U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

REFINERY INCIDENT

(1 Killed, 8 Injured, Offsite Environmental Impact)

MOTIVA ENTERPRISES LLC
DELAWARE CITY REFINERY
DELAWARE CITY, DELAWARE
JULY 17, 2001

KEY ISSUES:

- MECHANICAL INTEGRITY
- ENGINEERING MANAGEMENT
- MANAGEMENT OF CHANGE
- HOT WORK SYSTEMS

REPORT NO. 2001-05-I-DE
ISSUE DATE: OCTOBER 2002

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

REFINERY INCIDENT

(1 Killed, 8 Injured, Offsite Environmental Impact)

MOTIVA ENTERPRISES LLC
DELAWARE CITY REFINERY
DELAWARE CITY, DELAWARE
JULY 17, 2001

KEY ISSUES

MECHANICAL INTEGRITY

ENGINEERING MANAGEMENT

MANAGEMENT OF CHANGE

HOT WORK SYSTEMS

REPORT NO. 2001-05-I-DE
ISSUE DATE: OCTOBER 2002

Abstract

This investigation report examines a refinery incident that occurred on July 17, 2001, at the Motiva Enterprises LLC Delaware City Refinery in Delaware City, Delaware. One worker was killed, eight were injured, and there was significant offsite environmental impact. This report identifies the root and contributing causes of the incident and makes recommendations on mechanical integrity, engineering management, management of change, and hot work systems.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent Federal agency whose mission is to ensure the safety of workers and the public by preventing or minimizing the effects of chemical incidents. CSB is a scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, CSB is responsible for determining the root and contributing causes of accidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved in chemical safety. No part of the conclusions, findings, or recommendations of CSB relating to any chemical incident may be admitted as evidence or used in any action or suit for damages arising out of any matter mentioned in an investigation report (see 42 U.S.C. § 7412(r)(6)(G)). CSB makes public its actions and decisions through investigation reports, summary reports, safety bulletins, safety recommendations, special technical publications, and statistical reviews. More information about CSB may be found at http://www.chemsafety.gov.

Salus Populi Est Lex Suprema
People's Safety is the Highest Law

Information about available publications may be obtained by contacting:
U.S. Chemical Safety and Hazard Investigation Board
Office of Prevention, Outreach, and Policy
2175 K Street NW, Suite 400
Washington, DC 20037
(202) 261-7600

CSB publications may be purchased from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
(800) 553-NTIS or
(703) 487-4600
Email: info@ntis.fedworld.gov

For international orders, see:
http://www.ntis.gov/support/cooperat.htm.

For this report, refer to NTIS number PB2002-108210.

Contents

EXECUTIVE SUMMARY 11

1.0 INTRODUCTION 25
1.1 Background 25
1.2 Investigative Process 25
1.3 Delaware City Refinery 26
1.4 Sulfuric Acid Processes 26
1.5 Sulfuric Acid Storage Tanks 27

2.0 DESCRIPTION OF INCIDENT 29
2.1 Pre-Incident Events 29
2.2 The Incident 31
2.3 Incident Aftermath and Emergency Response 34

3.0 ANALYSIS 37
3.1 Corrosion and Tank Inspections 37
3.1.1 Indications of Corrosion 37
3.1.2 Potential Mechanisms for Accelerated Corrosion 45
3.1.3 Generation of Flammable Atmosphere 48
3.1.4 Finite Element Analysis of Tank Failure 48
3.2 Engineering of Conversion From Fresh to Spent Acid 50
3.2.1 Process Engineering 50
3.2.2 Tank Inerting Design 52
3.2.3 Secondary Containment Systems 54
3.3 Management of Change for Tank Conversion 55
3.4 Management Practices–Tank 393 58
3.4.1 Lack of Recognition of Imminent Hazard Potential 58
3.4.2 Deferral of Inspections 59
3.5 Hot Work 62
3.6 Unsafe Condition Report 64
3.7 Spent Sulfuric Acid Classification 65
3.8 Review of Similar Incidents 66
3.8.1 Pennzoil, Rouseville 66
3.8.2 ARCO, Channelview 67
3.9 Regulatory Issues 67
3.9.1 Process Safety Management Coverage 67
3.9.2 Jeffrey Davis Aboveground Storage Tank Act 70

4.0 ROOT AND CONTRIBUTING CAUSES 73
4.1 Root Causes 73
4.2 Contributing Causes 74

Contents (cont'd)

5.0 RECOMMENDATIONS 75

6.0 REFERENCES 81

APPENDIX A: Tank 393 History 83
A.1 1992–Thickness Readings 83
A.2 1994–Internal Inspection 83
A.3 1998–Shell Leak 84
A.4 1999–Shell Leaks 85
A.5 2000–Shell Leaks 86
A.6 2001–Shell Leak 86

APPENDIX B: Logic Diagram 89

Figures and Tables

Figures

1 Layout of Acid Storage Tanks and Catwalk 29

2 Tank 393, Collapsed at Northeast Corner of Storage Tank Dike 33

3 Tank 394 in Foreground and Remains of Catwalk, From the North 34

4 Side of Tank 393 Showing Series of Patches 39

5 Elongated Hole on Roof of Tank 393 40

6 Hole in Roof of Tank 393 Through Which Temporary Hose Was Inserted 40

7 Modeled Pressure Rise in Tank 393 During Internal Deflagration 49

8 Floor of Tank 393 Showing Uplift Due to Internal Deflagration (Before Separation of Shell) 49

9 Inerting System Schematic 52

Tables

1 Tank 393 Deterioration and Repair History 38

2 History of Motiva API 653 Tank Inspector Findings and Recommendations 44

Acronyms and Abbreviations

ACC	American Chemistry Council (formerly CMA)
AFL-CIO	American Federation of Labor-Congress of Industrial Organizations
AIChE	American Institute of Chemical Engineers
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
AWS	American Welding Society
CCPS	Center for Chemical Process Safety
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cfh	Cubic feet per hour
CFR	Code of Federal Regulations
CMA	Chemical Manufacturers Association (now ACC)
CO_2	Carbon dioxide
CS	Carbon steel
CSB	U.S. Chemical Safety and Hazard Investigation Board
DCR	Delaware City Refinery
DNREC	Delaware Department of Natural Resources and Environmental Control
EPA	U.S. Environmental Protection Agency
ESI	Engineering Systems Inc.
°F	Degrees Fahrenheit
Fe	Iron
FEA	Finite element analysis
$FeSO_4$	Ferrous sulfate
HAZOP	Hazard and operability
H_2	Hydrogen
H_2S	Hydrogen sulfide
H_2SO_3	Sulfurous acid
H_2SO_4	Sulfuric acid
in./yr	Inches per year

LEL	Lower explosivity limit
LLC	Limited liability company
MOC	Management of change
MSDS	Material safety data sheet
NACE	National Association of Corrosion Engineers
NDT	Nondestructive testing
NFPA	National Fire Protection Association
NPRA	National Petrochemical and Refiners Association
OSHA	Occupational Safety and Health Administration
PACE	Paper, Allied-Industrial, Chemical & Energy Workers International Union
PEI	Petroleum Equipment Institute
PHA	Process hazard analysis
ppm	Parts per million
psi	Pounds per square inch
psig	Pounds per square inch gage
PSM	Process safety management
PSV	Pressure safety valve
RBI	Risk-based inspection
RMP	Risk management program
RP	Recommended practice
scfh	Standard cubic feet per hour
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SPCC	Spill Prevention, Control, and Countermeasures
STI	Steel Tank Institute
UL	Underwriters Laboratories
UT	Ultrasonic thickness
UTM	Ultrasonic thickness measurement
USC	United States Code
WGI	The Washington Group International, Inc.

Executive Summary

ES.1 Introduction

On July 17, 2001, an explosion occurred at the Motiva Enterprises LLC Delaware City Refinery (DCR) in Delaware City, Delaware. Jeffrey Davis, a boilermaker with The Washington Group International, Inc. (WGI), the primary maintenance contractor at DCR, was killed; eight others were injured.

A crew of WGI contractors was repairing grating on a catwalk in a sulfuric acid (H_2SO_4) storage tank farm when a spark from their hot work ignited flammable vapors in one of the storage tanks. The tank separated from its floor, instantaneously releasing its contents. Other tanks in the tank farm also released their contents. A fire burned for approximately one-half hour; and H_2SO_4 reached the Delaware River, resulting in significant damage to aquatic life.

Because of the serious nature of this incident, the U.S. Chemical Safety and Hazard Investigation Board (CSB) launched an investigation to determine the root and contributing causes and to issue recommendations to help prevent similar occurrences.

