time of the explosion, Napp was performing a blending operation to produce ACR 9031, a gold precipitating agent (GPA) under a toll blending arrangement with Technic Inc. (Technic) of Cranston RI. Lacking the necessary equipment to blend the ingredients, Technic entered into a contract with Napp whereby Technic purchased the components of GPA and had them delivered to Napp to be blended.

The Patterson-Kelley (PK) 125 blender used in the GPA blending operation was located in the PK-125 Blending Room, located in the Pulverizing and Blending Department on the South side of the facility, near the main warehouse area (see Figure 1).

Facility Chemical Review Procedures

Consistent with Napp's "New Product Review" standard operating procedure (SOP), new products that potentially will be used or manufactured at the Napp Lodi facility are subject to an evaluation of employee health and safety, permit requirements, regulatory compliance (FDA, EPA, NJDEP, etc.), equipment suitability, process limitations and product characteristics. The New Process Review is an internal procedure in which management officials, the Regulatory Affairs Manager, Chemical Manufacturing and Engineering Manager, Operations Director, and Vice President of Regulatory and R&D participate.

The objective of the "New Product Review" procedure was *"to establish a uniform policy for evaluating potential products before their use or manufacture on this site."*

The Regulatory Affairs Manager initially reviews the job request which may be rejected due to regulatory concerns or company policies. If accepted, the Regulatory Affairs Manager will

NAPP CHEMICALS, INC LAYOUT

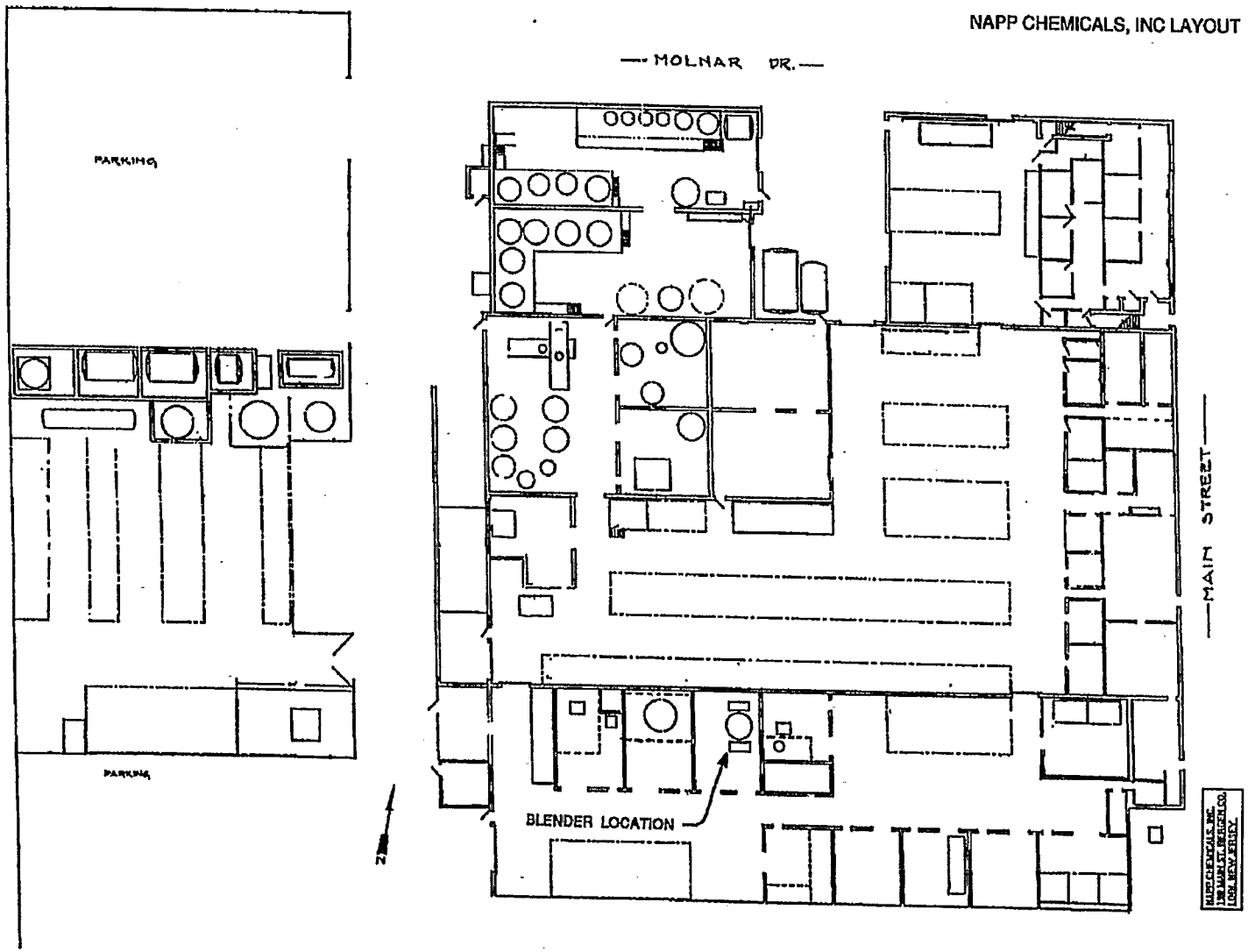


FIGURE 1

complete the New Product Review form, assemble relevant documentation, and circulate the package to other Napp management for further review. As part of that management review, the Chemical Manufacturing and Engineering Manager, the Operations Director, and the Vice President of Regulatory Affairs individually review (i.e., no concurrent team review) the package for safety, permitting, and process requirements. The last person to review the package returns it to the Regulatory Affairs Manager. Each participant in the review indicates his approval or rejection of the proposal on the New Product Review Form. All of the managers involved in the New Product Review approved of the processing of the GPA.

According to Napp's accident report: *"Material Safety Data Sheets and other information provided by Technic formed the primary basis for this review. Instrumental in Napp's acceptance of the project was the Company's review of its prior successful processing of approximately the same volume of these materials in the same blender and the absence of any disclosure from Technic of prior explosions, uncontrolled reactions or other accidents that had previously occurred during the blending of these materials."*

1.2 Process Information

GPA Blending Process

The GPA that Napp was blending is used to recover precious metals, such as gold, from aqueous cyanide solutions. The primary ingredients of the precipitating agent are aluminum powder and a reducing agent, sodium hydrosulfite. The precipitating agent also contains potassium carbonate, an alkali metal, as an activator. The ingredients were mixed in the following approximate proportions, by weight: 66% sodium hydrosulfite, 22% aluminum powder, and 11% potassium carbonate. A small amount (8 liters) of benzaldehyde was also to be added to the mixture for odor control.

To prepare the GPA, according to patent information, the three powdered components are mixed prior to use. The ingredients may be mixed in a simple cone blender or other mixing device. The intended blending time, from the time when all dry powders are charged until the time of unloading, is approximately 45 minutes.

Napp had once previously, in July 1992, blended a batch of ACR 9031 GPA for Technic, Inc., in its PK-125 blender. Before this operation, Napp technical personnel conducted a new product review. No formal record of this review was made, although production records were retained along with the Material Safety Data Sheet (MSDS) for each of the components of the GPA. The 1995 blending ingredients were virtually the same as in 1992. The 1995 blending operation was intended to be the same as in 1992; however, because of operation deviations, the 1995 batch operation was significantly different.

TYPICAL PATTERSON-KELLEY DRY SOLIDS BLENDER

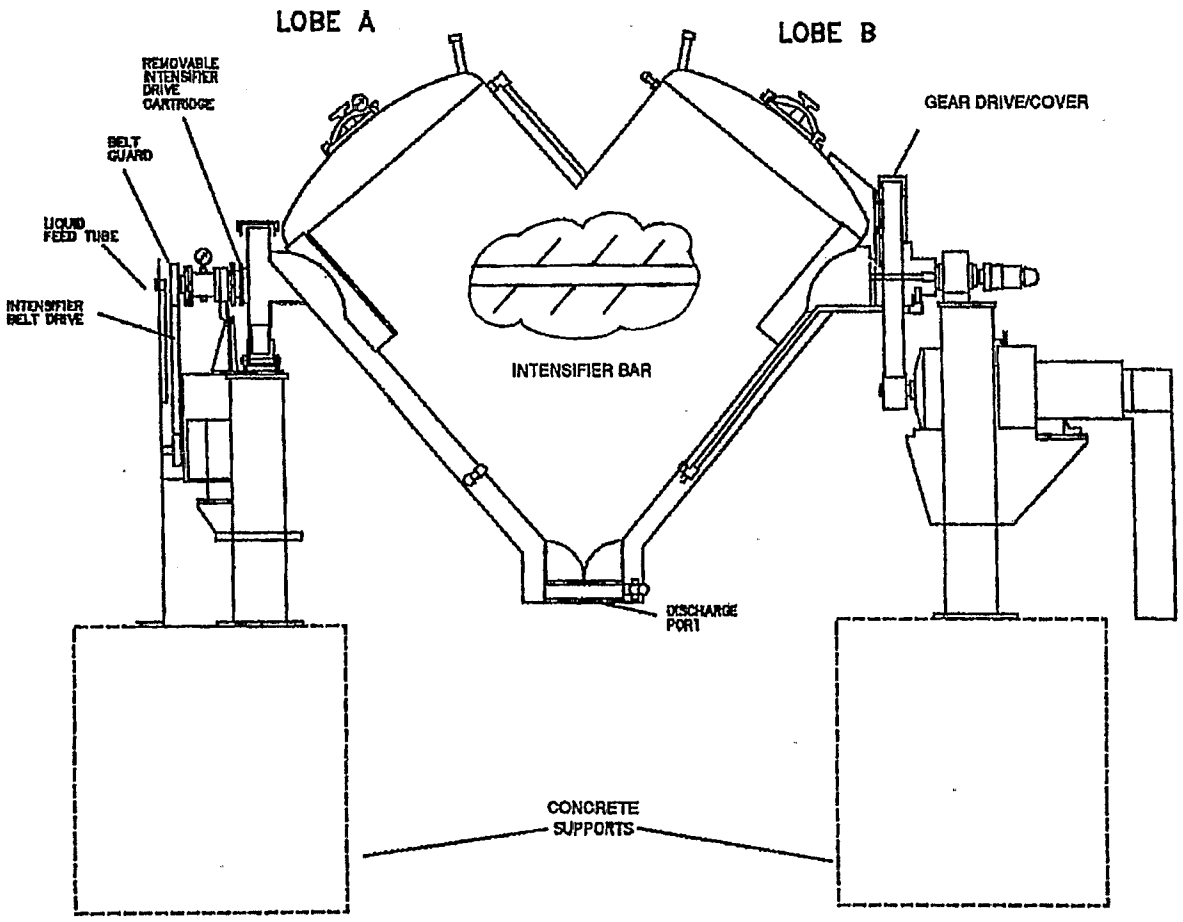


FIGURE 2

Patterson-Kelley 125 Blender

Figure 2 shows a typical Patterson-Kelley V-shaped blender. Patterson-Kelley builds each blender with options and features as specified by the purchaser. The blender at Napp had a working capacity of 6 cubic meters (125 cubic feet). It was approximately 6 meters wide (19 feet), including supports, and 3 meters (10 feet) high. The blender is a double-lobed stainless steel shell shaped like a heart. It is supported on its widest dimension by a horizontal trunnion attached to support tubes set in cement footings. It is insulated with a rigid foam material and encased in a steel jacket containing a water/glycol mixture for cooling and heating. The two access covers on top of the blender are used for loading raw materials, and one port is located at the bottom for off-loading product. A gear to one side of the blender (right side of Figure 2) rotates the shell of the blender through a 360-degree arc. Several water lines enter the jacket on this side. On the other side (left side of Figure 2) of the blender, a vacuum tube housing enters the blender. A graphite seal located inside the vacuum tube separates the seal's cooling water from the internal area of the vacuum tube and the blender. The purpose of the vacuum tube housing is to: (1) act as a conduit for establishing vacuum conditions when the blender is used for drying and other operations; and (2) contain other concentric lines, shafts, etc., including a liquid feed line (added by Napp) and the shaft used to rotate an intensifier bar (I-bar). The purpose of the I-bar is to enhance the mixing of materials being blended. The purpose of the feed line is to allow the controlled introduction of liquids to the materials being blended. The PK-125 blender can be used with or without the I-bar in service. The I-bar, Figure 3, transverses the inner walls of the blender connecting the inner sides of the blender on the same plane as the trunnion. See Figures 4-8 showing a larger but similar blender and associated equipment.

1.3 Chemical Information

The chemicals involved in the explosion were sodium hydrosulfite, aluminum powder, potassium carbonate, and benzaldehyde. The properties and hazards of these chemicals are discussed below.

Sodium Hydrosulfite

Sodium hydrosulfite (sodium dithionite), $Na_2S_2O_4$, is a whitish, crystalline solid, with moderately strong reducing properties. It is principally used in dying and bleaching operations.

The National Fire Protection Association (NFPA) (NFPA 49, Hazardous Chemical Data, 1994) rates chemical hazards on a scale of 0 (lowest degree of hazard) to 4 (highest degree of hazard). NFPA rates sodium hydrosulfite as 2 for health hazards (moderate) and notes that combustion byproducts may include sulfur dioxide. Sodium hydrosulfite is rated 1 for flammability and described as a combustible solid. NFPA rates it as 2 for reactivity and notes that exposure to moisture from humid air or small amounts of water can result in spontaneous chemical reactions that may generate sufficient heat to initiate thermal decomposition. The U.S. Department of Transportation (DOT) lists sodium hydrosulfite (49 CFR Part 172) in Hazard Class 4.2

INTENSIFIER BAR/VACUUM HEAD ASSEMBLY

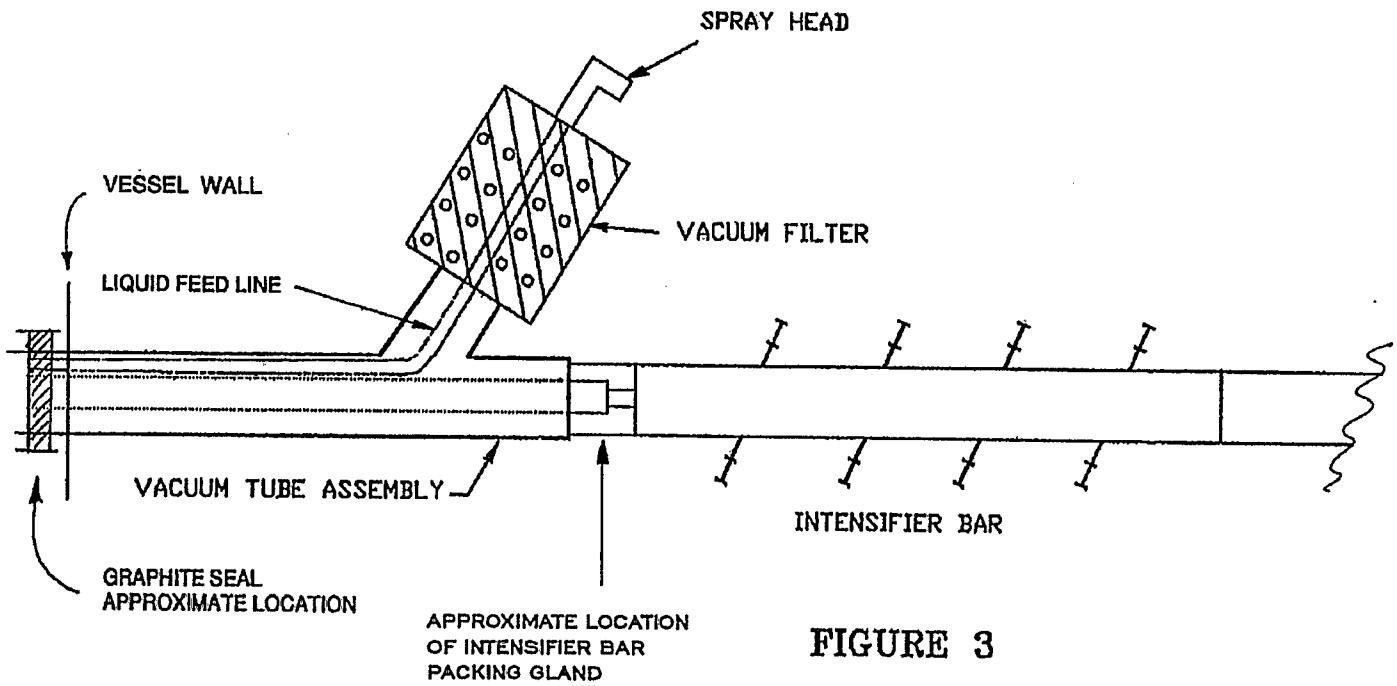


FIGURE 3

(spontaneously combustible material), Packing Group II. Packing Group II is assigned to materials that present a "medium degree of danger." The shipping label "SPONTANEOUSLY COMBUSTIBLE" is required for sodium hydrosulfite.

Sodium hydrosulfite is unstable in the presence of water, heat or humid air, giving off sulfur dioxide gas and other sulfur products in an exothermic reaction. Once initiated, the decomposition process of sodium hydrosulfite supports continued decomposition due to the generation of heat in the exothermic reaction. Therefore, once the decomposition has been initiated, it cannot be extinguished with smothering agents. To quench the decomposition, the temperature of the material must be lowered below the decomposition temperature.

The material safety data sheet (MSDS) for sodium hydrosulfite supplied by Technic notes in the event a container feels hot or begins to smoke it should be removed to an open area and "*flood with water.*"

The decomposition temperature of sodium hydrosulfite is identified on the MSDS as 130 C. Under Reactivity Data, the material is described as "stable" although moisture and heat in excess of 50 C are identified as conditions to avoid.

Aluminum Powder

Aluminum powder is light grey or silvery colored. Air dispersions (dust clouds) of aluminum particles, when mixed in proper proportions and exposed to a small amount of ignition energy, will burn with such rapidity that if contained an explosion may occur Aluminum powder has a number of uses related to its flammability and explosivity when dispersed in air, including use in explosives, propellants, and pyrotechnics. As a component of explosives, aluminum powder is used to increase explosive power.

NFPA (NFPA 49, 1994) rates aluminum powder as 0 for health hazards, indicating health hazards are minor. Under "Fire and Explosive Hazards," NFPA 49 describes aluminum powder as a "[f]lammable solid if finely divided. Forms explosive mixtures in a dust cloud in air. Bulk dust when damp with water may heat spontaneously. Hazard greater as fineness increases." The rating for flammability hazard is 3, the rating that applies to liquids and solids that can be ignited under almost all ambient temperatures. Aluminum powder has a rating of 1 for reactivity hazards. DOT lists aluminum powder, uncoated, on its Hazardous Materials Table in Hazard Class 4.3 (dangerous when wet material), Packing Group II ("medium" degree of danger). The shipping label "DANGEROUS WHEN WET" is required for uncoated aluminum powder.

Sax's "Dangerous Properties of Industrial Materials" fifth edition, (page 352) indicates that aluminum powder is a moderate explosion hazard when finely divided as dust and dispersed with gaseous SO_2, under appropriate conditions.

Water will react with aluminum dust to produce hydrogen gas, especially under alkaline conditions. Aluminum is normally protected by an oxide coating, but the coating is readily dissolved

by alkaline agents such as bicarbonate. Once the oxide coating is removed, the aluminum becomes very reactive. The oxide coating normally reforms rapidly and exothermically on contact with air. The uncoated condition is ideal for aluminum to become pyrophoric, i.e., burst into fire spontaneously under appropriate conditions.

The MSDS for aluminum powder, uncoated (atomized), as written by Valimet, Inc., and supplied by Technic to Napp states:

Under Section IV: Fire and Explosive Data:
"Special Fire Fighting Procedures: Avoid water"

Under Section VI: Reactivity Data:
"Incompatibility (Materials to Avoid): Water, acids, alkalis.
Hazardous Decomposition Products: Exothermic reaction with water, acids, alkalis to generate hydrogen and heat."

Benzaldehyde

Benzaldehyde is a colorless liquid. Benzaldehyde readily oxidizes to benzoic acid. To prevent contact with air, an inert gas blanket over the material is required.

Benzoic acid is a white crystalline material. When benzoic acid is heated above its melting point, some formation of benzoic anhydride and water takes place. When heated above 370C, it decomposes to benzene and carbon dioxide, with small amount decomposing to phenol and carbon monoxide.

Potassium Carbonate

Potassium carbonate is usually in the form of white crystalline granules. Because of its alkaline chemical nature, it is commonly used to raise the pH of mixtures and solutions. Potassium carbonate has some acute health hazards (irritant to all body tissue, possibly leading to tissue destruction), giving it an NFPA health hazard rating of 2. NFPA fire and reactivity ratings for the material are 0, indicating that it is a stable compound.

Gold Precipitating Agent

The MSDS for the gold precipitating agent supplied by Technic, Inc. notes:

"*Flammability Data:* *Contact with small amounts of water or humid atmosphere will cause a chemical reaction. The heat generated from this reaction is sufficient enough to ignite combustible material . . . Flood the material with water to ensure complete wetting, as this procedure will control the auto-ignition of the material.*

Extinguishing Media: Water spray should be used to extinguish fire

Usual Fire Fighting Procedures: Use water to keep fire exposed containers cool."

Unusual fire fighting techniques are asserted not to be applicable. Hazardous decomposition products specified are limited to oxides of sulfur, carbon dioxide and carbon monoxide. Incompatibles identified by Technic are limited to "oxidizing agents or materials, strong acids and moisture.

2.0 Description of the Accident

2.1 Events Preceding the Blending Operation

In January of 1995, Technic contacted Napp to inquire about the timing of an order of GPA. In February 1995, Napp informed Technic that the next available date to make GPA would be March 23, 1995. In preparation for that job, Napp decided to perform a new product review. The Regulatory Affairs Manager, Chemical Manufacturing and Engineering Manager, Operations Director, and the Vice President for Regulatory and R&D participated in the review which included the evaluation of the processing information available from 1992, the MSDS prepared by Technic for its GPA, the MSDSs of the components of the mix, as well as other information. They noted the water-reactive nature of the components of the GPA.