ES.2 Incident

Tank 393 was one of six 415,000-gallon carbon steel (CS) tanks originally built in 1979 and located in a common diked area. The tanks stored fresh[1] and spent[2] H_2SO_4 used in the refinery's sulfuric acid alkylation process. Over the years, the tanks had experienced significant localized corrosion. Leaks were found on the shell of tank 393 annually from 1998 through May 2001; all of the reported leaks were repaired, except for one discovered in May 2001. However, at the time of the incident, several additional holes in the roof and shell of tank 393 were unreported.

As leaks occurred and were repaired, the Motiva tank inspectors repeatedly recommended an internal inspection of tank 393. However, despite the imminent hazard presented by this particular tank, Motiva repeatedly postponed its inspection, originally scheduled for 1996. Between 1996 and 2000, even though tank 393 was emptied

As leaks occurred and were repaired, the Motiva tank inspectors repeatedly recommended an internal inspection of tank 393. However, despite the imminent hazard presented by this particular tank, Motiva repeatedly postponed its inspection, originally scheduled for 1996.

[1] Fresh H_2SO_4 typically contains 99 percent acid and 1 percent water.

[2] Spent H_2SO_4 typically contains 88 to 95 percent acid and up to 5 percent water, with the balance being hydrocarbons, including some light hydrocarbons that can vaporize.

three times to change its service between fresh and spent acid, Motiva maintained that inventory constraints prevented taking the tank out of service. In 2000, after the U.S. Environmental Protection Agency (EPA) identified 18 tanks that required internal inspection and after Motiva reduced its maintenance budget, the tank inspection program was reprioritized–which further deferred the inspection of tank 393 until January 2002.

Spent H_2SO_4 normally contains small amounts of flammable materials. Light hydrocarbons in the acid can vaporize and create a flammable atmosphere above the liquid surface if sufficient oxygen is present.

Tank 393 was one of four tanks originally designed for fresh H_2SO_4 that had been converted to store spent acid. Spent H_2SO_4 normally contains small amounts of flammable materials. Light hydrocarbons in the acid can vaporize and create a flammable atmosphere above the liquid surface if sufficient oxygen is present. To guard against this hazard, Motiva installed a carbon dioxide (CO_2) inerting system[3] and a conservation vent[4] with flame arrestor.[5] However, the system was poorly designed and did not provide enough CO_2 flow to prevent the formation of a flammable atmosphere in the vapor space of tank 393.

In June and July 2001, Motiva directed WGI to repair the catwalk that provided access to instrumentation on the roofs of the acid storage tanks. The catwalk had deteriorated due to acid vapors in the atmosphere around the tanks. The contractor employees worked this job on several days, cutting out damaged sections of the grating and welding down new sections.

On July 17, . . . a spark from the hot work most likely either entered the vapor space of tank 393 or contacted flammable vapors escaping from one of the holes in the tank and flashed back into it.

On July 17, as the contractors were working, a spark from the hot work most likely either entered the vapor space of tank 393 or contacted flammable vapors escaping from one of the holes in the tank and flashed back into it. An explosion in the vapor space of the tank caused the tank shell to separate from its floor, lift up and come down across the dike wall, and instantaneously release its contents of 264,000 gallons of spent H_2SO_4. The adjacent tank 396 also lost its contents; acid continued to leak from several of the remaining storage tanks for several weeks.

[3] Inerting refers to the use of a nonflammable, nonreactive gas to render the combustible material in a system incapable of supporting combustion.

[4] A conservation vent (also referred to as a PV valve) is a weight-loaded, pilot-operated, or spring-loaded valve used to relieve excess pressure or vacuum in a tank.

[5] A flame arrester is a device intended to prevent a flame from propagating through an open vent into a vessel.

Flammable and combustible material in the spent acid ignited, and a fire burned for one-half hour. The total mass of spent H_2SO_4 released–estimated by EPA at 1.1 million gallons–overwhelmed the area diking and plant containment and wastewater systems. Approximately 99,000 gallons of acid reached the Delaware River, killing fish and other aquatic life.

Mr. Davis, who had been working on the catwalk, was fatally injured. Eight other workers suffered acid burns, burning eyes and lungs, and nausea.

The total mass of spent H_2SO_4 released–estimated by EPA at 1.1 million gallons–overwhelmed the area diking and plant containment and wastewater systems.

ES.3 Key Findings

1. An explosion[6] in the vapor space of tank 393 generated sufficient pressure to separate the tank's floor-to-shell joint. The explosion most likely occurred when a spark from the maintenance work either fell through one of the holes into the tank–or contacted the flammable vapors near one of the holes in the tank roof and shell, and flashed back into the tank.

An explosion in the vapor space of tank 393 generated sufficient pressure to separate the tank's floor-to-shell joint.

2. Motiva did not consider the acid tank farm to be covered by requirements of the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) Standard (29 CFR 1910.119). The incident would likely not have occurred if good process safety management practices had been adequately implemented, such as mechanical integrity, management of change (MOC), and prestartup safety review.

   The OSHA PSM Standard is a systematic approach to safety and the prevention of catastrophic incidents. Enacted in 1992, the standard details 14 elements of good safety management. Processes containing any of a specific list of hazardous substances, including flammables, must adhere to these elements. However:

   - The PSM Standard does not cover H_2SO_4.

The [OSHA] PSM Standard does not cover H_2SO_4.

[6] The explosion was modeled by CSB as a weak deflagration that generated a maximum pressure of approximately 5.0 pounds per square inch gage (psig).

- Although flammables above a threshold quantity are covered, the Meer decision[7] determined that coverage does not extend to stored flammables in atmospheric tanks even if connected to a process. OSHA has not challenged this decision.[8]
- OSHA did not cite Motiva for violations of the PSM Standard following the July 17 incident.

3. Tank 393 and other acid tanks had a history of leaks. Major repairs were made to tank 393 in 1994, and the tank had at least one leak in each of the years 1998, 1999, 2000, and 2001. The leak reported in May 2001 was not repaired. Significant leaks also occurred in other H_2SO_4 tanks at Motiva, two of which were condemned and replaced due to corrosion.

4. In 1994, Motiva tank inspectors recommended that thickness measurements of tank 393 be conducted in 1996. In inspection reports written in 1999, 2000, and 2001, they recommended an internal inspection "as soon as possible." Motiva took no action on these recommendations.

5. Tank 393 was emptied three times (April and October 2000, and April 2001) as service was alternated between fresh and spent acid. Each of these occasions presented an opportunity to prepare tank 393 and conduct an internal inspection.

The design and implementation of the Motiva H_2SO_4 tank inspection program was inadequate.

6. The design and implementation of the Motiva H_2SO_4 tank inspection program was inadequate. Motiva's plan was to inspect its tanks at intervals prescribed by American Petroleum Institute (API) Standard 653[9] (i.e., every 5 years for external inspections and 10 years for internal inspections). However, API 653 notes that inspection frequencies must be modified based on the corrosivity of the stored material. Motiva inspectors recommended revised frequencies, but the inspections did not occur.

[7] U.S. Secretary of Labor v. Meer Corporation, OSHRC Docket No. 95-0341, 1995.

[8] Memorandum from John B. Miles, Jr., Director, Directorate of Compliance Programs, OSHA, to Regional Administrators, "Standard Interpretations, Coverage of Stored Flammables Under the Process Safety Management Standard," May 12, 1997.

[9] API Standard 653, Tank Inspection, Repair, Alteration, and Reconstruction, December 1995.

After an internal inspection in 1994, Motiva inspectors recommended thickness measurements for tank 393 in 1996; this did not occur. In addition, after 1994, no complete external inspections were conducted (i.e., inspectors only spot-checked shell thickness in the vicinity of leaks).

It is likely that an external inspection would have identified the holes in the roof of the tank and the need for a thorough internal inspection. API 653 requires the evaluation of flaws, deterioration, or other conditions that might affect the performance of a tank and the determination of its suitability for the intended service.

It is likely that an external inspection would have identified the holes in the roof of the tank and the need for a thorough internal inspection.

7. NACE International (National Association of Corrosion Engineers) RP 0294-94[10] recommends an internal inspection every 5 years and an external in-service inspection every 2 years for tanks in concentrated H_2SO_4 service. H_2SO_4 regeneration contractors[11] contacted by CSB follow these NACE guidelines.

8. Management did not consider the leaks in tank 393 to constitute an imminent hazard to safety or the environment. They stated in interviews their belief that patching the leaks allowed the tank to operate safely, even though inspectors noted that the repairs were temporary and required an internal inspection to ensure vessel integrity. They also believed that lowering the liquid level in the tank below the leak point addressed the hazard.