In March of 1995, in preparation for the blending of one batch of GPA, Technic began procurement of the various raw materials and made arrangements for their shipment to Napp. A slight delay in the scheduled blending of the GPA pushed the production date into April. On April 7, Technic sent Napp a purchase order, a duplicate of the GPA MSDS already in Napp's possession, and a sign-off by Technic's Director of Operations on the formulation sheet (batch recipe ticket) indicating that it was "OK to blend." The delivery of materials to Lodi commenced in March and was completed with the delivery of aluminum powder on or about April 4, 1995. The components of the blend included 1,800 pounds of powdered aluminum, 900 pounds of potassium carbonate, 5,400 pounds of sodium hydrosulfite, and eight liters of benzaldehyde. The blended GPA was to be packaged into 18 plastic-lined 55-gallon drums, supplied by Technic.

2.2 Preparations for Blending

Preparations for the processing to be performed commenced on Monday, April 17, 1995 when the PK-125 blender was rinsed with deionized water. Thereafter, the rinsewater was discharged. The intensifier bar was removed from the vessel, dismantled by mechanics, and cleaned.

The maintenance foreman instructed a maintenance employee to remove and change the packing gland associated with the intensifier bar on the PK-125 blender. This activity was standard procedure whenever there was a scheduled product change for one of the Napp P-K blenders. After removing the old packing gland and its housing, the maintenance employee observed water next to a bearing. Based on this observation, the maintenance foreman instructed the maintenance employee

to drain the water out of the area, replace the packing, and seal the blender. As part of the procedure to check the integrity of the seal and packing gland, the maintenance employee ran the blender and its intensifier bar for 15 minutes and visually inspected the interior of the blender to assure that the water-cooled seal and packing gland were not leaking. The mechanic found no evidence of leakage.

The blender was given a final rinse, and the rinsate was checked for the presence of contamination. Quality Control personnel "released" the blender and the room in which it was housed to Operations personnel and the cleaning log was signed signifying completion of the cleaning process, approving both for use in preparing the next product, the GPA.

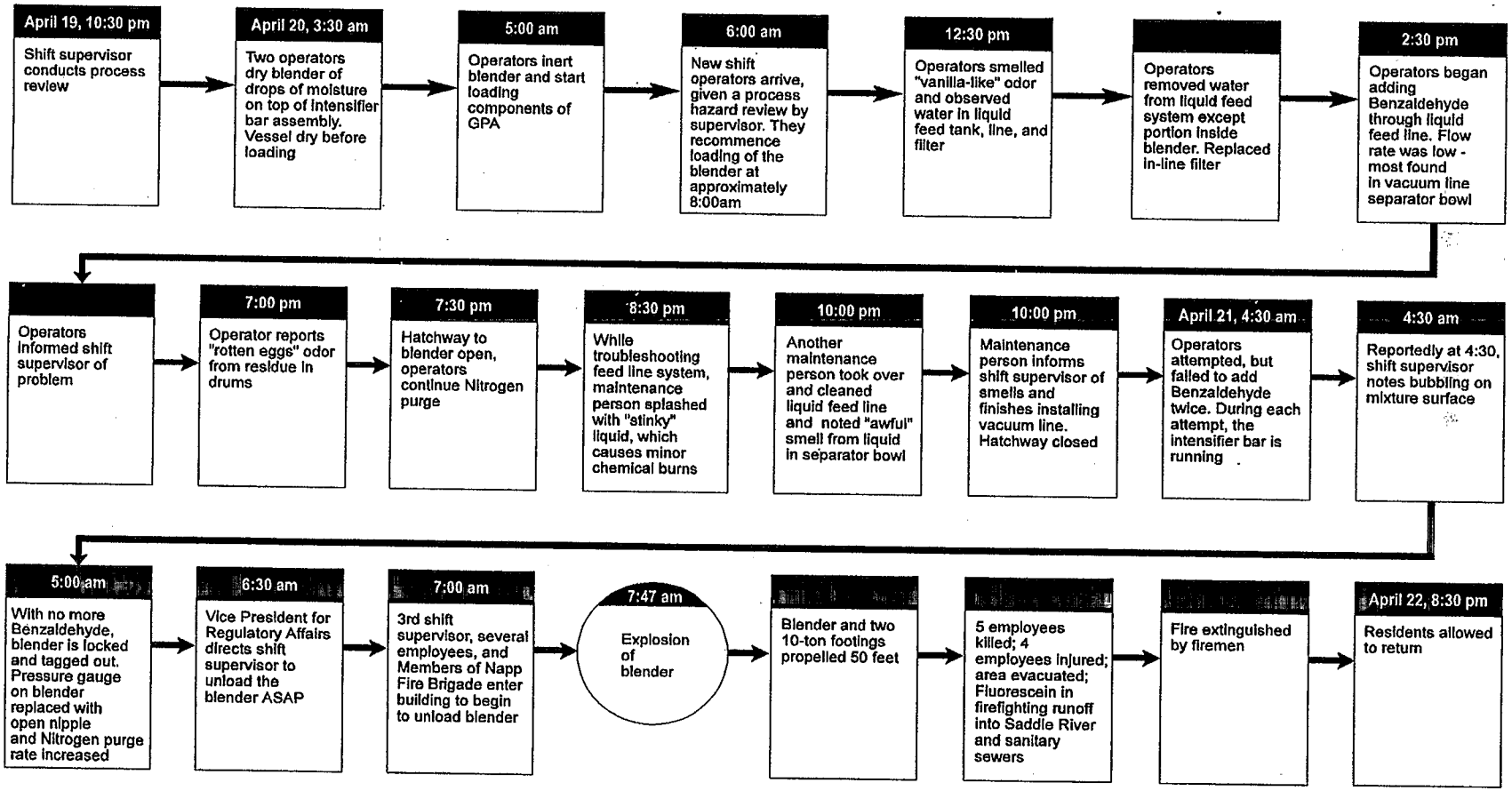
On April 19, prior to charging the materials, the first shift supervisor conducted a process review with operators on duty. It was a Standard Operating Procedure that any operator engaged in materials processing must complete a detailed review with the shift supervisor of the process and its hazards prior to commencing work. The review, which typically takes 45 minutes to an hour, was done for each operator involved in the Technic process, and included a discussion and review of the equipment set-up, the steps to be undertaken in the process, and a complete review of the MSDSs for GPA and each component of the mixture. The shift supervisor and two operators found a minor water leak from a water pipe in the back of the PK-125 room (not associated with the blender). The shift supervisor stopped the leak, dried up any water that remained, and covered the floor drains in the room to prevent contact of GPA with water in the sewer system in the event of a spill. A sign informing workers that water reactive chemicals were being processed in the PK-125 room was placed at the entry to the room.

At approximately 10:30 p.m. on April 19, the shift supervisor conducted a process review with the night shift crew. Exhibit 1 shows the timeline of events beginning at this point.

The process review with the operators concluded at approximately 11:15 p.m. The operators and leadmen then pre-weighed the GPA components, placing the unopened drums of sodium hydrosulfite and aluminum powder and bags of potassium carbonate on a digital scale and recorded the weight of the material and its container on a log. In the course of this activity, it was discovered that one of the bags of potassium carbonate had been broken and taped over and it weighed less than the others. To assure proper proportions for the GPA, a calculation was performed and the volume of the other raw materials was adjusted for the batch to be mixed.

At 3:30 a.m. on April 20, as part of the precharging verification, operators made a final check to assure the blender was ready (i.e., clean and dry) to be loaded. The two operators and a foreman discovered that the vacuum head area, inside the blender, was wet. They also observed water on the internal walls of the blender. Another employee saw a wet spot also described as "droplets of water on the stainless steel" at the intensifier bar shaft seal (connection). They believed this moisture was

Exhibit 1
Timeline of Events
April 21, 1995 Explosion of Blender at Napp Technologies, Inc. - Lodi, NJ



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caused by condensation.

Knowing that water reactive materials were to be loaded into the blender, the night shift foreman directed an operator to wipe off the portions where moisture was found. The blender was then heated using the water-glycol jacket on the PK-125 to further dry the interior surfaces. The blender was allowed to cool and was checked to ensure it was ready to be charged with the raw materials and found to be dry.

2.3 Blending Operation

Prior to the commencement of loading operations, the operators implemented a standard operating procedure that required that a vacuum twice be created within the blender and then broken with inert nitrogen gas. Thereafter, a slight nitrogen pressure was maintained to assure inert conditions within the blender. At approximately 5:00 a.m. on April 20, operators began to load the components of the GPA into the blender, but did not finish the work. At 6:00 a.m., a shift change occurred, and the first-shift day crew arrived to continue blending operations.

A process review of the GPA blend had been conducted for the new operators, and the hazardous nature of the raw materials was discussed. At approximately 8:00 a.m., the first shift operators recommenced loading of the blender alternating proportionately from one component to the next as had the previous operators. Because loading occurred only through one port of the "V"-shaped blender, and to distribute the materials evenly across the blender, the intensifier bar was rotated briefly. The loading of the blender concluded at approximately 11:00 to 11:30 a.m. Thursday morning. During the final charging, the blender was rotated to level (settle) the powders to allow all of the material to be loaded. An operator noted that the charge was not dusty when the blender was opened for the final addition. After charging was complete, the level of the powdered components completely covered the intensifier bar and was almost up to the middle of the vacuum head. Thereafter, the operators commenced the blending operation according to Napp's procedure, which called for blending the dry powders as follows: rotate the blender for ten minutes without the intensifier bar; five minutes with the intensifier bar; and ten minutes again without the intensifier bar. The dry blending was completed by mid-day.

The operators then made preparations to spray charge the benzaldehyde, a procedure requiring the use of a separate liquid feed tank connected by hoses to a spray nozzle atop the vacuum head within the blender. Operators noted a "vanilla-like" odor from a liquid feed tank for the blender, and water was observed inside the tank. Additionally, the operators found water in an internal filter located on the liquid feed line near the point of entry into the blender. However, because the components of the GPA, with the exception of the benzaldehyde, were already in the blender, the portion of the feed spray line located inside the blender could not be cleaned without contaminating the materials in the blender. The operators did not consider the liquid feed line to be functioning properly. The liquid spray head and spray system had not been completely dried prior to the charging of the blender. The operators placed a gallon of isopropyl alcohol (IPA) into the liquid feed tank and blew inert nitrogen through the tanks and lines into a bucket forcing the IPA through the system, with the exception of that portion of the line entering the blender and terminating at the spray nozzle.

They then blew nitrogen through the liquid feed system for 45 minutes to one hour to make certain the feed tank and lines were dry.

At approximately 2:30 p.m., the operators attempted to charge the benzaldehyde into the blender. In doing so, the operators placed the benzaldehyde in the liquid feed tank, charged the tank with nitrogen pressure, commenced rotation of the blender and intensifier bar, and relieved the pressure into the blender. The operators noted the feed rate was unusually low, and upon inspection, they noticed that most of the benzaldehyde had ended up in a vacuum line separator bowl and not in the blender (Figure 3A). Upon consideration of the failure of the liquid feed system to correctly spray the benzaldehyde into the blender, it was determined to examine the compression fitting to the liquid feed line to see if it was leaking.

An operator noted that the liquid in the bowl had a few drops of water or IPA on top of the benzaldehyde. No further analysis was performed on the liquid.

At 7:00 p.m. an employee entered the PK-125 room and smelled an odor described as "rotten eggs." The employee observed 18 drums which previously contained the raw materials. These drums sat uncovered. Assuming the residue inside the drums was the cause of the odor, he put the tops back on the drums.

At 7:30 p.m., a maintenance employee was instructed to troubleshoot the liquid feed system line. When the employee attempted to open the vacuum line to gain access to the feed line the employee was splashed with a "stinky" liquid. The maintenance employee received minor chemical burns and went to the locker room to wash off the chemical.

Between 7:30 and 10:00 p.m., one hatchway on the PK-125 blender remained open to the atmosphere. During this period the operators continued to run a nitrogen purge through the vacuum line into the blender so as to maintain an inert blanket in the head space of the blender.

At approximately 10:00 p.m., another maintenance employee completed the disassembly of the exterior portion of the vacuum line and took it to another room, where it was washed and dried. When the employee returned to the PK-125 room the employee smelled an odor that he described as a "dead animal" smell upon initially entering the PK-125 room. This employee also observed and smelled the liquid from the separator bowl which had been collected in a beaker. The employee described the smell as "awful." The maintenance employee cleaned up the liquid which had earlier spilled on the floor. By this time, it had been almost ten hours since the ingredients were placed into the blender (the blending should have taken not more than one hour to complete).

At 10:00 p.m., the maintenance employee informed the shift supervisor about the unusual odors in the PK-125 room. The maintenance employee finished reinstalling the vacuum line to the blender, and the shift supervisor went to the lab to obtain more benzaldehyde to inject into the blend.

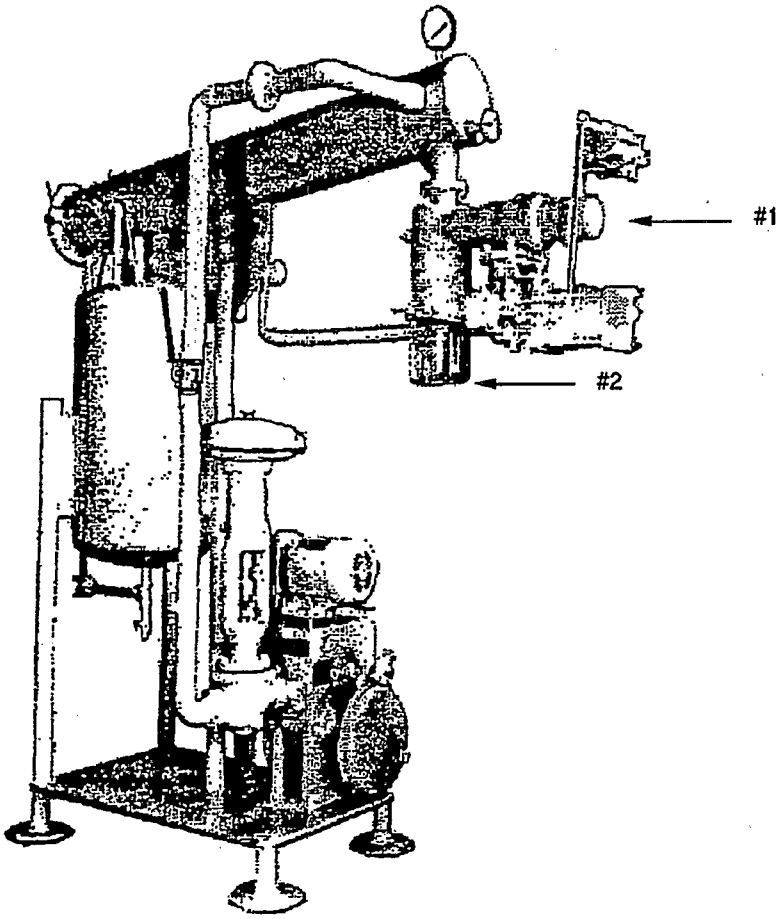

FIGURE 3A: TYPICAL VACUUM COLLECTION SYSTEM AS SUPPLIED BY PATTERSON-KELLEY. #1 SHOWS APPROXIMATE LOCATION OF INLET FROM BLENDER VACUUM LINE; #2 SHOWS VACUUM SEPARATOR BOWL.

Between midnight and 4:30 a.m. on April 21, 1995, the third shift attempted to inject benzaldehyde into the batch on two occasions; each attempt failed. Operators observed the benzaldehyde running back into the vacuum separator. During each attempt to add the liquid, the blender was rotated for about two minutes with the intensifier bar running. Suspecting that product was blocking the spray tip of the nozzle and preventing the injection of the liquid, operators opened the blender twice and removed and washed the spray nozzle. Operators reportedly observed a slight dusty powder wafting within the head space of the blender. This was reported to the shift supervisor, who then checked the inside of the blender and directed the operators to remove and clean the nozzle. After the final attempt to charge benzaldehyde into the vessel it was determined that no fresh benzaldehyde remained. It was by then approximately 5:00 a.m. and coming to the end of the third shift. The shift supervisor told the operators to perform a lock and tagout of the blender.

The shift supervisor noted that a pressure gauge on the blender was reading five pounds per square inch (psi). Inasmuch as the blend was to take place under atmospheric conditions, in a blender designed for non-pressurized service, concern arose that the rise in pressure could result in the two charging ports being blown out of the blender. Because there was a continuous flow of nitrogen into the blender, the pressure gauge was replaced with an open nipple, and the pressure was released into the PK-125 room. The nitrogen purge rate was then increased.

The shift supervisor reportedly observed an area of about 8 inches in diameter bubbling and smoking on the surface of the material inside the blender.

2.4 The Explosion and Fire

As employees arrived at the plant for the morning shift on April 21, they noticed a rotten egg odor. At approximately 5:30 a.m. the operators of the blender had observed puffs of white smoke coming from the exhaust nipple affixed to the PK-125. By 6:00 a.m. employees on the first shift had reported to their assembly areas. Nearly all Napp employees smelled the odor of rotten eggs, which by then had escaped the building and was noticeable in the parking lot behind the plant. At approximately 6:15 a.m. the plant was evacuated, through verbal instructions; no audible alarms were ever activated at the facility.

At about the same time, there was a discussion about whether the GPA should be unloaded from the blender. At approximately 6:30 a.m., the third shift supervisor placed a call to the Vice President for Regulatory Affairs (VPRA) and advised him of the situation. After asking a series of questions for more information, in a subsequent phone conversation at approximately 6:45 a.m., the VPRA directed the shift Supervisor to discharge the batch "ASAP." The VPRA suggested tumbling the blender with cooling medium (glycol) circulating in the water jacket. The shift supervisor stated that he did not want to rotate the blender because that would require capping the exhaust nipple that had been installed to relieve the pressure buildup inside the blender. The VPRA directed the shift supervisor to maintain the nitrogen purge into the blender. Additional phone calls were also made from the plant to other Napp management personnel.

During discussions regarding unloading of the blender and upon review of the GPA MSDS,

it was suggested that a fire hose would be strung out to the PK-125 room but not charged in order to prevent accidental discharge of water. Later, an additional hose was made available.

At approximately 7:00 a.m., the third shift supervisor went outside and approached the plant employees who had been evacuated to the rear parking lot. Several employees, including the first shift supervisor, returned to the blending room with him to assist with the unloading of the blender. Other employees, who were members of the Napp Fire Brigade, reentered the plant to stand by with fire hoses at the ready, but were instructed by the Production Manager not to charge them with water unless they were told to do so by another employee who would be closely watching the unloading operation. The maintenance supervisor stood in a doorway that led from the blending room to a hallway from which he could see both the unloading activities and the fire brigade member standing by awaiting a signal to charge the fire hose.

At approximately 7:47 a.m., three loud hissing noises were heard in succession. The noises were closely followed by a "whoosh" sound, then the explosion. The blender and its two 10-ton concrete footings were propelled in a westerly direction for a distance of approximately fifty feet. An employee standing by stated that he heard hissing noises, looked inside the blending room, and saw the other workers in animated activity. He turned to run, saw two bright flashes of what reminded him of lightning, and saw a yellow-orange ball of flame "like a snake's tongue" leap out of the room toward him. He was blown along the length of the corridor and out a passage door; he survived with minor injuries.

Four of the five employees in the PK-125 blending room were killed in the explosion and ensuing fire, and the fifth employee died of burns a week later. Four other employees escaped with minor injuries.

2.5 Emergency Response

At the sound of the explosion, Lodi police, fire, and EMS responded to the scene within minutes. Information concerning the chemicals stored at the facility was promptly made available to responders. Nine persons injured in the explosion were transported to a local hospital. Approximately 300 residents in the vicinity were evacuated from their homes, as well as a nearby elementary school.

Other responding agencies included EPA, OSHA, United States Coast Guard, Federal Bureau of Investigation, NJ Department of Environmental Protection (NJDEP), NJ State Police Office of Emergency Management, Bergen and Passaic County Health Departments, Bergen County Prosecutor's Office and the Arson Squad. Hundreds of volunteer fire and ambulance personnel also responded, as did more than 20 other municipal police.

Continuous air monitoring was conducted by seven NJDEP teams for the duration of the fire. Downwind monitoring was conducted by NJDEP, Bergen and Passaic County Health Departments.

Observable during the firefighting response was a discharge of the chemical fluorescein, a

bright green dye, which was stored at the Napp facility. Fluorescein-contaminated firefighting runoff water entered the Saddle River through the storm drains and by direct overland flow. Fluorescein-contaminated runoff also entered the sanitary sewer line feeding the sewage treatment plant. The Passaic Valley Sewage Commission was notified of the release. Napp Technologies hired a cleanup contractor to contain firefighting runoff. Evidence of firefighting runoff was seen in the Saddle River in the form of a bright green discoloration for two miles downstream to its confluence with the Passaic River.

A USEPA mobile laboratory vehicle was used to acquire downwind air samples of inorganic/acid gases, organic, and ketones. In addition, water samples were obtained at seven locations for off-site analysis. Water samples were analyzed for volatile organic compounds, base-neutral-acids, metals, pesticides, and PCBs.

Fish kills were confined to the Saddle River, for approximately 2 miles downstream to the confluence with the Passaic River. No fish kills were observed in the Passaic River. The residential evacuation order for Lodi and the surrounding communities was lifted on April 22 at 8:30 p.m.

2.6 Napp Fire Brigade Members and Emergency Responders

Among the Napp employees involved in the attempt to remove the GPA from the blender were several who were members of the Napp fire brigade and had been trained in incipient fire fighting techniques.