Management did not consider the leaks in tank 393 to constitute an imminent hazard to safety or the environment. . . . They also believed that lowering the liquid level in the tank below the leak point addressed the hazard.

9. Tank 393 was converted from fresh to spent acid service in March 2000 with minimal engineering support. Conversion involved the addition of CO_2 inerting and a conservation vent/vacuum breaker with a flame arrestor.

   - In its work order for the conversion, Motiva did no engineering and did not request engineering support from WGI.

[10] NACE Recommended Practice (RP) 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures, 1994.

[11] H_2SO_4 regeneration contractors take spent acid from refiners, convert it back to fresh acid, and return it for reuse.

Sizing of inerting flow requirements for normal and upset conditions was inadequate, and the CO_2 gas flow was insufficient to maintain a nonflammable atmosphere in the tank.

- Sizing of inerting flow requirements for normal and upset conditions was inadequate, and the CO_2 gas flow was insufficient to maintain a nonflammable atmosphere in the tank.
- The tank lacked a weak seam roof or other emergency venting provisions, which would likely have prevented it from separating at the floor and catastrophically releasing its contents.

10. Motiva did not use its MOC system for the conversion of tank 393 from fresh to spent acid service. As a result, the conversion did **not** benefit from the following good practices:

Motiva did not use its MOC system for the conversion of tank 393 from fresh to spent acid service.

- Review and sign-off on the proposed changes by subject area experts (e.g., corrosion, tank design) and higher level management.
- Process hazard review.
- Prestartup safety review.

11. The vapor space of tank 393 was not adequately inerted. Design deficiencies provided an insufficient flow of CO_2 to keep the internal atmosphere below the flammable range.

CO_2 was not hard-piped into tank 393, but rather was supplied via a temporary rubber hose running off the inerting system of an adjacent tank (396).

- CO_2 was not hard-piped into tank 393, but rather was supplied via a temporary rubber hose running off the inerting system of an adjacent tank (396). Because of the long length and small diameter of the hose, an insufficient amount of CO_2 reached tank 393.
- The hose supplying CO_2 was not attached to tank 393. It was dropped into a hole in the roof, where a nozzle had been located before it corroded. The temporary hose setup was in use for over a year; it was not converted to conventional hard piping, as on the other acid tanks.
- A common overflow line connected the vapor space of tank 393 to two tanks open to the atmosphere.

12. The vapor space above the liquid surface in tank 393 contained flammable vapor. Spent H_2SO_4 from alkylation units normally contains sufficient flammable hydrocarbons to generate a flammable atmosphere given the presence of oxygen.

As the tank contents settle, some of the hydrocarbons evaporate into the vapor space and may reach flammable concentrations.

13. Because of the holes in the tank and an ineffective inerting system, tank 393 exhibited severe localized corrosion beyond that considered normal in concentrated H_2SO_4 service. Both rainwater and water moisture in the ambient air entered the tank through holes caused by the corrosion. H_2SO_4 becomes more corrosive as its concentration decreases with the addition of water.

Because of the holes in the tank and an ineffective inerting system, tank 393 exhibited severe localized corrosion beyond that considered normal in concentrated H_2SO_4 service.

14. An operator submitted an Unsafe Condition Report[12] on June 27, 2001, after rejecting a hot work permit on the acid tank catwalk because of high flammable vapor readings. This report cited the holes in tanks 393 and 396, and noted that a hose inserted into an open hole in the tank roof supplied the inerting gas for tank 393.

    In the 3 weeks between submission of the Unsafe Condition Report and the day of the incident, Motiva investigated but did not correct the deficiencies noted or implement temporary safeguards, such as banning hot work in the vicinity of the holes.

In the 3 weeks between submission of the Unsafe Condition Report and the day of the incident, Motiva investigated but did not correct the deficiencies noted or implement temporary safeguards . . .

15. Motiva allowed hot work to be performed in the vicinity of a tank with holes in its roof and shell. Hot work should not have been authorized; Motiva was aware of the condition of the tanks and that they contained flammables. In addition, once the work was authorized, inadequate precautions were taken to prevent an ignition of flammable vapors. On July 17, and on several occasions in the days prior to the incident, contract workers used burning and welding equipment to cut out and replace sections of the catwalk above the acid storage tanks.

    - Contractors, permit writers, and approvers were unaware of the hazards posed by conducting hot work in the vicinity of the holes on the tops of tanks 393 and 396.

Hot work should not have been authorized; Motiva was aware of the condition of the tanks and that they contained flammables.

[12] Unsafe Condition Reports can be written by plant workers to bring management and union attention to safety and health issues that are not adequately addressed by the immediate supervisor.

On at least two previous occasions in the weeks prior to the incident, hot work permits to work on the catwalk grating had been denied–once because of excessive amounts of sulfur dioxide gas, and a second time because of a high reading for flammable vapors.

- On at least two previous occasions in the weeks prior to the incident, hot work permits to work on the catwalk grating had been denied–once because of excessive amounts of sulfur dioxide (SO_2) gas, and a second time because of a high reading for flammable vapors. However, despite this history, the July 17 hot work permit did not specify the need for periodic retesting or continuous monitoring of the atmosphere around the work area for flammables.

ES.4 Root Causes

The repeated recommendations of the tank inspectors that tank 393 be taken out of service "as soon as possible" for an internal inspection were unheeded.

The CO_2 inerting supply to tank 393, installed in 2000, was incapable of maintaining a nonflammable atmosphere.

1. **Motiva did not have an adequate mechanical integrity management system to prevent and address safety and environmental hazards from the deterioration of H_2SO_4 storage tanks.**
   - The repeated recommendations of the tank inspectors that tank 393 be taken out of service "as soon as possible" for an internal inspection were unheeded.
   - A leak in the shell of tank 393, observed in May 2001, was not repaired. Instead, the tank liquid level was lowered below the leak point, and the tank remained in service.
   - Management failed to recognize the imminent hazard posed by the holes in tank 393 and did not promptly initiate repairs or take the tank out of service.
2. **Motiva engineering management and MOC systems inadequately addressed conversion of the tanks from fresh to spent acid service.**
   - The CO_2 inerting supply to tank 393, installed in 2000, was incapable of maintaining a nonflammable atmosphere.
   - CO_2 was supplied to tank 393 via a temporary hose run off the inerting system of an adjacent tank. The hose was dropped into a hole in the roof of tank 393.
   - No engineering calculations were made to determine proper sizing for the inerting system.
   - The tank conversion was completed without review of changes by technical experts, process hazard analyses, or prestartup safety reviews–all elements of a proper MOC program.

3. **The Motiva hot work program was inadequate.**

   - Motiva scheduled and permitted hot work to be conducted above and around tanks that contained flammable vapors and had known holes; tank 393 had a leak in its shell and open holes in its roof, and tank 396 also had an open hole in its roof.
   - After authorizing the hot work, Motiva management did not institute adequate precautions to ensure worker safety, such as continuous monitoring.

Motiva scheduled and permitted hot work to be conducted above and around tanks that contained flammable vapors and had known holes . . .

ES.5 Contributing Causes

1. **The Motiva refinery system for investigating Unsafe Condition Reports, informing workers about such reports, and tracking the satisfactory resolution of issues was inadequate.**

   - In the 3 weeks between submittal of the Unsafe Condition Report on June 27 and the day of the incident, management did not correct the reported deficiencies or implement temporary safeguards.
   - Motiva operators would likely not have authorized hot work in the vicinity of the tank if they had understood the hazards, nor would contract employees have conducted the work.

2. **The Motiva Enterprises LLC management oversight system failed to detect and hold Motiva refinery management accountable for deficiencies in the refinery's mechanical integrity, engineering management, and MOC systems.**

ES.6 Recommendations

Occupational Safety and Health Administration

Ensure coverage under the Process Safety Management Standard (29 CFR 1910.119) of atmospheric storage tanks that could be involved in a potential catastrophic release as a result of being interconnected to a covered process with 10,000 pounds of a flammable substance.

Delaware Department of Natural Resources and Environmental Control

Ensure that regulations developed for the recently enacted Jeffrey Davis Aboveground Storage Tank Act require that facility management take prompt action in response to evidence of tank corrosion that presents hazards to people or the environment.

Motiva Enterprises– Delaware City Refinery

1. Implement a system to ensure accountability for mechanical integrity decision making. Include the following specific items:
   - Review of inspection reports by subject area experts, such as metallurgists or equipment design engineers, to ensure adequate analysis of failure trends and suitability for intended service.
   - Establishment of a planning system to ensure the timely repair of equipment.

The Center for Chemical Process Safety (CCPS) publication, Plant Guidelines for Technical Management of Chemical Process Safety, Chapter 3, "Accountability Objectives and Goals," presents a model for such a system.

2. Review the design of existing tankage that contains or has the potential to contain flammables to ensure that, at a minimum:
   - Inerting systems are installed where appropriate and are adequately sized and constructed.
   - Emergency venting is provided.
3. Ensure that management of change reviews are conducted for changes to tank equipment and operating conditions, such as:
   - Tank service and contents.
   - Tank peripherals, such as inerting and venting systems.
4. Revise the refinery hot work program to address the circumstances that require use of continuous or periodic monitoring for flammables.
5. Upgrade the refinery Unsafe Condition Report system to include the following:
   - Designation of a manager with decision-making authority to resolve issues.
   - Establishment of a mechanism to elevate attention to higher levels of management if issues are not resolved in a timely manner.
   - Identification of a means to ensure communication of hazards to all potentially affected personnel.

   Work with the Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE) Local 2-898 to design and implement the improved system.

Motiva Enterprises LLC

1. In light of the findings of this report, conduct periodic audits of storage tank mechanical integrity and design, Unsafe Condition Reports, hot work, management of change, and accountability systems at Motiva oil refineries. Ensure that the audit recommendations are tracked and implemented. Share the findings with the workforce.
2. Communicate the findings and recommendations of this report to the workforce and contractors at all Motiva refineries.

American Petroleum Institute (API)

1. Work with NACE International (National Association of Corrosion Engineers) to develop API guidelines to inspect storage tanks containing fresh or spent H_2SO_4 at frequencies at least as often as those recommended in the latest edition of NACE Standard RP 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures.
2. Revise API tank inspection standards to emphasize that storage tanks with wall or roof holes or thinning beyond minimum acceptable thickness that may contain a flammable vapor are an imminent hazard and require immediate repair or removal from service.
3. Ensure that API recommended practices address the inerting of flammable storage tanks, such as spent H_2SO_4 tanks. Include the following:
   - Circumstances when inerting is recommended.
   - Design of inerting systems, such as proper sizing of inerting equipment, appropriate inerting medium, and instrumentation, including alarms.
4. Communicate the findings and recommendations of this report to your membership.

NACE International (National Association of Corrosion Engineers)

1. Work with the American Petroleum Institute to develop API guidelines to ensure that storage tanks containing fresh or spent H_2SO_4 are inspected at frequencies at least as often as those recommended in the latest edition of NACE Standard RP 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures.
2. Communicate the findings and recommendations of this report to your membership.

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE) Local 2-898

Work with Motiva management on the design and implementation of an improved Unsafe Condition Report program.

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)

National Petrochemical and Refiners Association (NPRA)

Building and Construction Trades Department–AFL-CIO

Communicate the findings and recommendations of this report to your membership.

1.0 Introduction

On July 17, 2001, an explosion and fire occurred at the Motiva Enterprises LLC Delaware City Refinery (DCR), in Delaware City, Delaware. One contract employee died and eight workers were injured when a spent sulfuric acid (H_2SO_4) storage tank failed and released its contents, which ignited. Approximately 1.1 million gallons of spent H_2SO_4 was released; 99,000 gallons reached the Delaware River.

Investigators from the U.S. Chemical Safety and Hazard Investigation Board (CSB) arrived at the facility on July 20. Because of the presence of large quantities of H_2SO_4 and an ongoing search and rescue operation, the area was an active emergency response site for many weeks. As a result, investigators initially had limited access to examine physical evidence. The Delaware Fire Marshal controlled site access during this period. CSB examined physical evidence from the incident as it became available, conducted interviews with Motiva and contractor personnel, and reviewed relevant documents.

CSB coordinated its work with a number of other organizations conducting investigations, including:

- Occupational Safety and Health Administration (OSHA).
- U.S. Environmental Protection Agency (EPA).
- Delaware Department of Natural Resources and Environmental Control (DNREC).
- U.S. Coast Guard.
- Delaware Fire Marshal's Office.
- Delaware Attorney General's Office.
- Delaware State Police.

1.3 Delaware City Refinery

The Motiva Enterprises Delaware City Refinery began operation in 1956 as the Tidewater Oil Company. In 1967, Tidewater merged with Getty Oil, which was in turn acquired by Texaco in 1984. From 1989 to 1998, the refinery was known as Star Enterprise; it was part of a joint venture between Texaco and Saudi Aramco. In 1998, the refinery became part of Motiva, which was a joint venture between Texaco, Saudi Refining Company, and Shell. In 2001, Texaco terminated its participation in the Motiva partnership as a condition of its merger with Chevron.

At the time of the incident, the refinery had approximately 650 employees and 300 contractors onsite. It is located close to the Delaware River, in New Castle County, Delaware.

1.4 Sulfuric Acid Processes

H_2SO_4 is used as the catalyst in the refinery's alkylation process. In this process, smaller molecules–such as isobutane and butylene–are combined in the presence of H_2SO_4 to form compounds called alkylates, which are high-octane components of gasoline.

After being used in the alkylation process, the H_2SO_4–now referred to as spent acid–typically contains 88 to 95 percent H_2SO_4 and up to 5 percent water. The balance is hydrocarbons, including some light hydrocarbons that can vaporize.

To recycle the acid, Motiva sent it through a regeneration process in which it was heated and decomposed to sulfur dioxide (SO_2) and water. The SO_2 was then reacted with air and converted to sulfur trioxide (SO_3), which was subsequently converted to H_2SO_4 through contact with water in an absorber. The fresh H_2SO_4 has a composition of approximately 99 percent acid.

1.5 Sulfuric Acid Storage Tanks

Six storage tanks, numbered 391 through 396, were originally built in 1979 for the storage of fresh H_2SO_4. As operations changed, the tanks were converted to serve as storage for spent H_2SO_4 by the addition of carbon dioxide (CO_2) inerting[1] and the installation of conservation pressure/vacuum vents[2] with a flame arrestor.[3] Tanks 391 and 396 were converted in 1997, and tanks 392 and 393 were converted in 2000.

At the time of the incident, and for some time previously, the Motiva H_2SO_4 regeneration system could not handle the entire load of spent acid generated in the alkylation unit. DCR supplemented its regeneration capacity by using an offsite contractor.

[1] Inerting refers to the use of a nonflammable, nonreactive gas that renders the combustible material in a system incapable of supporting combustion (NFPA 69).

[2] A conservation vent (also referred to as a PV valve) is a weight-loaded, pilot-operated, or spring-loaded valve used to relieve excess pressure or vacuum in a tank (API, 2000).

[3] A flame arrester is a device intended to prevent a flame from propagating through an open vent into a vessel.

2.0 Description of Incident

2.1 Pre-Incident Events

Beginning in late June 2000, boilermakers from The Washington Group International, Inc. (WGI), the primary maintenance contractor at DCR, were repairing the weakened and corroded catwalk at the acid tank farm (Figure 1). SO_2 vapors from the storage tanks combined with moisture in the air to form sulfurous acid (H_2SO_3), which was causing the deterioration of the catwalk.

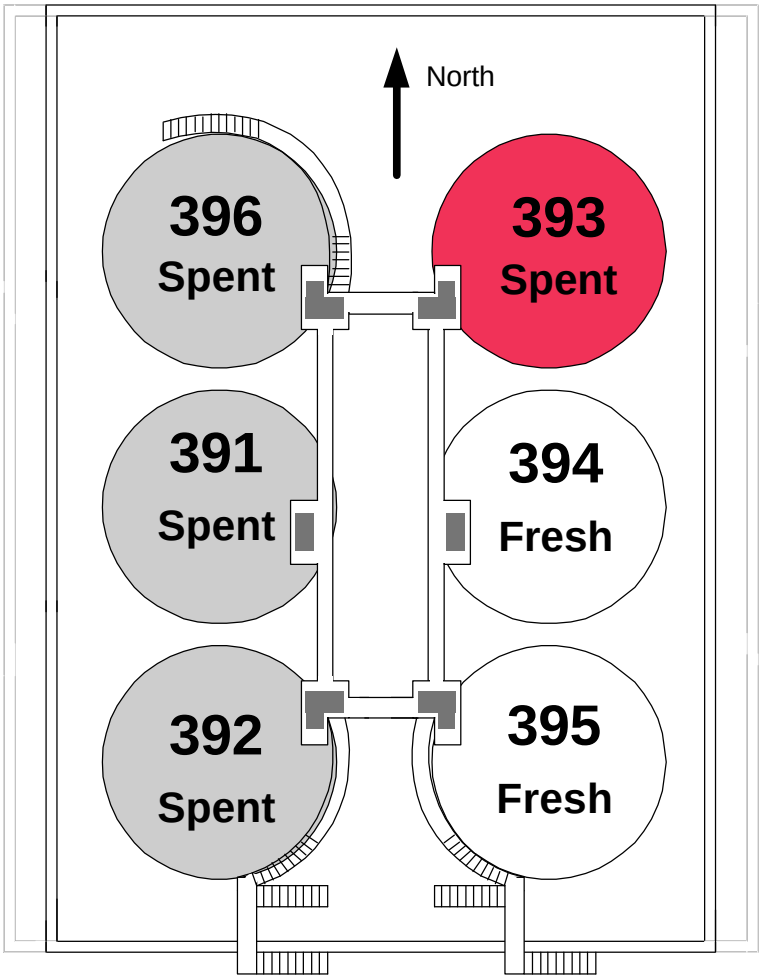


Figure 1. Layout of acid storage tanks and catwalk.