Napp fire brigade members and other Napp emergency responders were directed by management to respond to the ongoing chemical emergency. Nine of the twelve employees who were inside the building immediately preceding the explosion (during the unloading of the GPA) were also members of the Napp fire brigade. Training records revealed that some employees were given a lecture on chemical fires, but no formal training was conducted related to fighting chemical fires or emergencies. A course on hazardous materials was presented to the fire brigade in November 1993, but the records note that none of five listed managers, including three of the deceased employees, attended the session. The same training records indicate that four of the five managers failed to attend six fire brigade training sessions in 1993 (the fifth manager attended one session), and the same individuals failed to attend similar training courses, including one on hazardous materials and one on emergency response in 1994. In 1995 the same individuals missed three fire brigade training sessions, including one on fire behavior given 10 days prior to the explosion. The Napp Plant Safety Standard for Fire Protection Organization specifically defines the function of the Plant Fire Brigade as, among other things, to "answer all fire calls." It also states that the "intent of the Brigade is to fight incipient stage fires only." It further states that "The Brigade will perform a contain and hold function on any major interior structural fire until the Lodi Fire Department arrives."

3.0 Analyses and Significant Facts

3.1 Analyses

After the accident, investigators analyzed the chemical residues in the blender and the remains of the blender itself. These analyses are discussed in detail in Appendix A. Appendix A also includes information on the injuries suffered by the victims of the explosion.

The chemical analysis showed the presence of sodium, potassium, and aluminum, consistent with the blender contents. Phenol and methylphenol compounds were also found in large amounts. These compounds were probably due to the insulating material remnants which were originally located in the annulus between the outer wall of the blender and the outer wall of the water-glycol jacket. These compounds could also be derivatives of the benzaldehyde that was added to the blender contents.

The analysis of the remains of the blender showed extensive erosion damage in parts of the interior and around several openings. Ejection of heated material from the inside of the blender is the likely cause of the erosion. The blender also showed extensive damage attributed to impact when the blender was propelled about 40 feet due to the explosion. The investigators looked in particular for possible damaged areas where water could have entered the blender. Metallurgical examination of the water-cooled graphite seal for the vacuum tube showed grooves that could have allowed water to leak into the blender.

Evaluation of injuries suffered by the victims indicate that the explosion at the Napp facility was a deflagration rather than a detonation. A deflagration releases energy at a lower rate, generates lower overpressures, and is less destructive than a detonation.

3.2 Significant Facts

Other facts considered by the accident investigation team in determining the causes of the accident are listed below.

<u>Napp's Analysis of Hazards of Blending Operation</u>

- The GPA was blended on one previous occasion by Napp in July 1992, using the same PK-125 blender. The manufacturer of the blender states that the blender is not designed to mix water reactive substances.
- Technic provided Napp with MSDSs for components of the GPA and an MSDS for the GPA.
- The MSDSs noted that aluminum and sodium hydrosulfite are water reactive.
- The MSDS for the GPA recommends "flooding with water" to control auto-ignition of the material.

- Napp's "new product review" procedure was conducted primarily based on information included in the MSDSs. Review was conducted individually (i.e., not by a team) by four managers of Napp to determine equipment suitability and health and safety concerns.

- Napp management was aware of the water reactivity of the materials in the blending operation.

Sources of Water and Heat

Literature review and a limited laboratory study of the hazards of the GPA mixture revealed that small quantities of water were capable of inducing a runaway reaction at relatively low temperatures. Further, the presence of aluminum powder in the mixture provided a substantial increase in the amount of heat released during decomposition (see Appendix B).

The following were possible sources of water and heat in or around the blender at the time of the accident, which were evaluated by the JCAIT as potential initiators of the event.

- The seal of the intensifier bar was water-cooled.

- Water was observed on internal surfaces of the blender prior to charging; a drying procedure was subsequently performed.

- Water was used to clean the blender.

- Water was noted in the liquid feed tank and feed line filter just before the feed line entered blender.

- The coolant in the blender jacket was a water/glycol mixture.

- Water was seen in the packing gland area/bearings of blender prior to the blending operation.

- Although the blender was blanketed with nitrogen, the ports were opened and atmospheric humidity could have been a source of water.

- The intensifier bar moving at a high speed through dry powders my have been a source of frictional heat.

- Particulate matter between bearing surfaces at the intensifier bar shaft in the packing gland area may have been a source of frictional heat.

Deviations from Napp's Expected Maintenance and Operating Procedures

- During a routine maintenance procedure, water was noted between a packing gland and

bearings inside the PK-125 blender. Because this location was inside the vacuum section of the intensifier bar, no water should have been present. The water was dried and the gland re-packed.

- At 3:30 a.m. on April 20, two operators and a foreman found that the vacuum head area inside the PK-125 blender was "wet." Water (droplets) was observed on the intensifier bar shaft connection as well as on the inside walls of the blender. The moisture was removed and the blender dried.

- The quantities of the ingredients were recalculated because Napp lacked the proper amount of potassium carbonate.

- Operators noted that the level of dry ingredients was above the level of the intensifier bar and up to the middle of the vacuum head. According to Patterson-Kelley, the level should be no higher than the middle of the intensifier bar.

- At 10:00 a.m. on April 20, operators detected a vanilla-like odor in the liquid feed tank (used to contain liquids prior to injection into the blender).

- Water was observed in the liquid feed tank and its filter system. All parts of the injection system external to the blender were cleaned and dried. Because the powdered ingredients were already in the blender, the components of the injection system inside the blender could not be cleaned or dried without contaminating the charged material.

- At 2:30 p.m. on April 20, operators were unable to inject benzaldehyde, the sole liquid component of GPA, into the blender. For approximately 14 hours, operators attempted to clear the liquid feed line and re-inject the benzaldehyde, while intermittently operating the intensifier bar and rotating the blender. The intensifier bar was used far longer than specified in the Napp procedure, in order to properly blend material.

- At 7:00 p.m. on April 20, an operator smelled a "rotten egg" odor inside the PK-125 room. The operator assumed it was from open drums which originally contained the raw materials which had been charged into the blender.

- Two distinct liquids, assumed by Napp employees to be benzaldehyde and drops of water or IPA, were seen in the vacuum separator bowl. No analysis to determine the components of the liquid was performed.

- At 9:30 p.m. on April 20, a maintenance employee noted an unpleasant odor inside the PK-125 room.

- By 4:30 a.m. on April 21, bubbling was reportedly observed on the surface of the materials in the blender.

- At approximately 6:00 a.m. on April 21, workers were verbally notified to leave the building. Arriving day shift employees were directed to remain in the rear parking lot of the building.

Conditions at the Time of Employee Reentry to Unload Blender

- Bubbling (in an area approximately eight inches in diameter) and smoking were noted on the surface of the material inside the blender approximately three hours earlier.

- The blending operation is normally conducted at atmospheric pressure. However, an exhaust nipple was relieving pressure from the nitrogen blanket and off-gas products of the batch from within the blender. Blender could not be tumbled and cooled due to the open vent.

- A strong sulfur smell was noted in the blending area.

- With the exception of 12 employees which were directed to assist in the off-loading of the blender, the facility remained evacuated.

Lack of Notification of Local Community Immediately Preceding Accident

- Napp solely used verbal notifications to evacuate the building. Use of an internal alarm would have automatically notified local emergency responders.

- During the attempt to remove the contents of the blender, Napp did not charge fire hoses that were laid out and held by Napp employees in case of ignition. The fire water system included a device that would automatically notify local fire officials if a pre-set flow rate was met. Since the system was not utilized, no alarm was initiated.

- The Napp facility was located in a residential area, with homes and other businesses nearby. Napp did not provide any warning to local community of an on-going chemical emergency.

4.0 Causes of the Accident

4.1 Possible Causes of a Chemical Reaction

The reports of unusual odors in the blending room and building, bubbling and smoking noted on the surface of the material in the blender, and pressure buildup in the blender all suggest that the explosion and fire were triggered by an unwanted and uncontrolled chemical reaction occurring in the blender.

The GPA was successfully blended by Napp and other companies without incident on several occasions prior to this accident. Based on this history and an evaluation of the chemical components of the GPA, the JCAIT believes the raw materials by themselves will not normally react with each other in the absence of an outside initiator such as water and/or heat. The JCAIT eliminated outside sources, including sabotage and "Acts of God," as possible causes, as there was no evidence to

support these possibilities.

The predominant reactions taking place most likely were:

- The exothermic reaction of sodium hydrosulfite with water;
- The exothermic reaction of aluminum powder with water;
- The exothermic thermal decomposition of sodium hydrosulfite, which would have been initiated by heat from the exothermic reactions with water; and
- The exothermic oxidation of hot aluminum powder, which would have been initiated when air contacted the blender contents.

The oxidation of hot aluminum powder could have resulted in a deflagration. The chemical reactions of sodium hydrosulfite, aluminum, and benzaldehyde are discussed in detail in Appendix B. Brief descriptions of other accidents in the past involving sodium hydrosulfite or involving aluminum powder are presented in Appendix C.

Reaction Initiation

Based upon the nature of the chemicals in the blender at the time of the accident, and the circumstances of the accident, the JCAIT investigated possible sources of water and heat as the initiator of the reaction. The following table identifies the possible sources of heat and water in the blender system. These sources are discussed in more detail following the table.

Initiator	Possible Source
Water	Water used to clean blender/inadequate drying
Water	Water used to clean liquid feed line
Water	Leak of coolant from blender jacket
Water	Moisture from raw materials
Water	Water in nitrogen
Water	Atmospheric humidity entering blender
Water	Water in liquid feed tank
Water	Water-cooled seal failure
Heat	Shear from intensifier bar through dry powder solids
Heat	Particulate material in internal bearings of blender

Based upon eyewitness testimony, the reaction seemed to be localized (as a hot spot) rather than a generalized reaction of the materials in the blender. The eight-inch wide bubbling area noted in the Description of the Accident also suggests that the hot spot was more near the center of the blended material rather than along the sides of the blender. The JCAIT therefore considered the various sources of water/heat, as discussed below, to determine which ones would likely have led to a reaction in the location observed.

Inadequate drying of blender before use. Water was used to clean the inside of the blender before it was used. If water remained in the blender, it would have reacted with the raw materials. However, before the raw materials were added, water found in blender was drained and fully dried. While the bubbling noted towards the middle of the blender reveals that the reactions did not take place at the walls of the blender (where any moisture would have been located prior to use), it is likely that any moisture in the blender before it was used would have been distributed throughout the batch.

Leak of coolant from blender jacket into the raw materials. A water/glycol mixture is used in the outer jacket of the blender to cool or heat the blender. A breach in the integrity of the blender wall could have allowed the water/glycol mixture to migrate from the jacket into the contents of the blender. The JCAIT conducted metallurgical analysis of the blender after the accident. This analysis revealed one crack near the off-loading port; however, the crack was considered to be from impact damage. (See Appendix A for additional details.)

Moisture from raw materials. Moisture present in any of the raw materials could have been sufficient to initiate a reaction. However, no signs of reactions (odors, heat) were detected by the operators charging the blender with raw materials. Also, Napp performed a quality assurance check on the raw materials, and no moisture was noted.

Moisture in nitrogen. Nitrogen was used throughout the blending process to inert the headspace in the blender and to prevent atmospheric moisture from reacting with the materials in the blender. Any moisture in the nitrogen would have been carried into the blender, and it would likely have caused reactions on the surface of the material in the blender. However, this nitrogen source included a filter to extract moisture from the supply. There was no evidence that suggests moisture was in the nitrogen.

Atmospheric humidity. Atmospheric humidity is known to react with sodium hydrosulfite and aluminum. Interviews revealed that a nitrogen blanket was placed on the contents of the blender when the blender was opened to the atmosphere, minimizing the effects of atmospheric moisture on the feed materials.

Water used to clean liquid feed line. Some information indicated that operators may have used water or steam to clear the liquid feed line in an effort to add the benzaldehyde. In this case, water would have been injected into the contents of the blender. However, the JCAIT confirmed that efforts to clean the liquid feed line after the initial attempt to inject benzaldehyde did not involve

water or steam.

Water in liquid feed line or tank. Water was noted in the liquid feed tank and line up to the in-line filter near the line's entry into the blender, prior to the attempts to inject benzaldehyde. The maintenance employees were not able to clean and dry the portion of the injection system that is inside the blender because the raw materials were charged into the blender. Several drying/vacuum procedures were performed prior to charging, yet the liquid feed line within the blender was not checked to ensure that it was dry. Any water left in this portion of the line could have been deposited in the blender as the operators attempted to add benzaldehyde. However, given that operators were not able to inject the benzaldehyde into the blender it is unknown if any water in the feed line actually entered the blender.

Water-cooled seal failure. Analysis of the graphite water-cooled seal for the intensifier bar after the explosion revealed wear patterns that could have allowed water to leak through the seal. Had the seal leaked, it is likely that the water would have been deposited in the material being blended. However, analysis did not determine whether the seal failed during the blending of the GPA or during a previous use of the blender by Napp. Before the blending of the GPA, a Napp maintenance worker noticed water near a packing gland in the blender, which could be a sign of failure of the seal. However, even though it is unlikely- based on previous cleaning operations- it is possible that water used to clean the blender could also have been the source of the water near the packing gland.

Heat generated by shear of intensifier bar moving through dry metal powder. The heat generated by the friction between the intensifier bar moving through the dry metal powders may have been adequate to initiate or contribute to the thermal decomposition of the sodium hydrosulfite. Thermal decomposition of sodium hydrosulfite is exothermic; therefore, once the decomposition was initiated, it could have continued. The intensifier bar was only used while mixing the blender contents. Overfilling the blender may have reduced the efficiency of the blending operation; therefore, heat generated would not have been distributed throughout the raw materials within the blender.

Heat generated due to particulate matter between the bearing surfaces inside the packing gland for the intensifier bar shaft. The area inside the packing gland for the intensifier bar shaft contains bearing surfaces. Had any particulate matter been between those bearings , the particulate matter and the bearings could have become excessively hot due to friction. With this area in contact with the raw materials inside the blender, heat generated due to the friction would be transferred to the raw materials. If this heat transfer is sufficient it may have been enough to initiate the sodium hydrosulfite.

4.2 Most Likely Causes of Chemical Reaction

Based on the witness testimony, physical evidence, and analysis, the JCAIT has determined that the reaction and explosion of the sodium hydrosulfite and aluminum powder was most likely initiated by two mechanisms: water introduced that initiated the exothermic decomposition of sodium

hydrosulfite; and heat which caused the sodium hydrosulfite to decompose. The JCAIT believes the most likely sources of water are the graphite water-cooled seal and the liquid feed line. The most likely source of heat was the shear of the intensifier bar moving at a high rate of speed through the dry powder.

Water from failed seal and liquid feed line. The JCAIT estimates that only a small amount of water was needed to initiate a reaction. If a large amount of water was injected into the material in the blender, the JCAIT believes a large hydrogen gas bubble would have been formed, causing a detonation with greater energy then was released in this accident. However, if a small amount of water was injected into the material in the blender, the reaction would begin a series of exothermic reactions over a longer period of time (see Appendix B). This theory is consistent with the findings of the accident investigation.

Through interviews and review of the blueprints of the blender, the JCAIT believes that if the water-cooled seal for the intensifier bar failed, it is likely that the water would have leaked into the material in the blender. Analysis of the seal after the accident revealed grooves that may have been deep enough to allow water to leak into the blender.

Additionally, the JCAIT can not rule out that any water in the liquid feed line may have been delivered into the blender when attempts were made to add benzaldehyde.

Heat generated by intensifier bar. The heat generated by the friction of the blades of the intensifier bar running through the dry chemicals in the blender may have been sufficient to initiate or contribute to the thermal decomposition of the sodium hydrosulfite. Thermal decomposition of sodium hydrosulfite is exothermic; therefore, it is possible that once the decomposition was initiated, sodium hydrosulfite in the blender continued to decompose, generating more heat. This reaction would have continued to create a "hot spot" in the material in the area below the intensifier bar. As the material was being removed by the Napp employees, the hot spot ignited, setting off the rest of the material in the blender.

4.3 Root Causes and Contributing Factors

Root causes are the underlying prime reasons, such as failure of particular management systems, that allow 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 facilitated the occurrence of the event. The root causes and contributing factors of this event have broad application to a variety of situations and should be considered lessons for the chemical processing industries which operate similar processes, especially the tolling industry.

Immediately following the accident, members of the JCAIT collected and recorded the details on the event and the circumstances leading up to the event, interviewed witnesses, and collected, photographed (see Figures 4-24) and analyzed physical evidence and documentation. In the following months, the JCAIT conducted engineering analyses of this information using elements of Events and Causal Factors and Hazard-Barrier-Target techniques and professional judgement to determine the root causes and contributing factors, and to generate recommendations to prevent a recurrence. The JCAIT concludes that the root causes and contributing factors of this accident are:

- <u>An inadequate hazards analysis was conducted and appropriate preventive actions were not taken.</u>

Through Napp's accident report and interviews with Napp employees, the JCAIT learned that most of the pre-operation hazards assessment as part of the "New Product Review" was based upon the information presented in the MSDSs for the GPA and its ingredients. MSDSs can provide adequate *chemical* hazards information but not necessarily *process* hazards information. For example, the information presented in the MSDS for the GPA was for a typical package size (up to one 55 gallon drum), not for the quantity being blended (22 drums).

Under the New Product Review Procedure using the MSDSs, Napp noted that aluminum, sodium hydrosulfite, and GPA were water reactive. However, this procedure and the MSDSs did not reveal or address accident history, identify and account for all of the potential sources of water, ways to eliminate or control these sources (engineering safeguards or procedures), recognition of water contamination of the raw materials or GPA, the immediate steps necessary to stop or handle an unwanted reaction inside the blender, and the proper technology and design of the equipment necessary to safely and effectively blend water reactive substances. In addition, the procedure did not identify that heat could also have an adverse affect on the substances in the blender. Without this information, appropriate prevention actions were not taken.

Napp successfully conducted the blending operation previously (1992) using the same process, procedures, and equipment and was unaware of any major accidents involving this product or process. However, Napp did not appear to know about, or at least consider the consequences of, past accidents that have occurred involving sodium hydrosulfite or aluminum powder.

The lack of an adequate process hazards analysis led to a lack of knowledge or understanding

that small amounts of water or heat could trigger a self-sustaining exothermic reaction at relatively low temperatures. This exothermic reaction lead to the catastrophic deflagration and fire. Napp removed sources of water in the blending room and took steps to ensure the blender and raw materials were kept dry. However, other sources of water were still present and Napp did not fully eliminate the possibility that water could contaminate the blending process and operation. Water was used to cool the mechanical seal in the intensifier bar and a water/glycol mixture was used in the heating/cooling jacket. Evidence also suggests that water may have been present in the liquid feed tank and piping system since they were not cleaned and dried prior to the startup of blending operations. This equipment was cleaned and dried during the blending operation. However, since the blender was already loaded, the liquid injection piping inside the blender could not be cleaned and dried. In addition, the intensifier bar offered a potential source of heat input from bearings and mixing shear (see equipment selection, below).

The JCAIT notes that OSHA allows the collection of the MSDSs to suffice for compliance with its information collection requirements for process safety information, provided the MSDSs contain information to the extent that enable the employer and employee involved in operating processes to identify and understand the hazards posed by these processes. Such specific information criteria include: reactivity data, thermal and chemical stability data, and hazardous effects of inadvertent mixing of different chemicals that could foreseeably occur. A review of MSDSs alone for highly hazardous processes in lieu of a formal process hazard analysis would not meet OSHA's requirements. Industry may not clearly understand this distinction which may have contributed to less than adequate hazards analyses since MSDSs were relied upon to conduct the company's new product review. As a result, thermal and chemical stability as well as inadvertent mixing of chemicals were not adequately addressed in the review process.

- Standard operating procedures and training were less than adequate.

Napp's standard operating procedures (SOPs) failed to adequately address emergency shutdown, including conditions under which emergency shutdown is required and the assignment of shutdown responsibility to qualified operators to ensure that emergency shutdown is executed in a safe and timely manner. Also, the SOPs did not address operating limits, including the consequences of deviations and steps required to correct deviations. Consequently, employees could not have been trained on these critical steps, hampering their ability to properly execute the blending process under the conditions occurring on April 20 and 21.

Napp did not recognize or understand the significance of the abnormal situation beginning on April 20 and culminating in the explosion and fire on April 21. According to Napp's procedures, the blending portion of the process should occur in less than an hour. However, employees attempted to correct a variety of deviations, including unusual odors, bubbling, pressure buildup, and difficulty adding the liquid portion, while the blending operation continued for many more hours than normal. The odors, bubbling on the surface of the contents of the blender, buildup of pressure and venting of gases from the blender all signaled that an undesired reaction had been initiated and was ongoing. There were no operating procedures to address the deviations observed, the corrective actions to be taken, or conditions under which an emergency shutdown should be triggered.

- The decision to re-enter the facility and off-load the blender was based on inadequate information.

The lack of a complete understanding of the chemical and process hazards led to a lack of knowledge of the significance of the conditions present at the time employees re-entered the facility to off-load the blender. Once the contents of the blender began reacting, the reactions were self-sustaining. As described above, the reaction had progressed to a point where employees were evacuated because of the sulfur smell coming from the blender. At the time the decision was made to unload the blender, Napp was aware of, and concerned for, the strong possibility of a fire. However, there is no evidence to suggest that Napp was aware that off-loading the blender may have exacerbated the reaction mechanisms by exposing the contents to air or that the contents could violently erupt and deflagrate. Any attempt to stop the reactions by smothering or providing a nitrogen blanket would have been ineffective (see the discussion of chemistry in Appendix B).

- The equipment selected for the GPA blending process was inappropriate.

Napp took steps to eliminate or control sources of water but elected to use blending equipment that incorporated sources of water in the design (water cooled seal, water/glycol jacket). Although regular maintenance of seals and cooling jackets helps to prevent failure and leakage, the possibility of a malfunction still exists, allowing water to contaminate the blender. The Aluminum Association, in their brochure *Recommendations for Storage and Handling of Aluminum Powders and Paste*, recommends "In mixing aluminum powder with other dry ingredients, frictional heat should be avoided. The best type of blender for a dry mixing operation is one that contains no moving parts, but rather effects a tumbling action such as a conical blender." The PK-125 blender, as previously noted, was a closed blender which, for the batch blended, contained a high speed intensifier bar for mixing. Shear from the movement of the intensifier bar through the dry powders may have been a source of frictional heat. In addition, particulate matter between bearing surfaces at the intensifier bar shaft in the packing gland area may have been a source of frictional heat.

- Communications between Napp and Technic were inadequate.

Inadequate communication between Napp and Technic also contributed to the lack of a complete understanding of the process hazards and their consequences. There is no standard or delineation of responsibilities in the toll manufacturing/blending industry which specifically assigns the responsibilities for input into hazard reviews at the toll manufacturer's facility.

Technic, Inc. is the patent holder of the GPA and is in the best position to know the hazards of its product. In this tolling operation, Technic contracted with Napp to perform the blending. Technic provided Napp with MSDSs for the raw materials and the finished product and a batch recipe ticket. As noted above, MSDSs provide *product* hazard information but generally do not provide *process* hazard assessment information. This investigation showed that Napp did not possess all the information necessary to make sound judgements regarding the responses to deviations from the procedures in the blending process. Napp is in the chemical processing industry; however, Napp did not have in-house expertise regarding the GPA, nor did it have experience in working with water

reactive materials. Although some of its employees had previously used the ingredients of GPA, Napp blended the GPA only one other time prior to this event (the previous blend was performed in 1992).

It should be noted that the MSDSs for sodium hydrosulfite and aluminum powder also gave contradictory emergency response directions. For sodium hydrosulfite, copious amounts of water should be used, while the MSDS for aluminum clearly stated "avoid water," "reacts with water," "exothermic reaction with water . . . to generate hydrogen and heat." The MSDS for the GPA advised the use of "A water spray . . . to extinguish fire." The JCAIT investigators have located numerous scientific references, which were presumably readily available to Napp management personnel as well, indicating that powdered aluminum that is moistened or wetted becomes a very serious fire hazard. The only information that Napp used to determine the emergency response procedures for handling emergencies involving the GPA was the MSDSs. However, the MSDSs do not provide sufficient information to guide a response to an uncontrolled reaction or fire, given the significant quantity of material in the blender. The recommendation in the MSDS for "small fires" was to flood with water; however, a small fire was not defined, and the amount of water necessary to flood the fire was not specified. For a fire involving an agent that is reactive with water, the addition of an inappropriate amount of water as part of an emergency response can have tragic consequences.

- The training of fire brigade members and emergency responders was inadequate.

Eight of the twelve employees who were inside the building immediately preceding the explosion (during the unloading of the GPA) were also members of the Napp fire brigade and trained to handle fire hoses. Napp was concerned about the potential for fire by arranging for hoses and personnel to be ready. However, employee training records indicate that the employees standing by with fire hoses were not trained to deal with chemical fires or emergency response operations involving chemical fires. Consequently, the lack of training of the fire brigade members and emergency responders may have contributed to the consequences since the personnel present had no training to recognize, understand, and assist with a potentially significant emergency situation.

5.0 Recommendations

Based upon the root causes and contributing factors of this accident described above, the JCAIT provides the following recommendations to prevent accidents like this one from happening in the future:

PHAs, SOPs and Training

Before handling any substance, facilities should ensure that all chemical and process hazards and the consequences and deviations associated with the chemical and process hazards are completely understood, evaluated, documented, and appropriately addressed through preventive measures. This assessment should also include accident history, chemical incompatibilities and equipment design and integrity. One way facilities can carry out this evaluation is using a formal process hazard analysis

(PHA) technique as required under the OSHA Process Safety Management Standard under 29 CFR 1910.119 or the EPA Risk Management Program Rule under 29 CFR part 68. The Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE) has prepared guidance on PHA methodologies. In addition, the hazard evaluation can identify failure areas that need to be addressed by safeguards such as engineering controls, maintenance and standard operating procedures. The standard operating procedures (SOPs) should address steps for normal operations (including startups and shutdowns), anticipated deviations from normal, the consequences of such deviations and the steps to correct them, emergency conditions and steps for emergency shutdowns and placing the operation into a safe mode. After SOPs have been developed, all operating personnel, including supervisors, should be trained on the newly developed SOPs. This training must also include recognition of deviations or upset conditions and their potential consequences and corrective actions or shutdowns.

Facilities need to clarify and understand their respective responsibilities for the discovery and assessment of chemical and process hazards and process safety information in tolling or other contracting agreements. Both parties must be clear as to who will be responsible for process safety information, including chemical hazards, technology of the process, consequences of upset conditions, and identification of any previous incidents involving similar processes. The chemical and petroleum processing industries should develop basic guidelines to be used in tolling or contracting agreements the safety of which may depend on sound communication of chemical and process hazards. EPA has requested that CCPS examine whether guidance for conducting process hazards analyses and safety information sharing in tolling agreements should be developed.

Recognition and Evaluation of Abnormal Situations

The value of a thorough assessment of the chemical and process hazards using methods such as a process hazard analysis (PHA) is greater understanding of the range of possible deviations, the consequences of the deviations, and corrective actions to safely bring the process under control. Without this information, evaluation and action to correct abnormal situations when they arise may become guesswork, placing the process, the facility, the employees, the community, and the environment at risk. Facilities should routinely review their chemical and process hazards assessments to make sure new information is included, monitor accident histories and lessons learned and consider applications to their processes, and investigate deviations, no matter how minor, to prevent more serious consequences.

Proper Use of Equipment

All facilities should ensure that equipment manufacturers' recommendations are followed and that equipment is installed, operated, and maintained as designed. Equipment manufacturers typically have a wealth of information regarding the maintenance and recommended uses of equipment they manufacture. Chemical processors and toll operators should regularly contact equipment manufacturers for updated information and seek advice should equipment application, installation, operation or maintenance needs deviate or require modification from equipment manufacturers' recommendations.

Many types of industrial vessels or other equipment use mechanical seals to permit external drive of internal equipment, such as pumps, mixers, or agitators. In certain applications, mechanical seals must be liquid cooled or purged to prolong seal integrity. While regular maintenance may help prevent failure and leakage, the possibility of a malfunction always exists. Facilities should ensure that liquids used to cool or purge seals are not incompatible with materials processed in the vessels or other equipment.

OSHA/EPA Review of Highly Hazardous Chemicals List

Appendix A of OSHA's existing Process Safety Management (PSM) standard (29 CFR 1910.119) lists the toxic and reactive chemicals covered by that standard. At the time of the process safety management rulemaking, OSHA decided to include only those chemicals having the NFPA (NFPA 49) ratings of 3 or 4 for reactivity. Chemicals rated 3 or 4 are those that are capable of undergoing detonation or explosive decomposition and generating the most severe blast or shock wave. NFPA 49 assigns sodium hydrosulfite a reactivity rating of 2 and aluminum powder a reactivity rating of 1. Because of this tragic event, OSHA is considering adding additional reactive chemicals to the Appendix A chemical list.

EPA and OSHA have agreed to harmonize their lists of substances under the PSM standard and the List of Regulated Substances for the Risk Management Program in 29 CFR part 68 promulgated under section 112(r) of the Clean Air Act. EPA's current list only addresses toxic and flammable substances. As part of the upcoming 5-year review of its list, EPA will consider other hazards, including reactive chemicals.

OSHA Review of Integration of Hazard Communication (HazCom) and Hazardous Waste Operations and Emergency Response (HazWoper) Standards, with the Process Safety Management (PSM) Standard

OSHA's HazCom and HazWoper standards, combined with the PSM standard, provide an integrated approach to worker health and safety. OSHA's Hazard Communication Standard (29 CFR 1910.1200) permits the MSDS for the components of a mixture to serve as the MSDS for the mixture. Employers that rely upon an MSDS created by other entities must be aware that the MSDS for raw materials may not identify all hazards which may be encountered when mixing, blending or processing them with other materials. This may be true even if there is no reaction anticipated or apparent. Moreover, an MSDS for the final mixture may specifically address the hazards of shipping container quantities, but may not apply to the hazards of larger quantities in the processing phase.

This accident demonstrates that a review of the MSDS is an inadequate substitute for performing a process hazards analysis. As noted above, OSHA allows the collection of the MSDSs to suffice for compliance with its information collection requirements for process safety information if the MSDSs contain information to the extent that they enable employers and employees involved in operating processes to identify and understand the hazards posed by these processes. Such specific information criteria include: reactivity data, thermal and chemical stability data, and hazardous effects of inadvertent mixing of different chemicals that could foreseeably occur. A review of MSDSs alone

for highly hazardous processes in lieu of a formal process hazard analysis would not meet OSHA's requirements. Industry may not clearly understand this distinction which, in this accident, may have contributed to a less than adequate hazards analyses. As a result, thermal and chemical stability as well as inadvertent mixing of chemicals were not adequately addressed in the review process.

In addition, many companies rely on MSDSs to communicate hazard and emergency response information with communities and first responders as required by EPA under the Emergency Planning and Community Right-to-Know Act. EPA and OSHA will consider whether additional guidance or outreach in the form of an Alert or other means is necessary to advise industry and first responders to make sure that MSDSs are not used beyond their intended design, to highlight areas where information can be misunderstood, and to make sure that hazards information is complete. The American National Standards Institute (ANSI) in cooperation with the Chemical Manufacturers Association (CMA) is working to revise an existing ANSI uniform MSDS format. CMA and ANSI and other industry organizations should also evaluate whether additional consensus standards or guidelines are needed for MSDS consistency and to avoid misunderstandings (e.g. the difference between chemical and process hazards) or faulty interpretations of terms (e.g. small fires or small amounts of water).

As a result of the devastating loss of five emergency responders in this event, OSHA clarified its HazWoper Standard (29 CFR 1910.120) and its Employee Emergency Plans and Fire Prevention Plans (29 CFR 1910.38) (Memorandum For All Regional Administrators; Subject: Update to HazWoper Emergency Response Guidance: Coordination with Local Fire Departments; Oct. 30, 1996). This clarification, while written for compliance officers, gives employers guidance for conducting appropriate emergency response actions as part of their emergency response plans contained in the subject standards.

Finally, as a result of this accident, OSHA issued a Hazard Bulletin about MSDSs in July 3, 1996, recommending that a process safety analysis be performed for all materials with catastrophic potential, even if not covered by the PSM standard. The analysis should include a cautious review of chemical hazards, incompatibilities and a thorough examination of all mechanical equipment. Standard operating procedures should be developed and the consequences of deviation ought to be identified. Further, employers that rely on MSDSs created by other parties must be aware that MSDSs for raw materials may not identify all hazards that might be encountered when mixing or blending with other materials. This may be true even if there is no anticipated or apparent reaction. MSDSs for the final mixture may specifically address the hazards of shipping container quantities, but may not apply to the hazards of the larger quantities needed to make the mixture.

6.0 Outcomes of OSHA/Napp Technologies Settlement

As part of the settlement between Napp Technologies and the Occupational Safety and Health Administration, Napp agreed to the following items: 1) conduct a comprehensive review of all SOP's for worker health and safety issues and compliance with worker safety and health standards; 2) conduct periodic comprehensive safety and health audits utilizing a qualified independent safety and health professional and develop action plans to abate all hazards found; 3) contract with a qualified

safety professional to train Napp Safety Council members (including supervisory, technical and employee representatives) to perform their duties effectively; 4) create an SOP institutionalizing review all facility processes to identify those that should undergo a more detailed process hazard analysis; and 5) designate a responsible management official whose primary responsibility will be to oversee Napp's safety and health program, worker health and safety issues and compliance with applicable health and safety standards.

Appendix A

Results of Analysis of the Accident

Chemical Analysis Results

The results of the chemical analyses of the residues in the blender taken by EPA's Environmental Response Team revealed the presence of percentage amounts of various metals such as sodium, potassium and aluminum. This was expected, inasmuch as these metals were part of the GPA mixture. In addition, the sampling revealed the presence of large amounts of phenol and methylphenol compounds. Phenol was detected in internal ash samples and in an external crevice ash sample. To a lesser degree 2-methylphenol and 4-methylphenol were also detected in the ash samples.

Phenol and the methylphenol compounds were likely due to the insulating material remnants which were originally located in the annulus between the outer wall of the blender and the outer wall of the water-glycol jacket. Additionally, a review of the chemistry of benzaldehyde suggests that the presence of phenol and phenol compounds can be explained as follows: the aluminum in the blender had reacted with the water and sodium hydrosulfite, causing an exothermic and reducing atmosphere to form inside the blender. This resulted in the conversion of whatever benzaldehyde had been successfully introduced into the blender to a methyl hydroxy (alcohol) intermediate. This material, in the reducing environment inside the blender, was transformed to toluene, another intermediate. The toluene was in turn converted to phenol, and to a lesser degree 2-methyl phenol, and 4-methyl phenol. This reaction is a classic electrophilic aromatic substitution in which methyl groups reform preferentially onto the benzene ring in the ortho and para positions (relative to the OH group in phenol), creating phenol, and the 2- and 4-methyl phenol species respectively. This chemistry tends to eliminate the possibility that phenol, rather than benzaldehyde, had been inadvertently added to the GPA blend.

Post-Explosion Analysis of Blender

After the accident, members of the Materials Reliability Division of the National Institute of Standards and Technology (NIST) analyzed the remains of the PK-125 blender. A visual examination of the blender revealed that the outer jacket of the blender was ripped loose at the access ports and was peeled away from the stainless steel shell of the blender. The damage initially appeared to be the result of a steam explosion inside the water jacket lining. The shell sustained little gross deformation except near the bottom unloading hatch assembly area.

The bottom portion of the blender, where the discharge port was located, was severely deformed, and most of the unloading hatch assembly was missing. Much of this damage was probably caused by impact when the blender was propelled through the block wall of the blender room and/or immediately afterwards as it came to rest. The metal surrounding the discharge port was most likely very hot, which would have facilitated deformation.

The metal surrounding the access ports had striation marks resembling those typical of oxyacetylene cuts in steel. The striation marks are believed to be due to erosion that occurred when material from inside the blender was violently ejected from the loading ports at high temperature and velocity.

Further visual observations were performed by NIST personnel off-site. The surface of the stainless steel shell was examined for any visible cracks through which water (from the water jacket) could have entered the blender. With the exception of a small crack (several millimeters long) located near the discharge port, there were no visible signs of cracking. This damage is believed to have occurred during the accident and was not part of the initiating event. No localized areas of melting or heat tinting were observed.

A metal tube, approximately 400 millimeters (mm) diameter, to which the support flange is fastened on Lobe A of the blender, is welded to the stainless steel shell inside the blender. This tube had a sheet metal cover/seal on the end. Through this cover, a series of concentric pipes and shafts (vacuum tube assembly) enter the blender. The cover, which is approximately 1.5 mm thick, was severely deformed and bent in a manner suggesting that the concentric pipes were torn or blown out of the blender in the accident. Inspection of the cover inside the blender showed severe erosion damage around the opening through which the concentric pipes entered the blender. These erosion markings are similar to those found on the access ports and indicate GPA material was ejected out of this opening of the blender as well.

The interior shell near the off-load port is slightly buckled. This deformation most likely resulted from impact damage during the accident. The damage on the outside of the blender around the off-load port is more extensive. The wedge-shaped configuration of the damage was probably caused by the impact during the accident.

The most notable features on the surface of the interior were the erosion marks. These markings likely resulted from the ejection of heated material from inside the blender during the accident. The erosion was confined principally to the surfaces of the interior that form the "V" between the two lobes. The erosion occurred mostly within a region that was approximately one meter wide near the seam between the two lobes of the blender. The heaviest erosion damage is limited to a region about 200 mm wide near the centerline. The surface at the seam is not eroded. Erosion appeared on the surfaces adjacent to the seam, in the lobes, and at the top of the lobes (around ports). In both lobes, it appears that the erosion on the top side of the centerline is most severe. In addition, the erosion at the tops of Lobes A and B differ: on Lobe B the erosion is dimple-like around the access port, resembling impact damage, and erosion on Lobe A is wavy lines (flow-like) cut into the surface of the shell.

The concentric pipes and shafts of the vacuum tube assembly enter the blender (Lobe A) through the support tube. On the outside of the blender, near the end of the vacuum tube assembly, is a water-cooled graphite seal that allows the agitator shaft to turn at high speed. Examination of the seal components showed that the inboard steel ring was fractured and that the inboard graphite seal had radial fissures and circumferential gouging. The depth of the grooving was measured on a

replicated surface of the inboard seal. The measurements were made on an optical microscope with a calibrated z-axis. Typically, the depth of the grooves varied from 25 to 125 microns. The width of the groove exceeded 1 mm in some regions; these grooves may have allowed water to pass through the seal over time.

Coroner's Report

This report will not detail the injuries sustained by those Napp employees who perished in the explosion. However, the physical condition of the victims provides some insight into the nature of the chemical reactions that occurred inside the PK-125 blender.

Autopsy information provided investigators by the Bergen County Medical Examiner indicates that the deceased employees suffered a combination of trauma, burns, and smoke/fumes inhalation. There were no physical signs that the victims had been subjected to the explosive force of a detonation. Rather, the physical signs indicated that what occurred was a deflagration, not a detonation. The main difference between the two is the rate of energy release and the amount of overpressure generated by the instantaneous and violent reactions of the materials involved. Had a hydrogen gas explosion occurred, it has been calculated that the entire plant, as well as a significant portion of the nearby homes, would have been destroyed in the blast. The extent of the damage, although catastrophic by any standards, was indicative of an explosion with a lower rate of energy release than that which would have been produced by hydrogen gas. This physical evidence indicates that the reactions that occurred involved the decomposition of sodium hydrosulfite and subsequent reaction products interacting with powdered aluminum.

Appendix B

Chemical Reactions

Sodium Hydrosulfite

Sodium hydrosulfite decomposes exothermically in the presence of heat, moisture, or air. Although sodium hydrosulfite is flammable, it is not explosive. Contact with small amounts of water or moist air will cause a chemical decomposition reaction that generates sufficient heat to ignite combustible materials. In one reported accident (Bretherick 1990), smoldering started when water entered a drum of sodium hydrosulfite, which then ignited when tipped over for disposal. In another case (Bretherick 1990), a batch of sodium hydrosulfite violently decomposed during drying in a graining bowl. The likely explanation was contamination with water and/or oxidant.

Exposure of sodium hydrosulfite to moisture, either from humid air or traces of water, can cause reactions that may generate enough heat to initiate thermal decomposition (NFPA 49, 1994). The reaction of sodium hydrosulfite ($Na_2S_2O_4$) with water can produce sodium bisulfite ($NaHSO_3$) and sodium thiosulfate ($Na_2S_2O_4$) (Equation 1). Because sodium bisulfite is an unstable solid compound (Kirk-Othmer 1983), it most likely decomposes to sodium metabisulfite ($Na_2S_2O_5$) and water (Equation 2). Sodium metabisulfite may then decompose to sodium sulfite (Na_2SO_3) and sulfur dioxide (SO_2) (Equation 3). Therefore, the bubbling of the GPA materials that was observed by a supervisor in the early morning of April 21 can be explained by the generation of sulfur dioxide. Because water is produced in this suggested reaction scenario, the overall reaction becomes self-sustaining; only a small amount of water is needed to initiate the exothermic reaction. As the reaction proceeds, the temperature of the blender and the GPA components would have increased.

(1) $2Na_2S_2O_4 + H_2O \rightarrow 2NaHSO_3 + Na_2S_2O_3$

(2) $2NaHSO_3 \rightarrow Na_2S_2O_5 + H_2O$

(3) $2Na_2S_2O_5 \rightarrow Na_2SO_4 + SO_2 + S$

Only catalytic amounts of water are needed to make the decomposition self sustaining. In closed vessels, decomposition is likely to occur simultaneously with pressure buildup at low temperatures.

Anhydrous sodium hydrosulfite has a tendency to decompose spontaneously as in the following equation (Equation 4), forming sodium thiosulfate and sodium sulfite and releasing sulfur dioxide. Because this reaction is exothermic, the temperature of the GPA components would have continued to increase. This increase in temperature would have accelerated the decomposition and, thus, the production of sulfur dioxide, resulting in violent surface bubbling of the reaction mixture.

(4) $2Na_2S_2O_4 \rightarrow Na_2SO_3 + Na_2S_2O_3 + SO_2$

The reaction is violent above 150 - 190C. Simple geometry influences the mode of decomposition. In 'heap' samples, insulation, and therefore self heating, is greater than in thin layers of the chemical. When a sample was heated at 15C per minute, a sudden exotherm of 47 kilojoules per mole (kJ/mol) occurred at 205C (Goodhead, 1974). Another investigator performing calorimetry experiments on sodium hydrosulfite found that there were two large exotherms preceded by a small one (Tartani and Contessa). The initial decomposition temperature was lowered by 50C (from 110C) in the presence of 0.5 to 1% water. The investigator concluded that in closed vessels, the two sets of reactions above (i.e., wet and anhydrous sodium hydrosulfite) occur simultaneously with buildup of pressure at low temperatures.

The intensifier bar rotating at a high speed, cutting through the aluminum powder and other GPA materials, may have generated frictional heat. Although tumbling the contents of the blender may have distributed some of the heat, the use of the intensifier bar may have contributed to the continuation of the sodium hydrosulfite/aluminum/water reaction.

Aluminum

Aluminum is a strongly electropositive metal and is very reactive, burning rapidly in air when strongly heated. Finely divided aluminum powder or dusts forms highly explosive mixtures in air (flash point of 645C). Ignition may be the result of heat, shock or abrasion; it may also be spontaneous due to humidity or moisture. A severe explosion occurred in a plant producing fine aluminum powder in 1983 (Bretherick 1990). Fires and explosions have occurred during grinding and polishing operations where sparks may have set off the reaction. Because of the extreme exothermic nature of its reaction with air, aluminum is used as a metal fuel. It is incorporated into explosives to increase the energy released. The use of substantial amounts of aluminum powder under high temperatures with the reduction of liberated carbon dioxide and water by the metal is used in conventional explosives enhances the energy release by up to 100%.