Sulfur dioxide vapors from the storage tanks combined with moisture in the air to form sulfurous acid, which was causing the deterioration of the catwalk.

The catwalk was located at the roof level of the storage tanks. It provided access to the gauge hatch used to physically measure the tank level and to various nozzles and instruments, including inerting system controls. At tank 393, the catwalk was located above the southwest section of the tank–an area that had several holes due to corrosion in both the tank roof and shell.

The boilermakers had worked the catwalk repair job at least four times prior to July 17. On at least two other occasions, however, they had arrived at the job site but could not work because unit operators were unable to approve a hot work permit . . .

The boilermakers had worked the catwalk repair job at least four times prior to July 17. On at least two other occasions, however, they had arrived at the job site but could not work because unit operators were unable to approve a hot work permit:

- The hot work permit was denied once because the outside operator considered SO_2 levels in the work area to be too high. The operator stated that an SO_2 reading of 10 parts per million (ppm) was obtained at the bottom of the stairs leading to the catwalk and the fumes were too strong to continue up the stairs.
- The hot work permit was also denied on June 27. The operator obtained a 1 percent reading on a hand-held combustible gas monitor[4] in the area where the work was to be performed and also noted a hole in the roof of tank 396.

The operator who denied the hot work permit on June 27 submitted an Unsafe Condition Report[5] on that day. The report stated:

> 393 TK is still being fed a blanket (CO_2) by a nitrogen hose [a rubber hose typically used for nitrogen] from the regulator on 396 TK. This hose is shoved in a hole in the top of the 393. The hole came from a nozzle that fell off because it was corroded so bad. 396 TK also has a (1½) nozzle that fell off because it was corroded so bad. Now it's open to atmosphere. Note: The one regulator is working for both tanks.

The report was initially distributed to the area supervisor, the safety department, and the joint (union/management) health and safety committee, and a copy was kept in the control room for other operators to read.

[4] Combustible gas monitors measure the percentage of the lower explosivity limit (LEL) present in the atmosphere. The LEL is the lowest concentration of a gas or vapor that must be present to support combustion in the presence of oxygen.

[5] Unsafe Condition Reports can be written by plant workers to bring management and union attention to safety and health issues that are not adequately addressed by the immediate supervisor.

2.2 The Incident

On July 17, 2001, four WGI boilermakers and their foreman received their assignment for the day, via a work order, to continue the job of replacing the grating on the catwalks in the acid tank farm. At approximately 7:45 am, the five boilermakers went to the acid area control room to obtain a hot work permit.

The permit allowed them to burn/weld and grind "on tank 396" (which was understood to mean the catwalk grating at tank 396) and gave instructions to stop hot work immediately if hydrocarbons were detected. The instructions on the permit called for a fire watch, acid gas respirators, warning signs, impervious gloves, face shields, and coordination with Operations. There was no requirement for the containment of sparks from the hot work.

The permit allowed them to burn/weld and grind . . . the catwalk grating at tank 396 and gave instructions to stop hot work immediately if hydrocarbons were detected. . . . There was no requirement for the containment of sparks . . .

To complete the hot work permit, the outside operator[6] went to the work area and conducted air monitoring for oxygen and the presence of flammable vapors (LEL), hydrogen sulfide (H_2S), and SO_2. The results of these tests, conducted with portable meters, were noted on the permit as "0." The outside operator filled out the gas test section of the permit and signed it.

The unit supervisor signed the permit as the cosigner; the WGI foreman signed in the acknowledgement section and left to check on other jobs. The permit for July 17 was good from 8:00 am until 4:30 pm.

Corrosion-damaged sections of grating were to be cut out and replaced by welding down new sections. The work plan was for two of the boilermakers to remove small sections, while the other two measured and prepared new pieces to replace what was cut out.

Corrosion-damaged sections of grating were to be cut out and replaced by welding down new sections.

Two of the boilermakers started out on the ground setting up equipment and then turned on the welding machine and came up onto the catwalk. After trying the oxy-acetylene cutting torch, they decided to use air carbon arc gouging because the torch was not hot enough to cut through rust on the corroded grating.

After trying the oxy-acetylene cutting torch, they decided to use air carbon arc gouging because the torch was not hot enough to cut through rust on the corroded grating.

[6] An outside operator typically works outside of a unit control room–taking readings on local gauges, and manipulating valves and other equipment under the direction of an inside operator, who monitors the control room instrumentation.

Air carbon arc gouging works by generating an electric arc between the tip of a carbon electrode and the work piece. As the work piece becomes molten, high velocity air streams down the electrode and blows away the molten metal. This process–which uses air at 80 to 100 pounds per square inch gage (psig)–ejects large amounts of molten metal over a wide area.

There was no communication between WGI and Motiva when WGI switched from oxy-acetylene to air carbon arc gouging, and a Motiva hot work requirement for "absolute spark control" was not observed.

There was no communication between WGI and Motiva when WGI switched from oxy-acetylene to air carbon arc gouging, and a Motiva hot work requirement for "absolute spark control" was not observed.

During the morning of July 17, portions of the grating around tank 396 were removed and replaced. The workers were ready to start working from tank 393 back toward tank 396 when they broke for lunch at noon.[7]

Upon returning at 12:30 pm, two boilermakers went onto the catwalk, while two remained on the ground to receive the sections removed earlier. The men on the catwalk stated that they had to lift a hose that was draped across the handrail between tanks 396 and 393 so that it would not get caught on the grating being lowered to the ground. This was likely the temporary rubber hose that supplied CO_2 inerting gas to tank 393.

The second boilermaker on the platform . . . reported that he felt a high pressure burst of air and turned to see his coworker stand up as tank 393 began to lift off its foundation pad and collapse toward the north, pulling down the catwalk.

At approximately 1:30 pm, one boilermaker was on the ground at the south end of the dike as the contract foreman drove up to the area between the tanks and the control room. The second boilermaker on the ground started up the stairs at tank 392 to the catwalk area. The two men already on the catwalk decided to start at tank 393 and work back toward the grating they had replaced in the morning, adjacent to tank 396.

At this time, the boilermaker working the air gouging equipment was kneeling and cutting out the first piece of grating above tank 393. The second boilermaker on the platform was standing south of 393 and had his back turned. He reported that he felt a high pressure burst of air and turned to see his coworker stand up as tank 393 began to lift off its foundation pad and collapse toward the north, pulling down the catwalk (Figure 2).

[7] The catwalk between tanks 396 and 393 is approximately 25 feet long.

Figure 2. Tank 393, collapsed at northeast corner of storage tank dike. (Note floor of tank 393 to the right of tank shell.)

The second boilermaker turned and ran to the south; he was starting down the steps at tank 392 when the explosion occurred and he met another coworker, who was coming up the stairs. Together they fell down the stairs and then helped each other exit the dike (Figure 3). At the same time, acid crashed against the dike wall to the south and to the north and splashed onto the ground outside the dike. As the acid flowed inside the dike, flammable material was burning on top of it. The acid overwhelmed the dike diversion system and flowed up through the grating on the streets outside the dike.

One of the boilermakers was overcome by acid fumes and was helped into the control room to get air. The acid surrounded the foreman's pickup truck, which ignited and burned. The acid continued to flow through the streets toward the control room and to the southwest.

As the acid flowed inside the dike, flammable material was burning on top of it. The acid overwhelmed the dike diversion system and flowed up through the grating on the streets outside the dike. . . . The acid continued to flow through the streets . . .

Figure 3. Tank 394 in foreground and remains of catwalk, from the north.

2.3 Incident Aftermath and Emergency Response

One contract employee was killed, and eight contract employees were injured. Most of the injuries included burning eyes and lungs and nausea due to exposure to fumes.

One contract employee was killed, and eight contract employees were injured. Most of the injuries included burning eyes and lungs and nausea due to exposure to fumes. One truck driver received acid burns to his face, hands, and legs. Three contractors were injured during the initial response effort to contain the acid.