In a finely divided form, aluminum will react violently with boiling water to form hydrogen and aluminum hydroxide; the reaction is slow in cold water. Under ordinary circumstances, aluminum is passivated by the formation of a layer of aluminum oxide. If this protecting layer is breached, reactions consistent with its strong electropositive character may occur. In handling fires where aluminum dust is present, one is warned not to use water. In one case where aluminum dust was ignited by sparks from a grinding machine, the activation of an automatic sprinkling system and the reaction of the water with burning metal resulted in the liberation of hydrogen, which, after mixing with air, exploded (Bretherick 1990). In the Bretherick case, the primary explosion created an aluminum dust cloud which exploded forcefully, producing more dust and encompassing more aluminum dust, resulting in four tertiary explosions in all.

Because of its high affinity for oxygen, aluminum is used in metallothermic reductions of metal compounds. These reactions produce enormous amounts of heat. For example, in its reaction with chromic oxide, molten chromium (melting point 1907C) is formed. Thermite-type reactions may also occur with non-metals such as sodium hydrosulfite, sulfur dioxide, and carbon oxides. Even though sodium hydrosulfite is a reducing agent, aluminum has such an affinity for oxygen that it can

extract oxygen from these compounds. A violent explosion occurred when an 8:3 molar mixture of aluminum powder and sodium sulfate was heated to 800C (Bretherick 1990). Application of sodium carbonate to red hot aluminum caused an explosion (Bretherick 1990). At high temperatures, aluminum powder also reacts violently with sulfur to form aluminum sulfide.

As examples, aluminum powder may react with sodium hydrosulfite or sulfur dioxide, produced from the decomposition of sodium hydrosulfite, according to the reactions:

$$4Al + 3SO_2 \quad 2Al_2O_3 + 3S$$

$$2Al + Na_2S_2O_4 \quad Na_2O + Al_2O_3 + 2S$$

The heats of reactions at 25C are -615.3 kJ/mol Al and -428.9 kJ/mol Al, respectively.[1]

In another case, butanol attacked an aluminum gasket at 100C, liberating hydrogen (Bretherick 1990). Other alcohols would react similarly. Benzyl alcohol is produced by the reaction of benzaldehyde with sodium hydrosulfite. Therefore, conditions may exist in the reaction vessel for a similar reaction of benzyl alcohol and aluminum powder to occur.

Reactions Occurring in Mixture

The predominant reactions taking place probably were the exothermic reaction of sodium hydrosulfite with water, or with water and oxygen; the exothermic reaction of aluminum powder with water; the exothermic thermal decomposition of sodium hydrosulfite, which would have been initiated by heat from the exothermic reactions; and the exothermic oxidation of hot aluminum powder, which would have been initiated when air contacted the blender contents. The reaction products expected are consistent with the results of the chemical analysis of the site (EPA Trip Report, July 5, 1995). The source of the large phenol concentration noted in the grab samples from the blender does not seem to be a result of the reactions of the reported mixture materials, but most likely occurred at some time during initial attempts to blend the GPA components.

Calorimetry Studies

The following are the results of accelerated rate calorimetry (ARC) studies of sodium hydrosulfite and a sample approximating the composition of the GPA. The purpose of the studies was to measure the heat released from these substances in the presence of water to determine the hazard posed by these substances. Calorimetric studies obtained from the literature and a limited study conducted by the Salt Lake Technical Center confirm that the mixture was extremely hazardous. These studies confirm that small quantities of water were capable of inducing a runaway reaction at relatively low temperatures and that the presence of aluminum in the mixture provided a substantial increase in the amount of heat released during the decomposition.

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[1] The heats of formation were obtained from CRC Handbook of Chemistry and Physics, 75th edition and Lange's Handbook of Chemistry, 13th edition.

A review of the literature disclosed a study entitled "Water Influence on Thermal Stability of Sodium Dithionite" (presented by V. Tartari and S. Contessa at the 5th International Symposium "Loss Prevention and Safety Promotion in the Process Industries," sponsored by the Societe de Chimie Industrielle, 28 rue Saint-Dominique, F75007, Paris. This accelerated rate calorimetry (ARC) study of the effect of water on the decomposition of sodium hydrosulfite ($Na_2S_2O_4$, sodium dithionite) demonstrated that addition of less than one percent of water to a sample of sodium hydrosulfite reduced the temperature at which self-heating begins from approximately 111C down to approximately 60C. Based on these results, the authors conclude that a small amount of water strongly influences the thermal stability of this material.

Additional, but limited, studies were conducted by the Salt Lake Technical Center using ARC methods to determine the effects of including aluminum in a mixture containing sodium hydrosulfite and potassium carbonate. Under these conditions, which mimic the insulated (adiabatic) conditions in the core of the mixer leading to thermal runaway, the net adiabatic temperature rise for 3.5 grams (g) of the mixture without the aluminum was 34C. For a comparable amount of the mixture including aluminum and approximating the composition of the ACR9031 mixture, the temperature excursion went off scale, and the experiment had to be scaled down. For 0.5 g of the mixture containing the aluminum, the net adiabatic temperature rise was 486C. From these data, the heats of reaction were determined. These studies demonstrated that the addition of the aluminum produced an eleven-fold increase in the amount of heat released per gram of mixture.

Appendix C

Accidents Involving Sodium Hydrosulfite and Aluminum

Sodium Hydrosulfite

The events leading to the explosion at Lodi involved the exothermic reaction of sodium hydrosulfite with water, followed by thermal decomposition of sodium hydrosulfite. A number of accidents are reported in the literature involving reaction of sodium hydrosulfite with water and generation of sulfur dioxide. Exhibit C-1 below provides short descriptions of some accidents involving fires, explosions, or reactions of sodium hydrosulfite, culled from media and other sources. This exhibit does not include reports of spills of sodium hydrosulfite where no serious consequences resulted, but evacuations were carried out as a precaution.

Exhibit C-1
Accidents Involving Fires, Explosions, or Reactions of Sodium Hydrosulfite

Location	Date	Description	Effects on People
Savannah, GA	4/1/95	Large fire may have resulted from tank leaks that caused the mixing of crude sulfate turpentine and sodium hydrosulfite.	None reported
Chemical plant, Wuxi, Jiangsu, China	3/24/95	Drums containing sodium hydrosulfite exploded (no details available).	6 killed, 5 injured
Commercial laundry, Rhode Island	6/14/94	A small chemical fire was reported in a storage drum containing sodium hydrosulfite.	None reported
Philadelphia, PA	3/23/94	Water, possibly from a roof leak, hit a 30-gallon drum of powdered sodium hydrosulfite, generating fumes.	4 workers injured, 12 evacuated
Accrington, Lancashire, UK	3/5/92	Drum of sodium hydrosulfite came in contact with moisture and began giving off sulfur dioxide. Several gallons of water were used to dilute chemical.	8 people (company staff) evacuated
Los Angeles, CA	11/28/90	A 35-gallon drum filled with sodium hydrosulfite burned.	2 firms evacuated
Paper manufacturer, Madawaska, ME	11/6/90	A spill of 5,000 pounds of solid sodium hydrosulfite led to a release of sulfur dioxide.	11 workers injured
Trucking Company, Galveston County, TX	6/9/90	A trailer of sodium hydrosulfite caught fire.	16-block area evacuated; no injuries

Exhibit C-1 (continued)

Location	Date	Description	Effects on People
Rail depot, Kensington, Victoria, Australia	4/20/90	Sodium hydrosulfite leaked from a shipping container that held 122 drums and reacted with moisture to form a huge toxic cloud. Firemen neutralized the leak.	1300 residents evacuated
Landfill in Orlando, FL	1/26/90	Fire started when a small amount of calcium hypochlorite was added to a drum containing sodium hydrosulfite.	Evacuation reported
Chemical plant, Phoenix, AZ	4/6/89	A drum of sodium hydrosulfite ignited while in storage.	None reported
Chemical plant, Rocky Mount, NC	6/28/89	Rain apparently fell into a rusted 30-gallon container of sodium hydrosulfite, causing a chemical reaction that formed a vapor cloud.	16 people treated, 1 hospitalized
Dye plant, Los Angeles, CA	5/25/89	Fire of sodium hydrosulfite reported.	Evacuation reported
Henrico, VA	2/15/89	Sodium hydrosulfite "ignited itself" inside a 35-gallon drum in the parking lot.	None reported
Chemical truck, Daglingworth, Gloucestershire, UK	1/13/89	Driver of truck carrying drums of sodium hydrosulfite noticed one on fire. Water was sprayed onto drums, which then exploded. Sixty-foot cloud of sulfur dioxide formed.	Residents told to stay inside
Chemical truck on highway, Covington, LA	1/1/89	A truck carrying 43,000 pounds of granular sodium hydrosulfite burst into flames.	12 miles of interstate highway closed, residents evacuated in a 1-mile radius
Chemical distribution, and storage company, NC	3/88	A fire was blamed on improper cleanup of a chemical spill. Employees accidentally punctured a drum of sodium hydrosulfite; the spill area should have been deluged with "massive amounts" of water.	None reported
Northenden, Greater Manchester, UK	1/20/87	A drum of waste sodium hydrosulfite periodically ignited and released toxic fumes. Firemen used water to cool the drum.	20 nearby residents evacuated suffering from nausea and sore eyes
Liverpool, Merseyside, UK	11/11/85	A chemical fire broke out in the hold of a cargo ship. As a drum of sodium hydrosulfite was being offloaded, some material was spilled and instantly ignited, causing a flash fire.	7 people injured by inhaling vapor

Exhibit C-1 (continued)

Location	Date	Description	Effects on People
Dye plant, Leicester, Leicestershire, UK	10/16/85	Water got into a drum of sodium hydrosulfite, which ignited, giving off poisonous fumes.	1 injury, evacuation reported, residents complained
Penang, Malaysia	11/24/80	A vessel carrying 4,800 drums of sodium hydrosulfite caught fire. Some of the drums were transferred to barge, but many had their lids blown off in the heat. Dense poisonous fumes were given off.	None reported
Avonmouth, Avon, UK	6/10/80	A truck containing 160 drums of sodium hydrosulfite overturned. Heavy rains caused severe problems.	42 people injured

Sources: Newspaper reports (on-line literature search), United Kingdom's Major Hazard Incidents Data Service (MHIDAS) database, EPA's Accidental Release Information Program (ARIP) database

Aluminum Powder

The Lodi explosion likely involved the aluminum powder in the mixing vessel. Aluminum powder has been reported in a number of accidents with fires or explosions. Fine aluminum powder, like other finely powdered materials, has the potential to explode when dispersed in air. In addition to dust cloud explosions involving aluminum, there are several reports in which mixtures of aluminum powder and other chemicals exploded (e.g., an explosion of aluminum powder and glass-making chemicals in a mixing machine). A case of ignition of aluminum powder in hot weather is also reported. Exhibit C-2 presents brief descriptions of some accidents that involved fires or explosions of aluminum powder, culled from media and other sources.

Exhibit C-2
Accidents Involving Fires or Explosions of Aluminum Powder

Location	Date	Description	Effects on People
Glass factory, Pittsburgh, PA	9/4/93	A mixture of aluminum powder and glass-making chemicals exploded in a mixing machine. The cause of the explosion is unknown.	1 worker killed
Aluminum flake processing plant, Darwen, Lancashire, UK	9/91	An explosion blew the roof off the plant and caused a fire. The cause of the explosion is unknown; a possible cause is failure to stop process while maintenance was being carried out.	1 worker killed, 2 injured

Location	Date	Description	Effects on People
Aerojet industry, Sacramento, CA	7/26/91	A compound of potassium perchlorate and aluminum powder exploded.	1 worker cut and seriously burned
Truck on highway, VA	7/24/91	Aluminum powder ignited while being transported in hot weather. The aluminum powder was reported to be properly contained, but the container might have deteriorated during a heat wave.	None reported
Newburgh, IN	5/16/90	A gap in an exhaust duct allowed aluminum fines and dust to be dispersed in the air. Welding sparks ignited the dust, creating a fireball.	1 worker injured
Darwen, Lancashire, UK	3/27/89	An exothermic reaction occurred in an aluminum powder storage area, starting a fire which consumed about 40 metric tons of aluminum. The fire spread to other parts of the factory and was allowed to burn itself out.	None reported
Mixing plant, Eaton Township, OH	7/2/86	An aluminum powder compound exploded at a mixing plant, lifting the roof off. The cause of the explosion was unknown.	8 workers injured
Aluminum powder company, Gwynedd, Anglesey, UK	7/16/83	Explosion in powder collection system sent fireball hundreds of feet in the air; two more explosions and a fire followed. All buildings within 200 yards were wrecked, and debris blocked rail line.	5 people injured
Chemical works, Widnes, Cheshire, UK	2/6/83	A dust explosion occurred during filling operation when aluminum powder was being put into drums.	1 person killed
Aluminum works, Hermillion, France	2/2/80	Several buildings were destroyed in 3 explosions. Fire raged for 6 hours.	None reported
Albany, CA	1/23/78	Explosion occurred in building where aluminum powder was precipitated and graded. Considerable damage inside and outside plant.	1 person injured
Metalwork plant, Chicago, IL	4/16/53	Plant demolished by fire following dust explosion ignited by polishing machine.	35 people killed, more than 20 injured

Sources: Newspaper reports (on-line literature search), United Kingdom's Major Hazard Incidents Data Service (MHIDAS) database, Occupational Safety and Health Administration (OSHA) database

Appendix D

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Appendix E

Photos of Napp Technologies Equipment and Facility

Figures 4 - 24

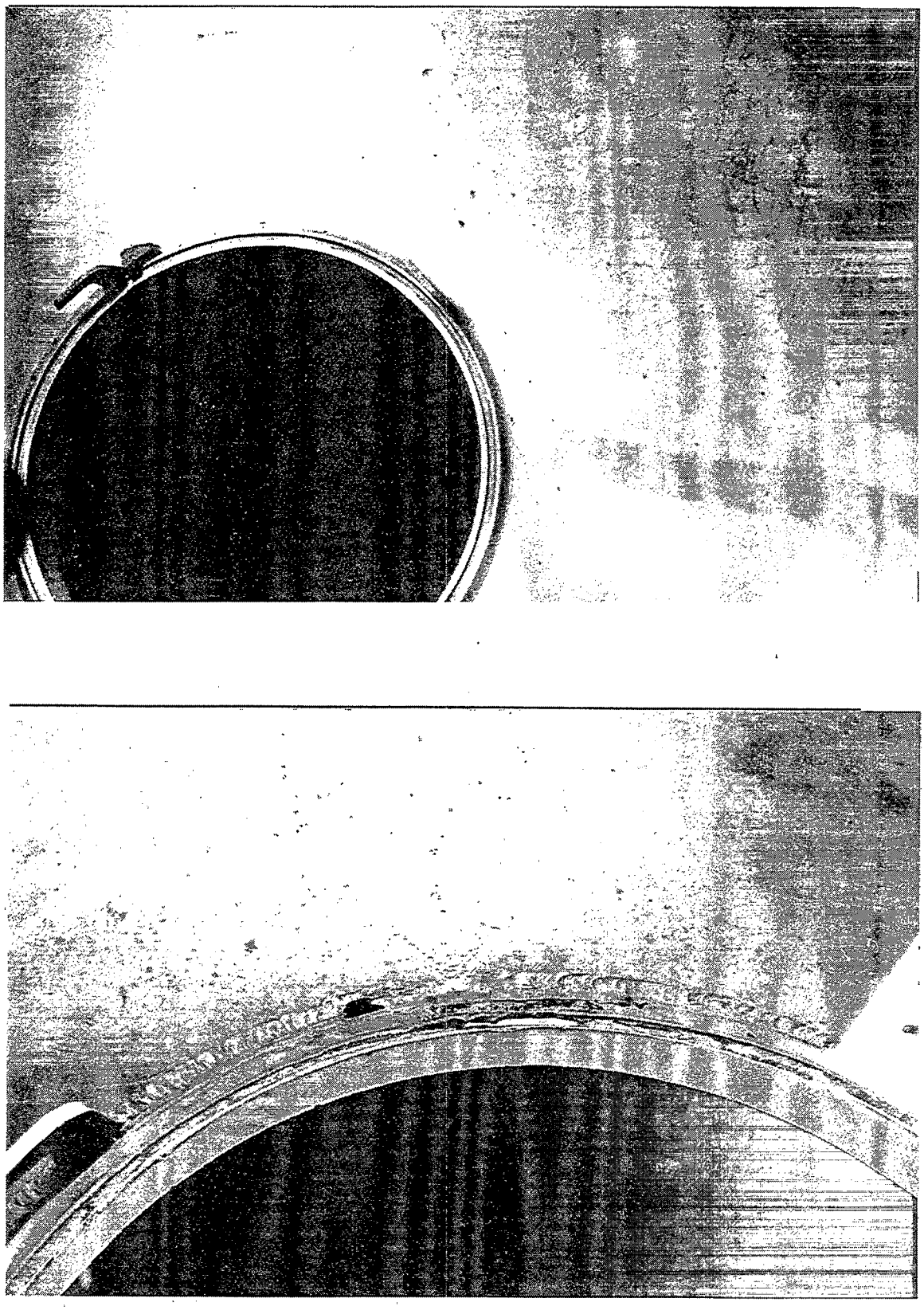


Figure 4: One of the top loading ports on the 150 cubic foot blender showing how the insulation jacket is attached (weld) and access door tabs.

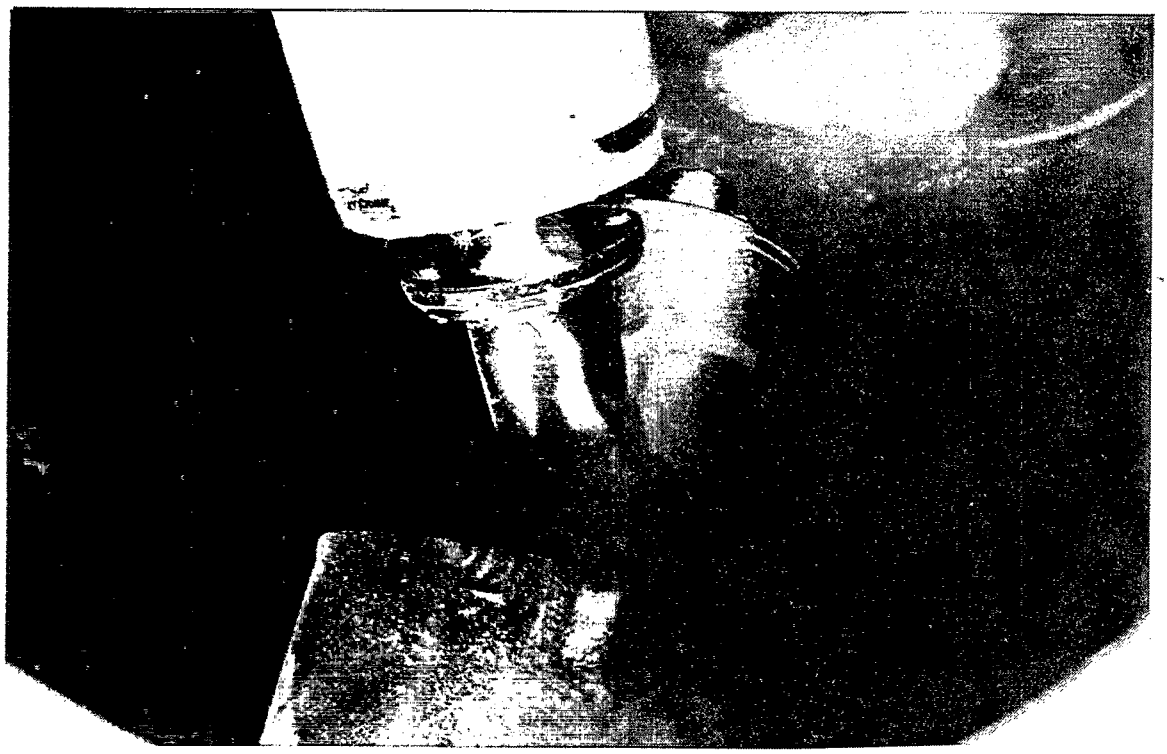


Figure 5: Inside a PK-150 cubic foot blender, looking through top access port, the vacuum head and spray nozzle configuration can be seen.

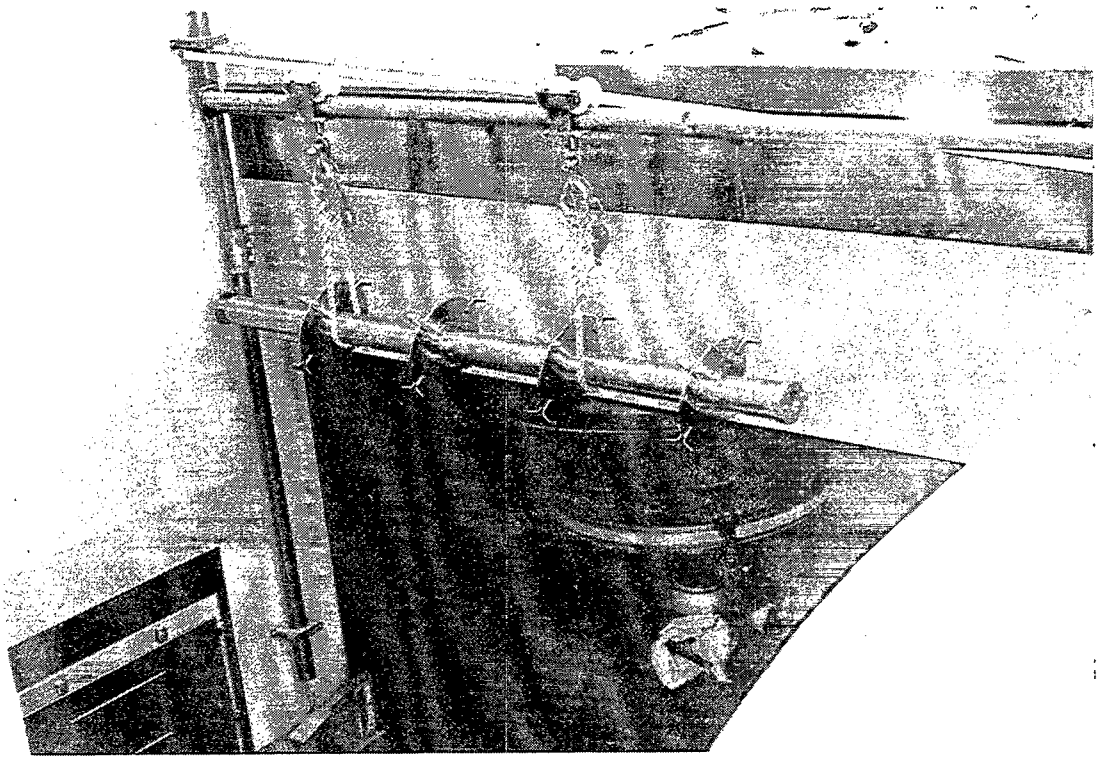


Figure 6: The intensifier bar for a PK-150 cubic foot blender shown in its storage position.