The first Motiva fire brigade truck arrived on scene within 5 minutes of the explosion and sprayed a large amount of water into the tank farm area. The tank farm was equipped with spill collection boxes inside the dike that ran to a common header. The header ran to a valve box south of the tank farm, where it entered an internal sump system that directed flow to an acid neutralization system. However, on July 17, the large amounts of acid and firewater overwhelmed the system, and acid flowed up through the sewer gratings onto the streets outside the diked area.

The spill eventually reached both the oily water and stormwater sewers. The material in the oily water sewer flowed to the plant's wastewater treatment facility, which may have contained or treated some of the acid before it was discharged to the Delaware River. The material in the stormwater sewer flowed untreated through a Delmarva Power & Light channel and then into the river. Acid also flowed northwest from the tank farm area into a tributary of Red Lion Creek. Motiva was able to pump a portion of the acid into fly ash settling ponds.

Motiva estimated that 99,000 gallons of H_2SO_4 was released into the Delaware River. The spill resulted in approximate fish and crab kills of 2,500 and 250, respectively.

Immediately following the incident, there was concern that the remaining acid tanks could catastrophically fail due to damage from the fire and the spill of acid. Because of acid contamination and the amount of acid remaining in the undamaged tanks, workers were unable to enter the diked area until August 17, when the tanks were emptied–32 days after the incident. The search for Mr. Davis continued until September 18.

Motiva estimated that 99,000 gallons of H_2SO_4 was released into the Delaware River.

Because of acid contamination and the amount of acid remaining in the undamaged tanks, workers were unable to enter the diked area until August 17, when the tanks were emptied–32 days after the incident. The search for Mr. Davis continued until September 18.

3.0 Analysis

3.1 Corrosion and Tank Inspections

Sections 3.1.1 to 3.1.4 discuss the most likely scenario for the failure of tank 393, as summarized below:

- Flammable vapors and gases were normally present in the vapor space of the spent H_2SO_4 storage tanks.
- The tank 393 inerting system was fundamentally incapable of maintaining the oxygen concentration in the vapor space below the level necessary for combustion.
- The inerting system was further compromised by holes in the tank roof and shell.
- Hot work on the catwalk near the top of tank 393 generated sparks that either entered the tank and ignited the flammable mixture inside–or contacted flammable vapors outside the tank, near one of the holes, and flashed back inside.
- A deflagration inside the tank generated enough pressure (estimated by CSB to be 5 pounds per square inch gage [psi]) to cause the shell of the tank to separate from the floor.

Flammable vapors and gases were normally present in the vapor space of the spent H_2SO_4 storage tanks.

Hot work on the catwalk near the top of tank 393 generated sparks that either entered the tank and ignited the flammable mixture inside–or contacted flammable vapors outside the tank, near one of the holes, and flashed back inside.

3.1.1 Indications of Corrosion

The six carbon steel (CS) tanks in the DCR acid tank farm (391 through 396) were originally built in 1979 per API 650[8] and were identical except for the orientation of nozzles. The tanks each had a diameter of 47 feet, a height of 32 feet, and a nominal capacity of 415,000 gallons. Each tank was composed of four rows or courses of metal plates, each course 8 feet high. The initial thickness of the bottom course was 9/16 inch, the next course up was 7/16 inch, and the top two courses and the roof were 5/16 inch.

[8] API Standard 650, Welded Steel Tanks for Oil Storage, 1998.

3.1.1.1 Tank 393

Tank 393 had a history of localized corrosion and leaks throughout the last 8 years of its life. Using data from inspection reports, Table 1 summarizes the history of leaks and repairs on tank 393. Figure 4 shows several of the patches on the shell of the tank. (See Appendix A for additional details.)

Table 1
Tank 393 Deterioration and Repair History

Date	Inspection Findings
1992	**Thickness readings:** approximately half of the corrosion allowance is used up in large sections of the entire exposed area
1994	**Internal inspection:** corrosion groove ¾ inch wide and extending 270 degrees around shell, 4 inches above floor plate; repaired with a buildup of weld metal
June 1998	**Shell leak:** leak ¾ inch long and 3/32 inch wide, 18 feet above tank floor; repaired with 6-inch-diameter steel plate
April 1999	**Shell leak:** 1/8-inch-diameter hole, 18 inches above repair made in 1998; repaired with 8-inch-diameter patch
September 1999	**Shell leak:** 1-inch-long by 3/16-inch-wide hole, directly above previous leaks; repaired with 35- by 11-inch-wide patch to cover areas of reduced thickness
April 2000	**Shell leak:** horizontal leaks due to grooving extending through shell wall in same area as previous leaks; 12- by 29-inch-long CS patch recommended
July 2000	**Shell leak:** leaks from April 2000 were covered with an epoxy patch instead of the recommended CS patch; the patch leaked and was replaced with a CS patch
May 2001	**Shell leak:** 3- by 1/8-inch-wide leak directly above a previously installed patch; recommended 22- by 22-inch repair patch was not installed

Figure 4. Side of tank 393 showing series of patches.

Post-incident analysis revealed three additional openings in the roof and shell of tank 393 that were believed to have been present prior to the incident:

- A 5.5-inch-long mushroom-shaped perforation just under the roof-to-shell joint, near the overflow line.
- A 14-inch elongated hole in the area of the bubbler system nozzles on the roof of the tank. This hole, which originally housed a 2.5-inch-diameter nozzle on the roof, was under insulation (see Figure 5).
- A 1.5-inch hole in the roof, created when a nozzle–originally used for a level indication system–fell off due to corrosion. The temporary CO_2 inerting hose was inserted into this hole (Figure 6).

Post-incident analysis revealed three additional openings in the roof and shell of tank 393 that were believed to have been present prior to the incident . . .

Figure 5. Elongated hole on roof of tank 393 (covered by insulation at time of incident).

Figure 6. Hole in roof of tank 393 through which temporary hose was inserted.

3.1.1.2 Corrosion in Other Acid Tanks

In addition to tank 393, other DCR acid tanks experienced significant corrosion over the years.

- **Tank 391**–An internal inspection in 1993 found severe horizontal corrosion rings approximately 8 feet above the floor of the tank. One band was 6.5 inches wide and extended 270 degrees around the circumference of the tank. A second band was ¼ inch wide and extended a full 360 degrees around the tank. The corroded areas were removed and replaced with fresh metal.
- **Tank 394**–Ultrasonic thickness measurements (UTM) in 1992 revealed corrosion in a vertical pattern in the area of the level bubbler instrument. Three- to 6-foot-wide patches were installed 24 feet up the side of the tank.
- **Tank 395**–In 1992, UTM readings indicated that the corrosion allowance was almost completely used up, and a maximum liquid height restriction of 25 feet was imposed. In 1995, an internal inspection found significant corrosion on the shell and roof. The tank was condemned, and a replacement tank that used the existing tank floor and the bottom 6 inches of the shell was installed.
- **Tank 320**–This tank was one of four acid tanks (320, 321, 322, and 398) located at the H_2SO_4 alkylation unit. Accelerated corrosion was observed in an internal inspection in 1996; the shell had deteriorated to a thickness that warranted retirement per API 653.[9] The tank was demolished and replaced.
- **Tank 398**–An internal inspection in 1998 revealed that the roof and shell were holed through in "numerous locations." The holes were in a vertical band extending from the roof down through the shell toward the ground. This pattern of corrosion was similar to that on tank 393. Eight- by 8-foot replacement plates were installed in both the shell and the roof of the tank, and severely corroded roof nozzles were replaced.

[9] API Standard 653, Tank Inspection, Repair, Alteration, and Reconstruction, December 1995.

3.1.1.3 Tank Inspections

As discussed in Section 3.4, the inspection of tank 393 was repeatedly delayed. Motiva employees told CSB investigators that its tank inspection program followed the requirements of API 653; however, several inspections required by the standard were **not** conducted, as noted below:

- An internal inspection scheduled for 1999.
- Full external inspections and UTM inspections, which could have provided key information on the deteriorating condition of tank 393. Inspections were limited to the areas around leaks.

API 653 requires that "flaws, deterioration, or other conditions" (e.g., change of service, relocation, corrosion greater than the original corrosion allowance) that might adversely affect the performance or structural integrity of the shell of a tank be evaluated to determine suitability for intended service. It further recommends that the interval between inspection of tanks be determined by service history, unless "special reasons indicate that an earlier inspection must be made."

API 653 requires that "flaws, deterioration, or other conditions" . . . that might adversely affect the performance or structural integrity of the shell of a tank be evaluated to determine suitability for intended service.