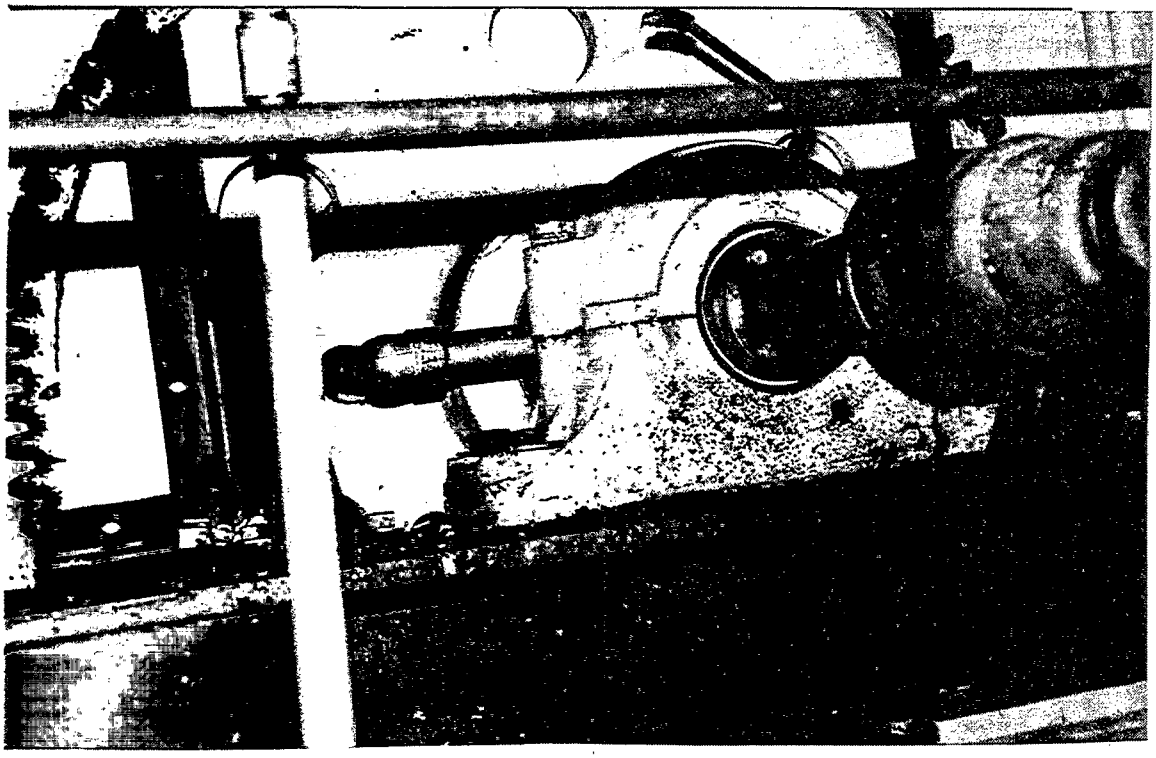


Figure 7: The gear drive and bearing that supports one side of a 150 cubic foot blender.

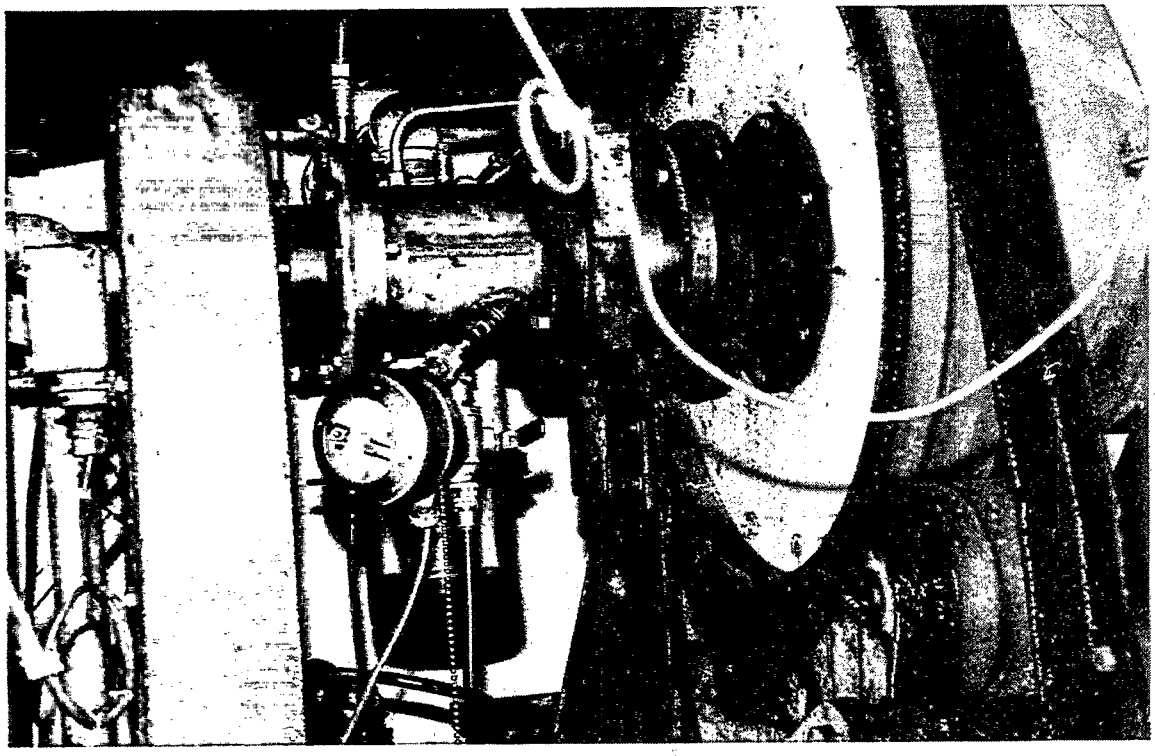
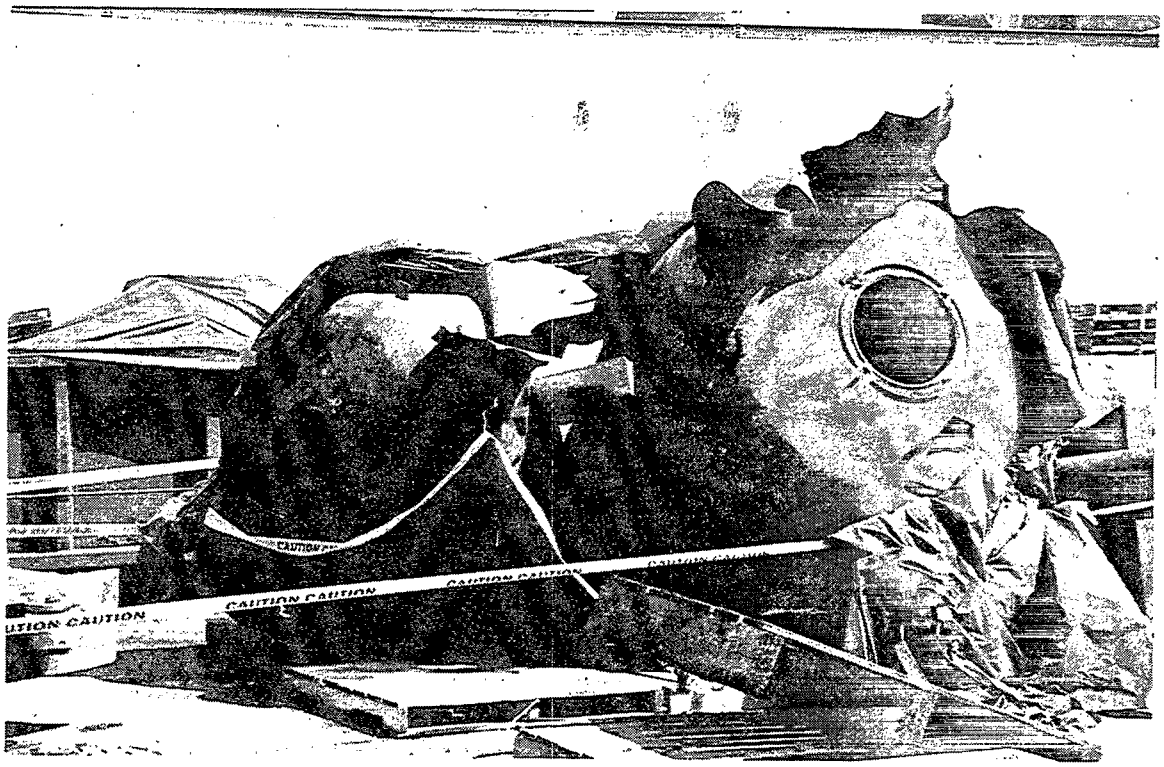


Figure 8: The other side support (intensifier bar drive side) of a 150 cubic foot blender.



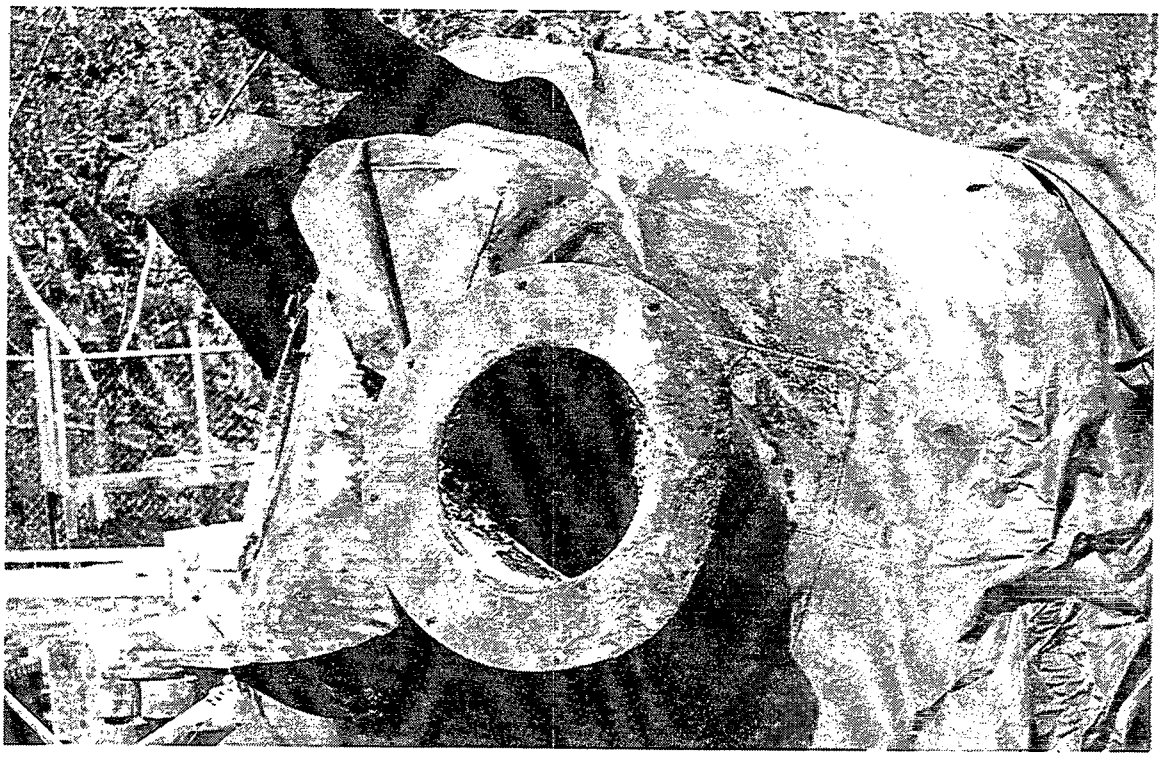


Figure 9: The general condition of the 125 cubic foot blender: a) the top access ports and damaged insulation jacket, and b) the flange to which the belt drive attaches.

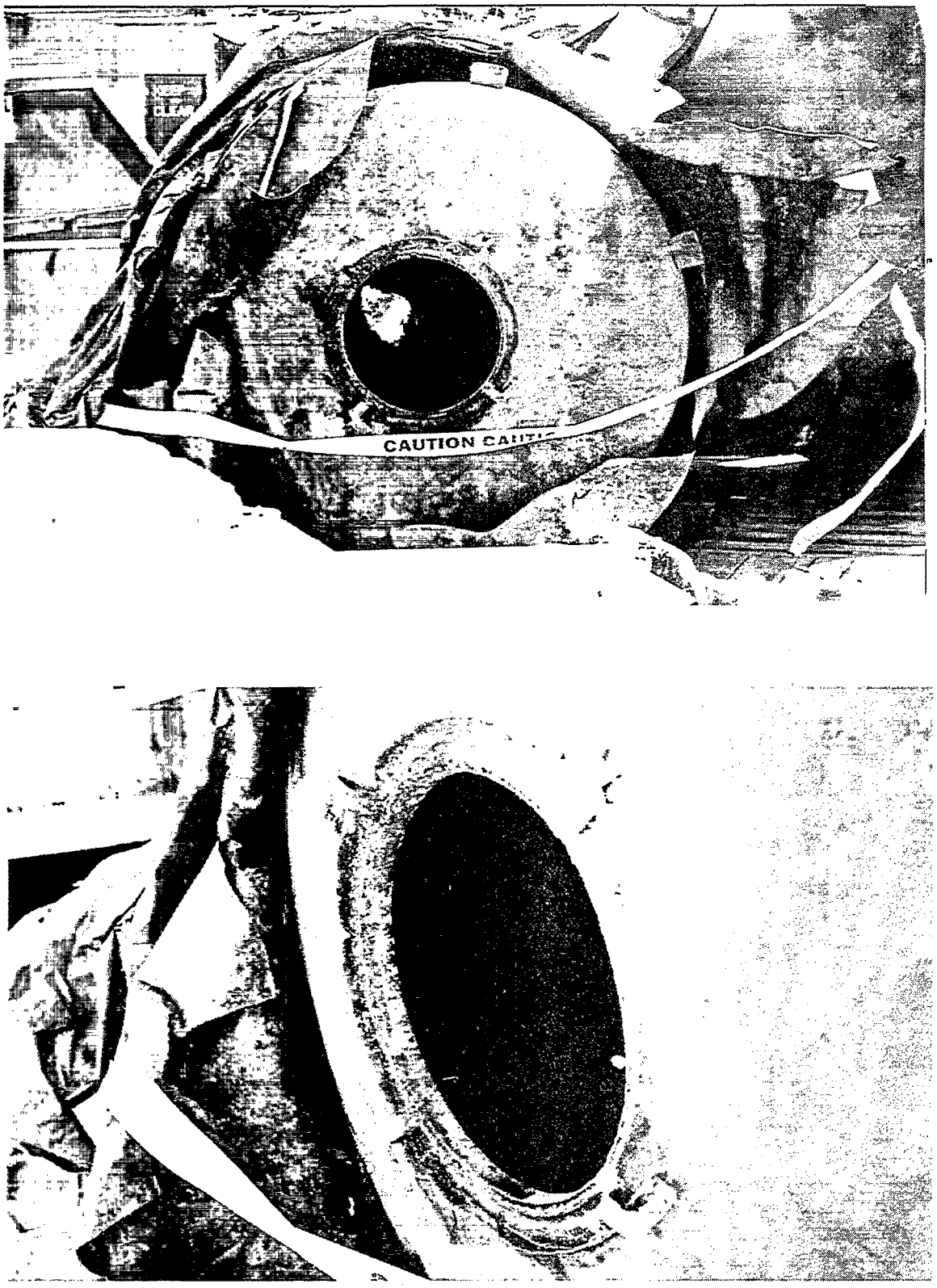


Figure 10: Top access port: a) looking through a top port and out the bottom off-load port, and b) close-up view of a top port.

Figure 11: The bottom off-load port of the blender was severely damaged in the accident: a) the stubs of the flange bolts that held the door to the port are visible, b) general deformation to the water jacket and shell.

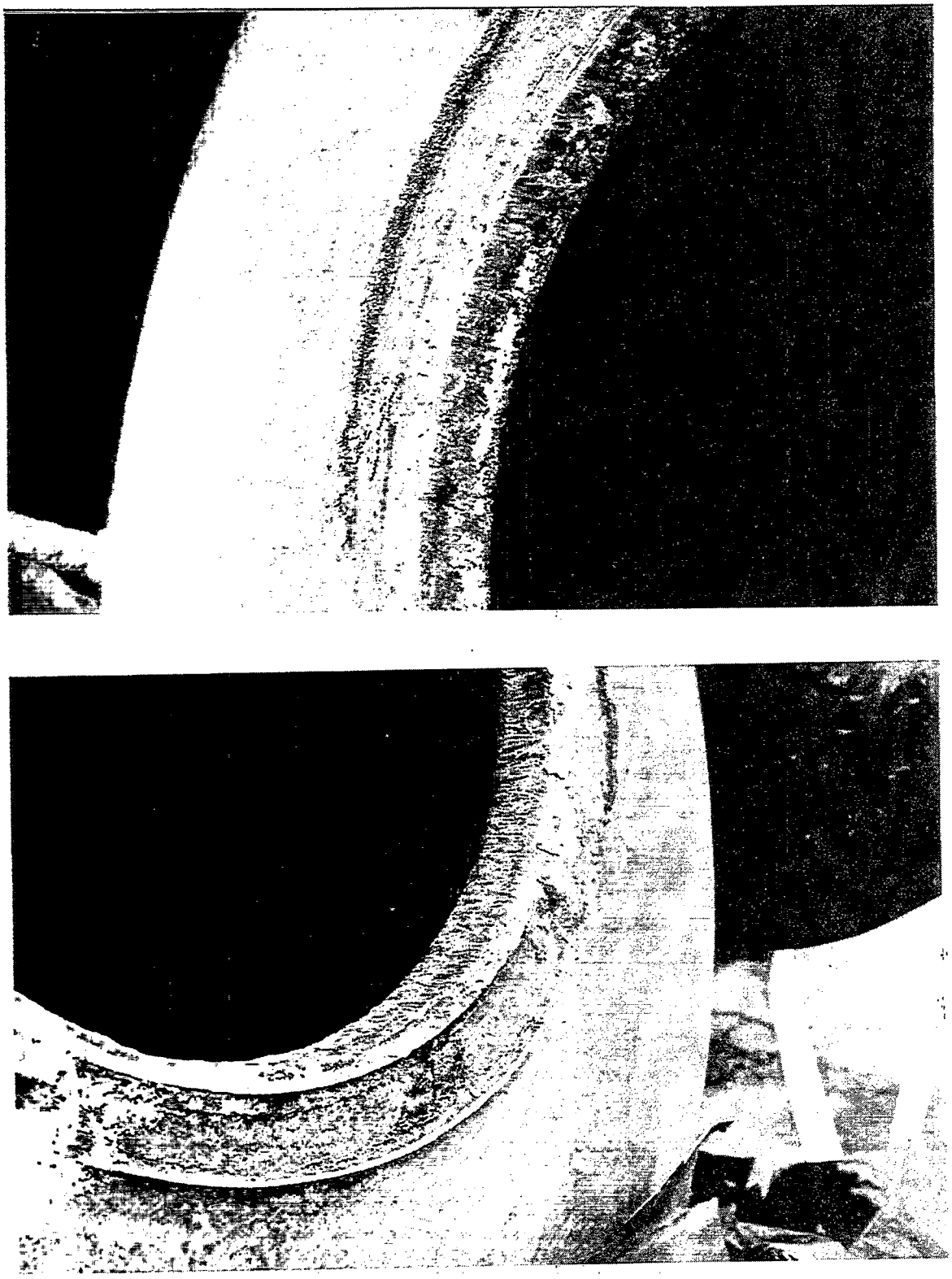


Figure 12: The striation markings on the top access ports.