Service history includes corrosion rates measured during previous inspections or anticipated based on tanks in similar service. API 653 states that the inspection interval shall be set to ensure that the thickness of the bottom plate is sufficient, and that in no case shall the internal inspection interval exceed 20 years.

Risk-based inspection (RBI) is an alternative to inspecting by service intervals. API notes that RBI can have the effect of increasing or decreasing the 20-year interval. Historic tank leakage and failure data are integral to an RBI assessment.

Trade organization publications and open literature provide guidelines on the frequency of tank inspections. NACE International recommends "minimum" inspection frequencies for tanks in concentrated H_2SO_4 service. In RP 0294-94,[10] NACE recommends that all tanks receive three forms of regular inspection:

[10] NACE Standard RP 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures, 1994.

- Routine external visual examination
- External in-service examination every 2 years
- Internal inspection every 5 years.

NACE RP 0294-94 also states that, if any storage tank is likely to have suffered significant damage–regardless of inspection schedule–"it shall be taken out of service and subjected to a detailed inspection." Inspection frequencies may be decided on the basis of "operating conditions, experience, inspection results, fitness-for-service evaluations and risk analysis." It is likely that adherence to this NACE guideline would have resulted in even shorter inspection intervals for tank 393.

NACE RP 0294-94 also states that, if any storage tank is likely to have suffered significant damage–regardless of inspection schedule–"it shall be taken out of service and subjected to a detailed inspection."

In Materials Selector for Hazardous Chemicals, Dillon (1977) advises that an internal inspection is necessary to detect and evaluate most types of corrosion in concentrated H_2SO_4 tanks. He notes that external inspection is effective only in monitoring uniform corrosion rates.

One factor in determining inspection frequency is maintenance history. The guidance on inspection frequency, which is based on published technical articles, recommends that tanks in excess of 1,000-ton capacity be internally inspected every 5 years.

Motiva conducted an internal inspection of tank 393 in 1994. The inspection report noted that the corrosion allowance would be used up for the bottom sections of the tank shell in approximately 4 years and recommended thickness measurements or "sonoray"[11] in 1996. This inspection was not conducted.

Leaks developed in the shell of tank 393 in each year from 1998 through 2001. Starting in 1999, the inspection department recommended that the tank be inspected internally "as soon as possible." However, other than spot testing for thickness in the vicinity of specific leaks, no internal or external inspections were conducted on the tank after 1994. Table 2 details the history of inspection recommendations.

Starting in 1999, the inspection department recommended that the tank be inspected internally "as soon as possible." However, other than spot testing for thickness in the vicinity of specific leaks, no internal or external inspections were conducted on the tank after 1994.

[11] Sonoray is a synonym for ultrasonic thickness (UT) testing of tank walls and roofs using high frequency sound waves.

Table 2
History of Motiva API 653 Tank Inspector Findings and Recommendations

Date	Comments From Inspection Reports
1992	Approximately half of the corrosion allowance is used up in large sections of the entire exposed area.
1994	At the present rate of corrosion, this tank will have used up all of the corrosion allowance for the bottom two shell courses in approximately 4 years. Inspection department to sonoray in 2 years to monitor corrosion and calculate for continued service.
June 1998	This tank is overdue for an external sonoray survey as recommended in [1995].
July 1998	Remove this insulation again in 2 years for inspection department to sonoray shell.
September 1999	Due to recent tank failure, it is recommended that this tank be taken out of service as soon as possible for an internal inspection and sonoray survey.
April 2000	Due to the recent leaks on this tank, it is recommended to remove it from service for an internal inspection as soon as possible.
July 2000	This tank to be taken out of service as soon as possible for an internal inspection due to corrosion on the shell.
May 2001	This tank has a history of leaks and internal corrosion. It should be taken out of service as soon as possible for an internal inspection and permanent repair.

There was no system by which engineering staff or metallurgical experts were tasked with identifying failure trends or assessing suitability for service.

Inspection reports were distributed to a wide range of DCR managers and staff, including the hierarchy of line managers responsible for the acid tanks, Motiva and WGI maintenance departments, the engineering department, and the safety department. The trend of leaks in tank 393 and the other acid tanks was not identified. There was no system by which engineering staff or metallurgical experts were tasked with identifying failure trends or assessing suitability for service.

Motiva should also have conducted a full external inspection of tank 393. API 653 recommends full external inspections at least every 5 years, while NACE International recommends a 2-year frequency. An external inspection requires the removal of insulation "to the

extent necessary to determine the condition of the exterior wall of the tank or the roof." A thorough inspection of the tank with the insulation removed would likely have uncovered the extensive corrosion and penetrations due to corrosion in the upper shell and roof.

Motiva failed to follow good practice guidelines and recognize that the pattern of leaks on the outside of the tank was an indication of accelerated corrosion inside. Also, the history of leaks and replacements of other tanks in H_2SO_4 service was a further indication of the pattern of accelerated corrosion. The inspection recommended by the Motiva tank inspectors would likely have identified the severe corrosion in tank 393. It is likely that the holes in the tank would have been detected and repaired if the company had conducted an external inspection.

The inspection recommended by the Motiva tank inspectors would likely have identified the severe corrosion in tank 393.

3.1.2 Potential Mechanisms for Accelerated Corrosion

The inspections of tank 393 between 1992 and 1998 showed that the general rate of corrosion was in line with expected values for tanks in concentrated H_2SO_4 service (approximately 5 to 20 mils per year [0.005 to 0.020 inch per year (in./yr)]). However, the prevalence of leaks in the tank in the 3 years prior to the incident, along with the indications of horizontal grooving, demonstrated the acceleration in localized corrosion. The breaches in the tank shell discovered post-incident indicate that the problem was even more widespread than known. Published literature details the major corrosion mechanisms that should be considered for H_2SO_4 tanks.

. . . the prevalence of leaks in the tank in the 3 years prior to the incident, along with the indications of horizontal grooving, demonstrated the acceleration in localized corrosion.

3.1.2.1 Diluted Sulfuric Acid Within the Tank

H_2SO_4 in CS tanks reacts with iron in the shell to form a ferrous sulfate product and hydrogen according to the reaction:

$$\text{Fe (iron)} + H_2SO_4 \text{ (sulfuric acid)} \Rightarrow FeSO_4 \text{ (ferrous sulfate)} + H_2 \text{ (hydrogen)} \qquad \text{[Eq 1]}$$

The $FeSO_4$ forms a protective layer between the wall of the tank and the acid. Any condition that deteriorates this protective film–such as diluting the acid with additional water, high temperature, or agitation–leads to accelerated localized corrosion. In the presence of low concentration H_2SO_4 (i.e., containing a high amount of water), the $FeSO_4$ layer is absorbed into the acid solution, which compromises the protective layer and can lead to accelerated corrosion. Because of this potential, carbon steel is not recommended for H_2SO_4 service if the acid concentration is below 70 percent.

In the presence of low concentration H_2SO_4 . . . the [protective] ferrous sulfate layer is absorbed into the acid solution . . .

Accelerated corrosion occurs in concentrated H_2SO_4 tanks when water dilutes the acid, either generally or–as was the likely mechanism in tank 393–in localized areas where water accumulates. In tanks with an ingress of water, the localized concentration of the acid mixture may be lower (e.g., at the surface of the liquid).

Accelerated corrosion occurs in concentrated H_2SO_4 tanks when water dilutes the acid, either generally or–as was the likely mechanism in tank 393–in localized areas where water accumulates.

A number of routes were available for additional water to enter tank 393:

- The holes in the upper portion of the tank and the roof provided a pathway for rainwater to enter and run down the sides, contacting the surface of the acid solution.
- Additionally, the holes in the tank compromised the already inadequate CO_2 inerting system (Section 3.3.2), which allowed moisture-laden ambient air to enter the tank and subsequently condense on the inside surfaces of the roof and shell.
- The acid dilution from rainwater and atmospheric moisture increased corrosion and exacerbated the shell and roof holes, which in turn allowed more moisture to enter the tank.

The holes in the upper portion of the tank and the roof provided a pathway for rainwater to enter and run down the sides, contacting the surface of the acid solution.

The extensive series of horizontal grooves observed in the shell of the tank after the incident indicate corrosion at the liquid level surface as water mixed with the acid.

The extensive series of horizontal grooves observed in the shell of the tank after the incident indicate corrosion at the liquid level surface as water mixed with the acid.

The tank level measurement device, referred to as the "bubbler system," used instrument air as a medium. A small flow of instrument air (i.e., bubbles) entered the tank near its floor through the level probe. This air introduced some turbulence into the acid, near the wall of the tank, which likely made a small contribution to the corrosion rate by disturbing the protective $FeSO_4$ layer. Instrument air

also contains moisture, much of which would likely be absorbed soon after coming in contact with the acid solution; however, the moisture would have some effect on the dilution of H_2SO_4 because of the proximity of the bubbler tap to the wall. The bubbler system also introduced a small amount of oxygen directly into the tank.