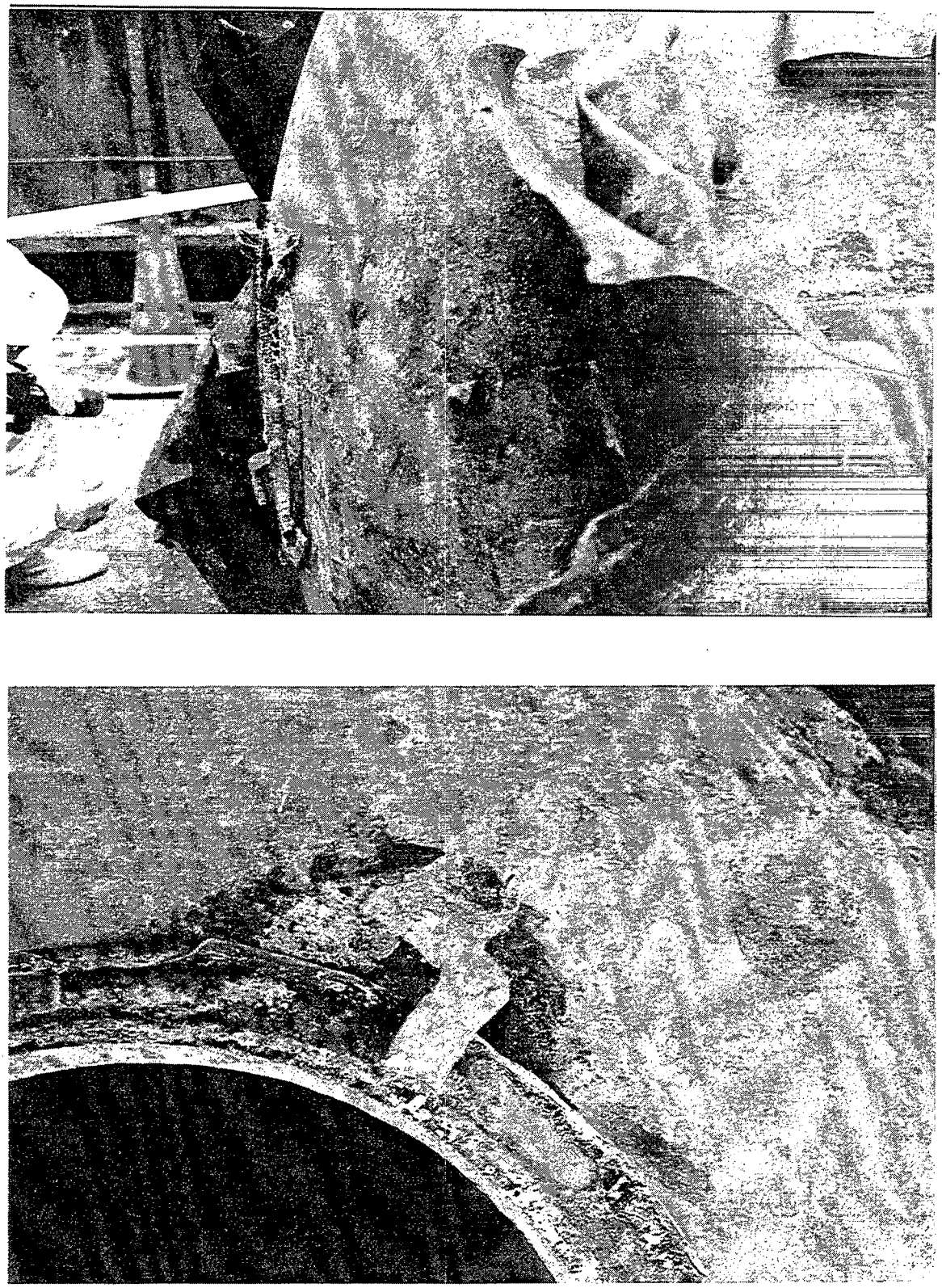
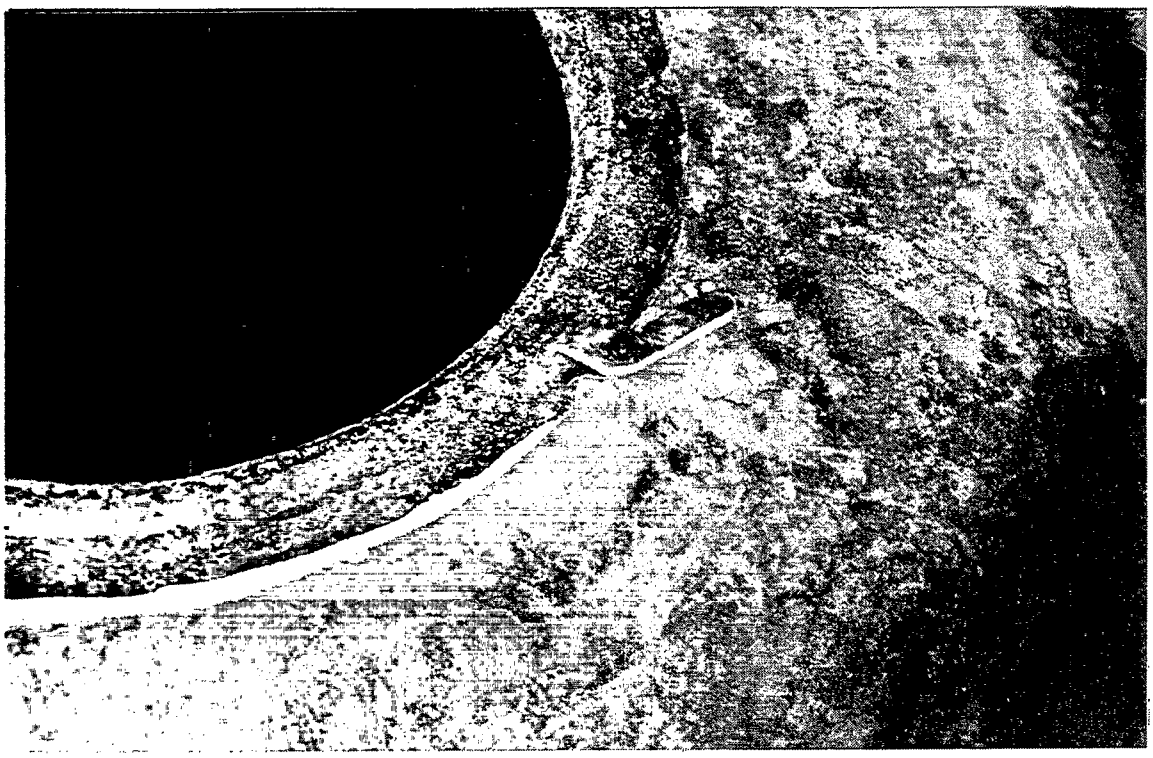


Figure 13: The tabs that held the top access port door are bent down against the stainless steel shell.



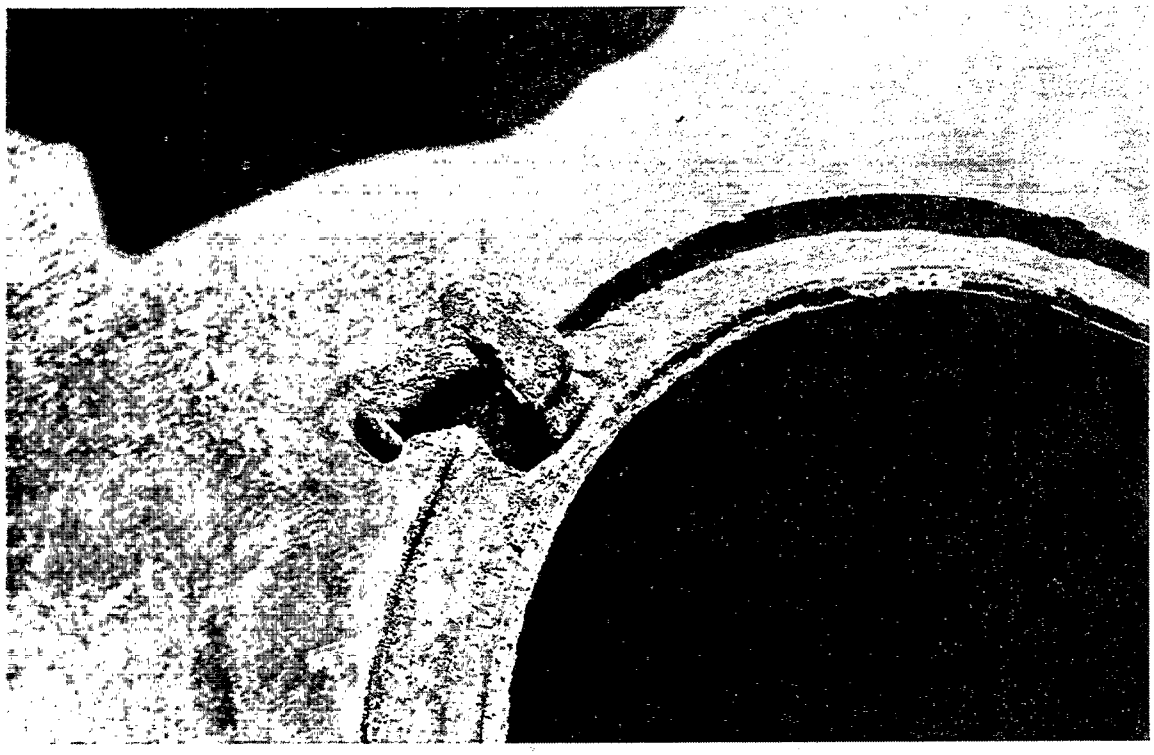
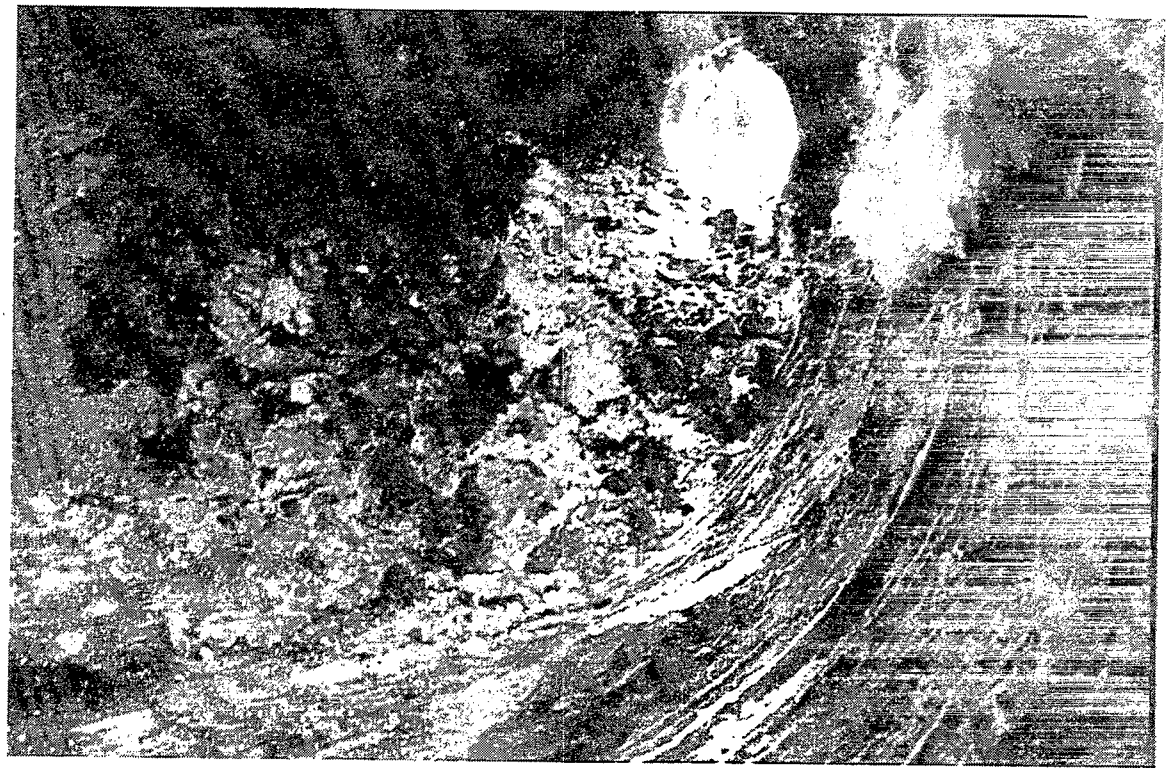


Figure 14: The insulation jacket has torn away from where it was attached to the stainless steel shell and the access door tabs are bent over against the shell.



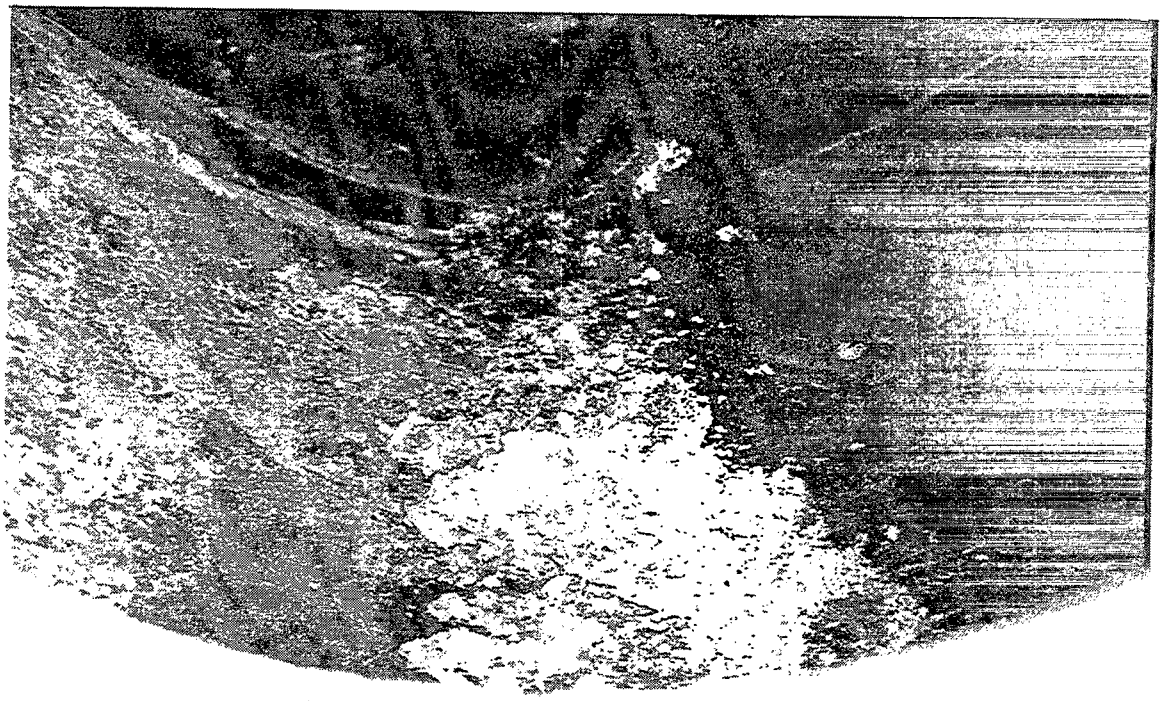


Figure 15: The inside of the blender: a) area near the bottom off-load port, b) just inside one of the top access ports.

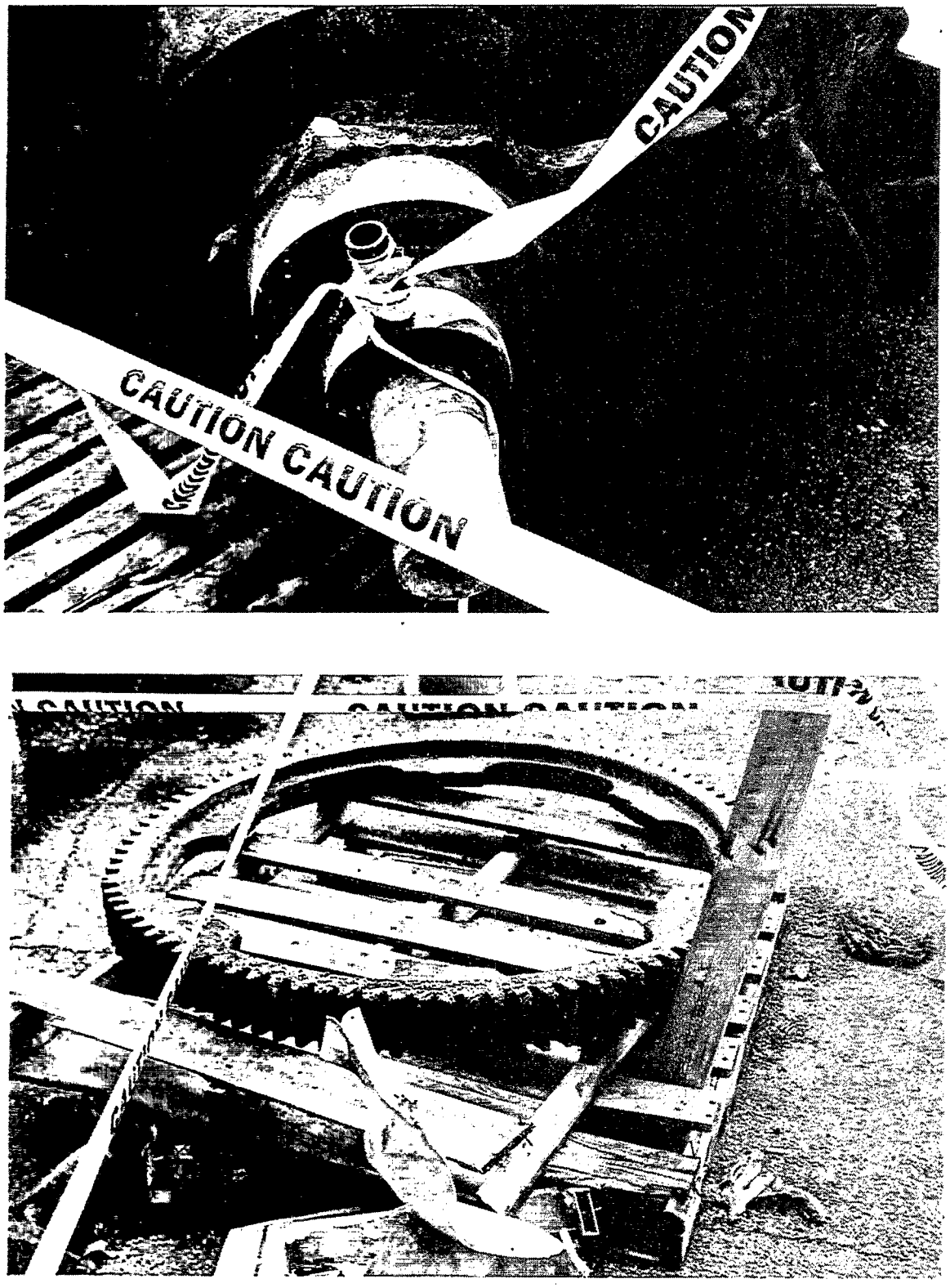


Figure 16: The gear drive side of the blender: a) the shaft (drive side) and b) the portion of the gear that fractured and separated from the blender in the accident.

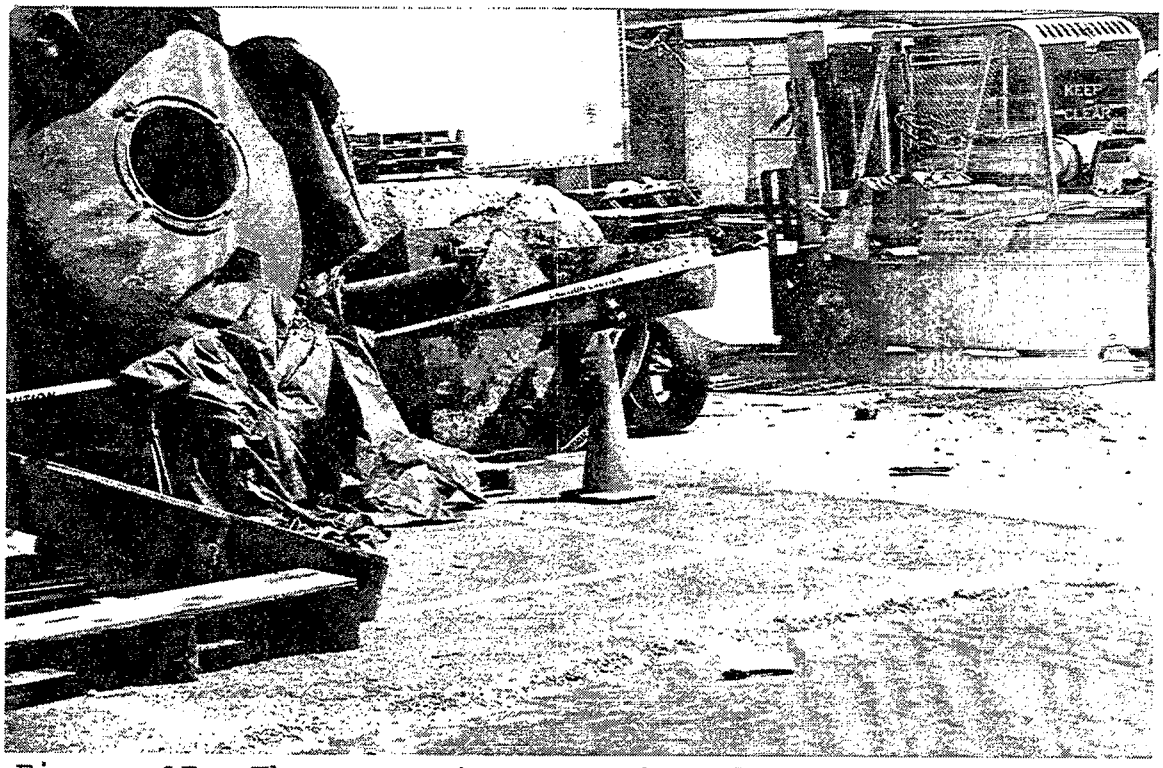


Figure 17: The concrete support and bracket that secured the bearing on the gear drive side of the blender.

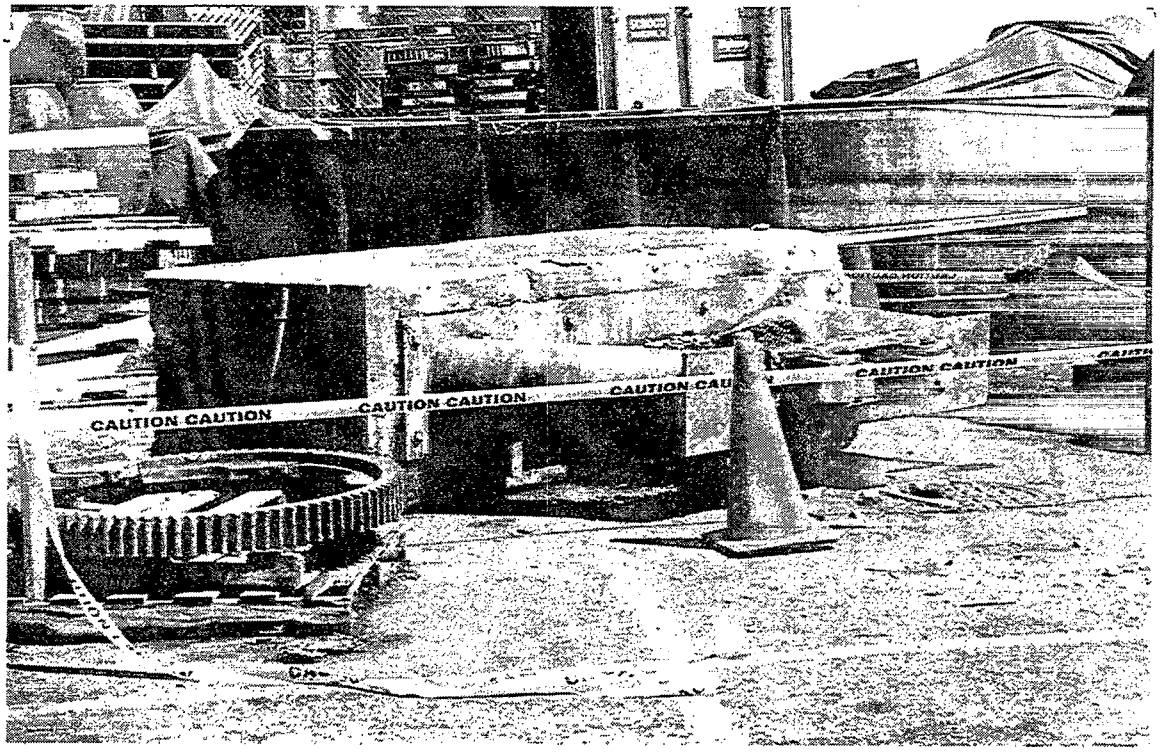
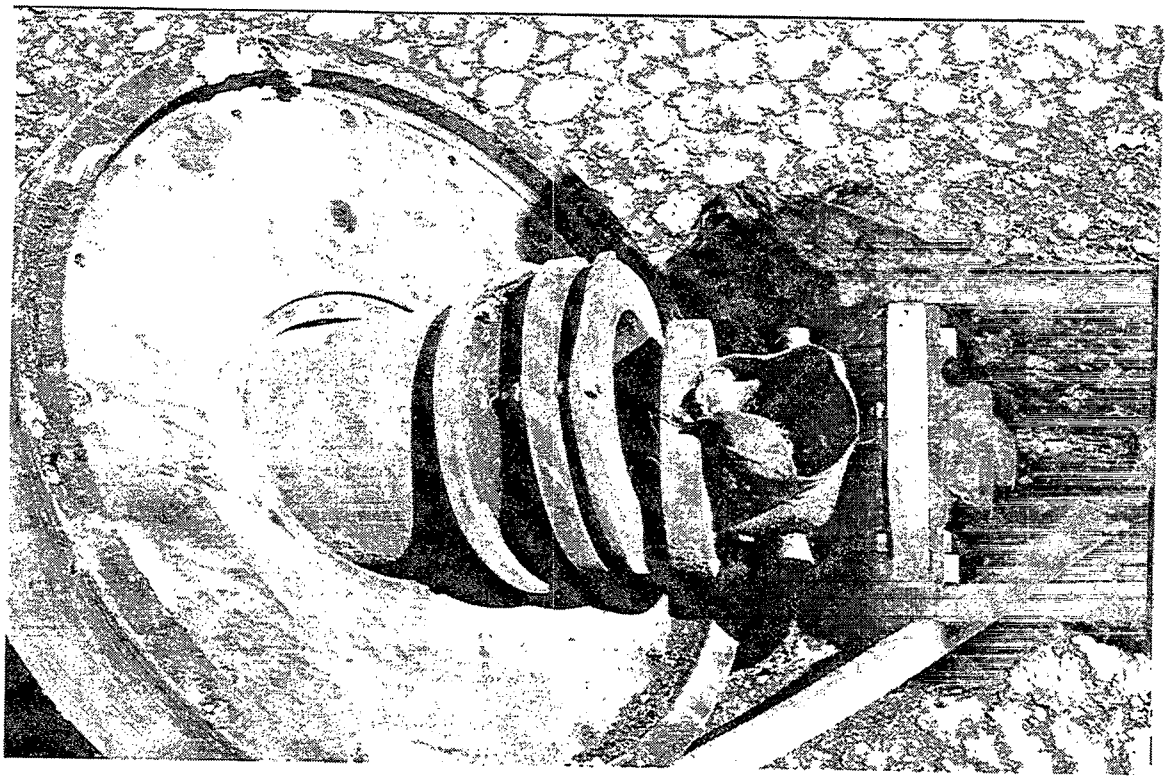


Figure 18: The concrete support and rollers that supported the belt drive side of the blender.

Figure 19: The flange on the belt drive side of the blender: a) the bolt stubs are visible, b) the flange is bent.



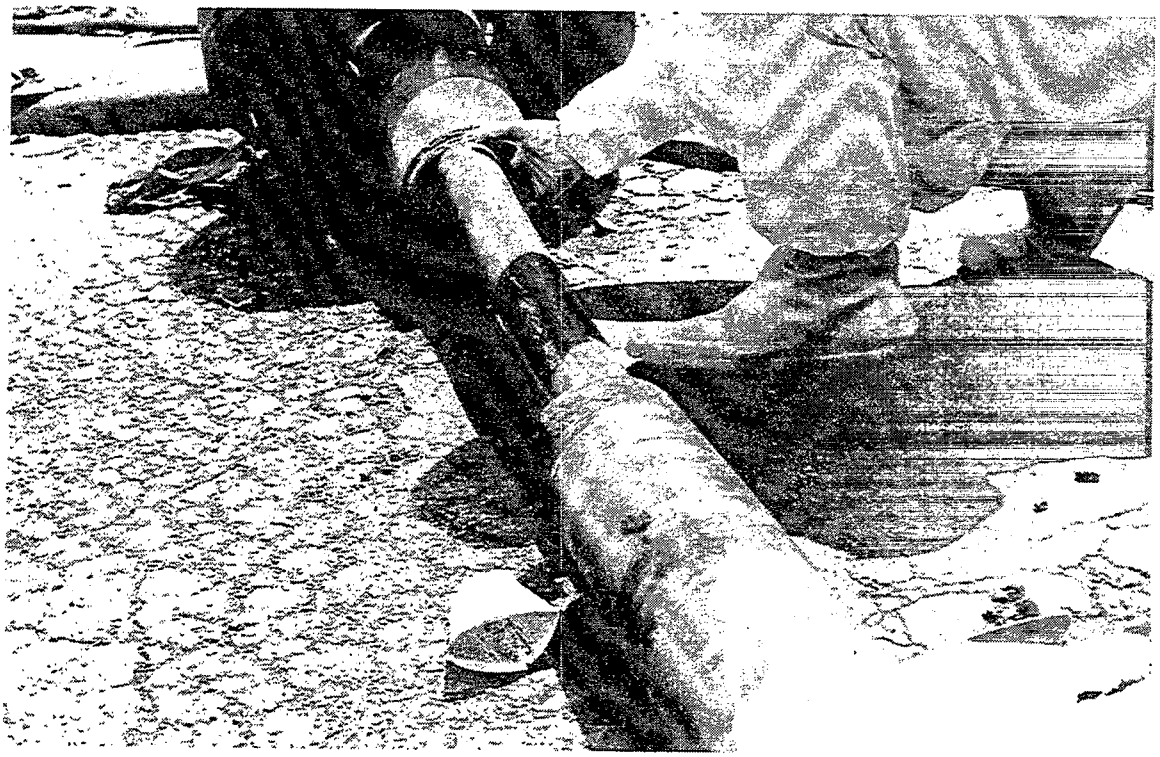


Figure 20: The wheel that supported the blender on the belt drive side and the shaft components: a) the wheel and shaft, b) the concentric shafts and tube that went into the interior of the blender.

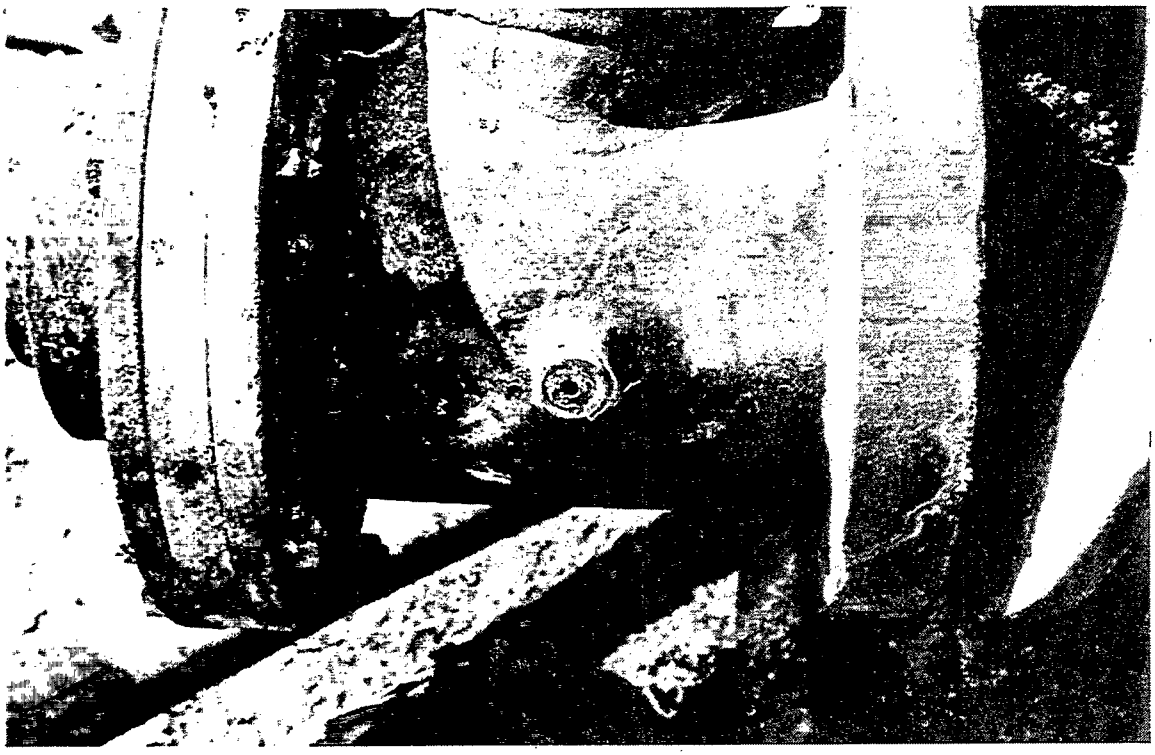


Figure 21: Close-up views of the end of the shaft shown in Figure 20.

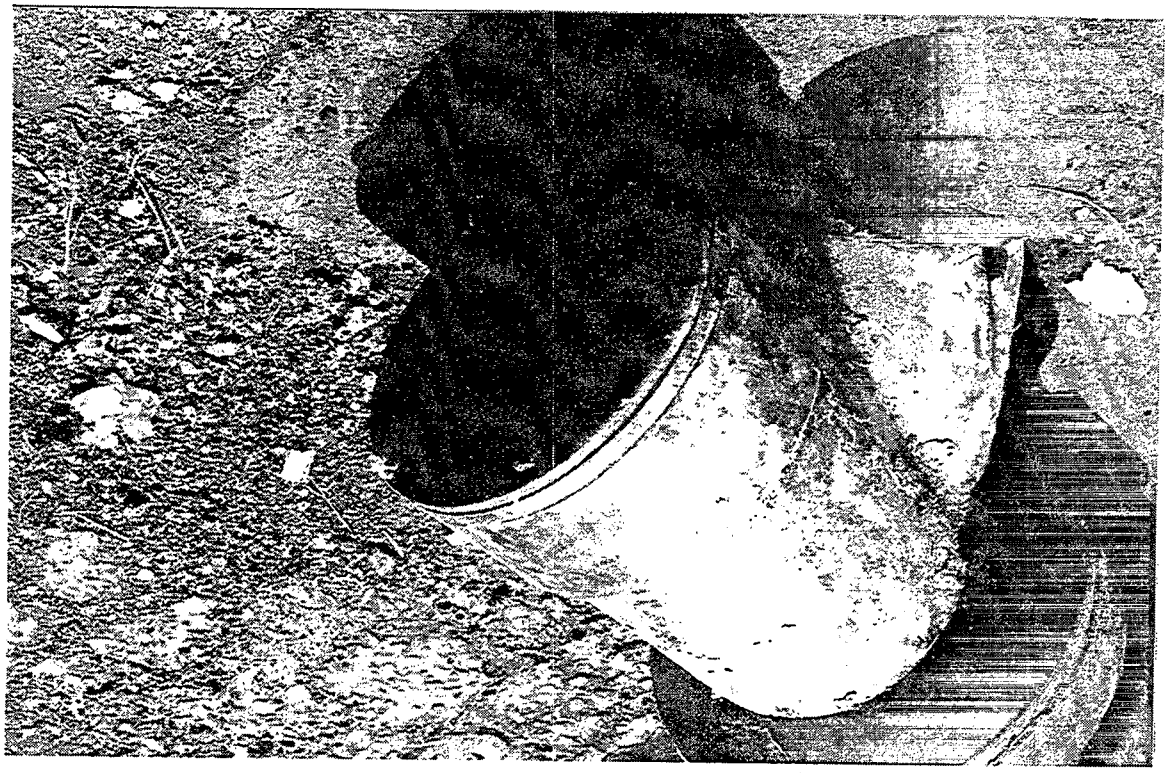
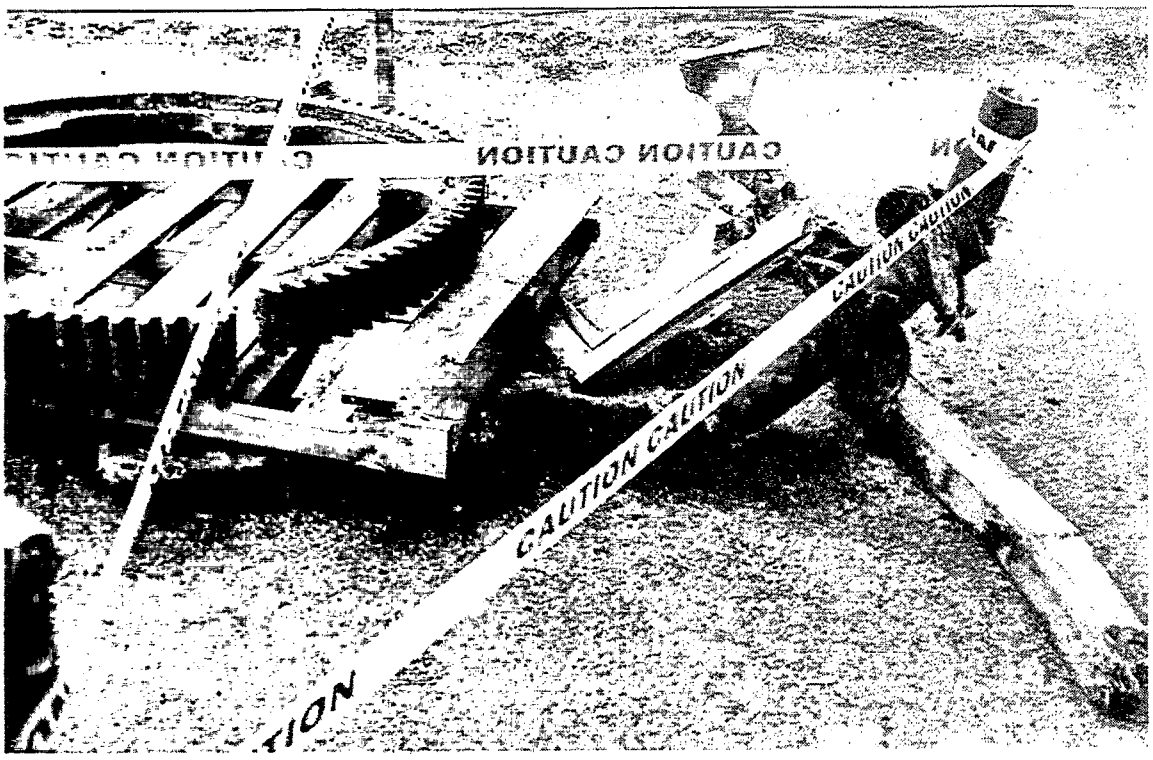


Figure 22: The end of the shaft, shown in Figure 20, holds the vacuum head, spray nozzle, and the connecter for the intensifier bar shaft: a) Y-fitting where the vacuum and water spray nozzle branch off the tube, b) the can that surrounds the vacuum head.



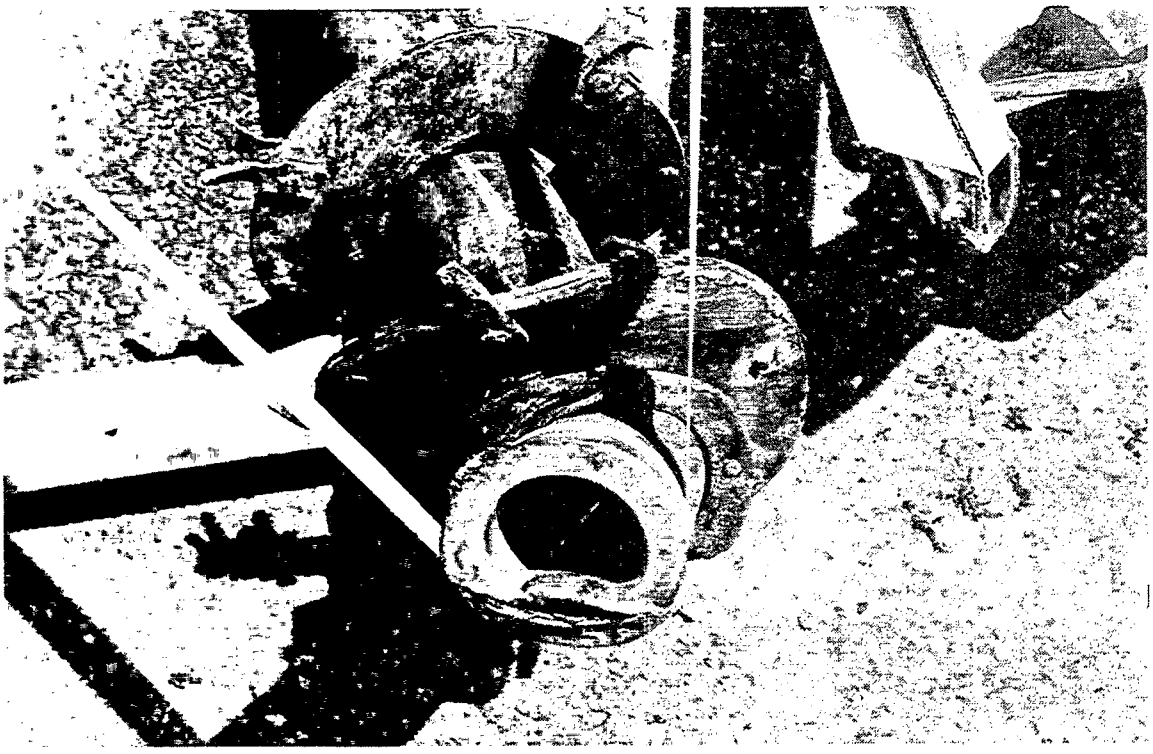


Figure 23: The intensifier bar: a) the shaft of the bar is severely deformed, b) two of the mixing plates are left, both are broken away from the shaft.

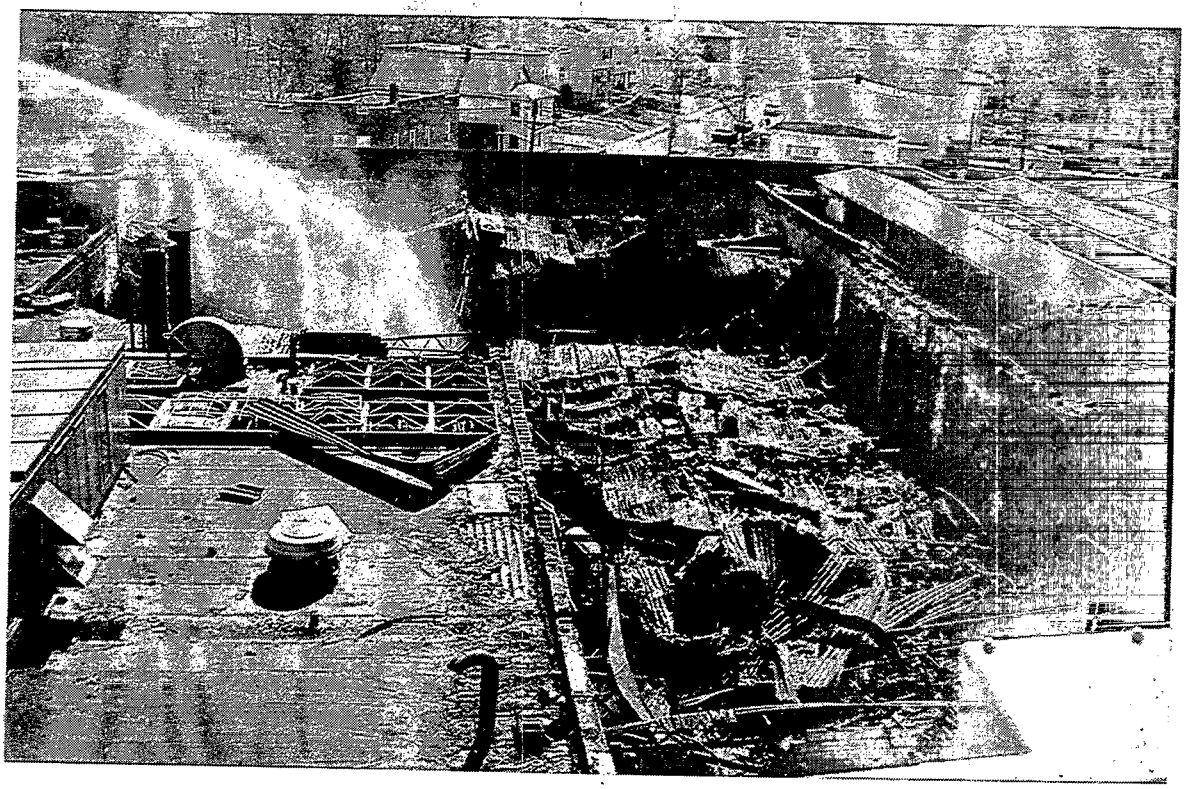


Figure 24: The Napp facility after the explosion and fire showing location in the plant where the processing took place and the location of the facility with respect to residential area in background.