The corrosion of carbon steel by H_2SO_4 proceeds at a faster rate as the temperature of the acid increases. Most of the holes in tank 393 were in the west and southwest quadrant. Because of the history of leaks and repairs in this area of the tank, insulation had been removed from a wide section of the shell, which then exposed it to direct heating from sunlight.

The corrosion of carbon steel by H_2SO_4 proceeds at a faster rate as the temperature of the acid increases . . . insulation had been removed from a wide section of the shell, which then exposed it to direct heating from sunlight.

3.1.2.2 Carbonic Acid

Tank 393 was inerted with CO_2. When this gas is used as an inerting agent, there is a possibility that it will react with water to form carbonic acid. Although carbonic acid has a much lower corrosion rate than diluted H_2SO_4, it would still have contributed to accelerated corrosion, especially in the vapor space of the tank.

3.1.2.3 Generation of Hydrogen Gas

The corrosion of steel produces hydrogen bubbles (see Equation 1), which can disrupt the protective $FeSO_4$ film locally, resulting in higher rates of corrosion. Hydrogen gas is also extremely flammable and would have contributed to the likelihood of flammable vapor being present in the vapor space of tank 393. However, H_2 is a very light gas and would tend to escape through the holes in the tank roof.

3.1.3 Generation of Flammable Atmosphere

. . . hydrocarbons produce a flammable atmosphere because they are lighter than the acid and float to the top of the liquid in the tank.

The Encyclopedia of Chemical Processing and Design states that because of the possible formation of a hydrocarbon layer in the spent acid, "a [spent sulfuric acid] storage tank should be designed and operated as if it contained volatile hydrocarbons" (McKetta, 1995).

Typically, spent acid leaving the H_2SO_4 alkylation area contains less than 1 percent hydrocarbons; however, the hydrocarbons produce a flammable atmosphere because they are lighter than the acid and float to the top of the liquid in the tank. This layer includes isobutane and alkylates (C5–C16 isoparaffins with high octane numbers, a composition similar to that in the alkylation process reactor). Volatilization of the isobutane moves flammable vapors into the space above the liquid in the tank (Albright, 2002).

As discussed in Section 3.2.2, inadequate inerting allowed sufficient ambient air to enter tank 393 to produce a flammable mixture.

3.1.4 Finite Element Analysis of Tank Failure

. . . the peak pressure within the tank–5.0 psig–would have been reached approximately 1 second after ignition of the vapors.

CSB contracted with Engineering Systems Inc. (ESI), of Aurora, Illinois, to examine the mechanical failure of tank 393. ESI conducted a finite element analysis (FEA) using a modeling tool developed by Kansas State University. The model predicted that the peak pressure within the tank–5.0 psig–would have been reached approximately 1 second after ignition of the vapors.

Yielding at the shell-to-floor weld was predicted to have begun at approximately 4.0 psig. Furthermore, by the time the peak pressure of 5.0 psig was reached, the stresses at the corner welds exceeded the tensile strength of the tank (ESI, 2002; Figure 7).

Figure 8 shows the floor of tank 393. The curved edges clearly indicate the uplift that occurred prior to separation of the shell from the floor.

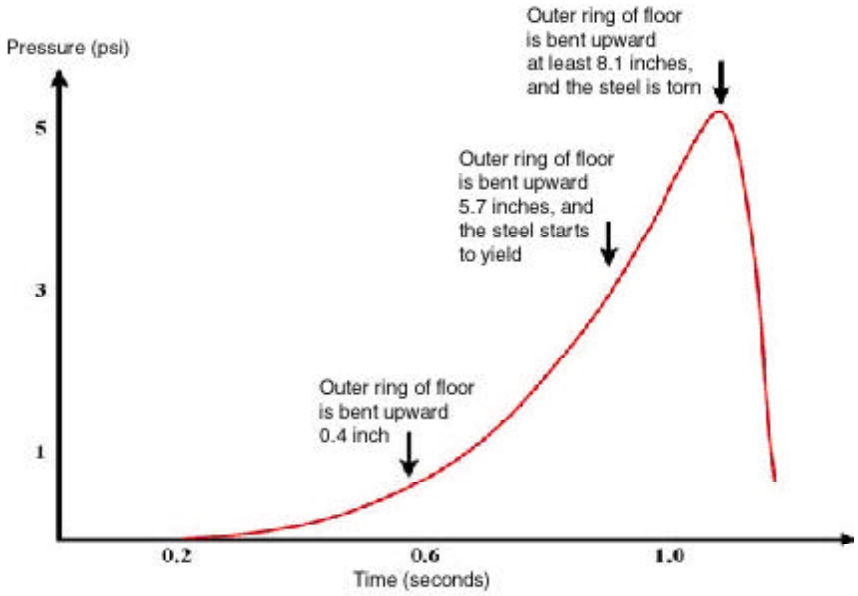


Figure 7. Modeled pressure rise in tank 393 during internal deflagration.

Figure 8. Floor of tank 393 showing uplift due to internal deflagration (before separation of shell).

3.2 Engineering of Conversion From Fresh to Spent Acid

In March 2000, tank 393 was converted from fresh to spent H_2SO_4 service. This change involved the installation of an inert gas[12] system, a conservation vent,[13] and a flame arrester.[14] These modifications were necessary because spent acid–unlike fresh acid–normally contains a small amount of light hydrocarbons that vaporize and form a flammable mixture above the liquid level. The intent of the modifications was to protect against a fuel/air explosion in the tank vapor space.

3.2.1 Process Engineering

Investigators discovered only minimal evidence of process engineering in support of conversion of the storage tanks from fresh to spent acid service. There was no documentation of engineering work on the inerting systems. An engineering analysis would have determined that the proposed system–connecting the CO_2 supply from tank 396 to tank 393–could not supply an adequate flow of CO_2 to maintain an atmosphere in the tank capable of preventing the ignition of flammable vapors (Section 3.2.2).

An engineering analysis would have determined that the proposed system–connecting the CO_2 supply from tank 396 to tank 393–could not supply an adequate flow of CO_2 to maintain an atmosphere in the tank capable of preventing the ignition of flammable vapors.

Motiva issued a work order to WGI to initiate the conversion of tank 393 to spent service. The work order stated: "Purchase and install flame arrestor and vacuum breaker. Also need CO_2 hose connected to tank." To conduct engineering for a project, Motiva supervision typically wrote a request for engineering support; however, no engineering was requested for tank 393. WGI installed a vent and flame arrestor, sized the same as those on tanks 391 and 396, and connected the temporary hose for CO_2 per the directions in the work order.

During the initial conversion of two other tanks in the acid tank farm (391 and 396) in 1997, engineers verified that the proposed conservation vent size was sufficient to provide adequate ventilation for

[12] Inert gas refers to a nonflammable, nonreactive gas that renders the combustible material in a system incapable of supporting combustion (NFPA 69).

[13] A conservation vent (also referred to as a PV valve) is a weight-loaded, pilot-operated, or spring-loaded valve used to relieve excess pressure or vacuum in a tank (API, 2000).

[14] A flame arrester is a device intended to prevent a flame from propagating through an open vent into a vessel.

normal flow of liquid into and out of the tank.[15] However, no documentation was available for determining the adequacy of the vent for thermal breathing.[16]

When tank 393 was converted in 2000, no calculations were documented. The contractors replicated the sizing of the vents used in the 1997 tank conversions.

There is no evidence that Motiva conducted engineering analyses of other scenarios that could result in abnormal or emergency tank venting, such as failures of the inerting system (allowing excessive flow of inert gas to enter the tank) or an external fire that volatilizes hydrocarbon liquids in the tank. API 2000 discusses the need for an adequate engineering design for these specific scenarios.[17]

The original design of tank 393, as a fresh H_2SO_4 tank, did not necessitate an emergency pressure relief system, such as a frangible roof.[18] However, the conversion to spent acid service invalidated the original premise.[19]

---

[15] One of the sizing criteria for conservation vents is to ensure that sufficient air or inert gas enters the tank when liquid is pumped out, or leaves the tank when liquid is pumped in, to displace the volume of liquid leaving or entering the tank. If insufficient vapor is added to replace the volume of liquid leaving the tank, the pressure drops and the resulting vacuum may damage the tank. Conversely, if insufficient venting occurs when pumping liquid into the tank, it may be subject to damaging overpressure.

[16] Thermal breathing refers to the movement of gas into or out of a tank when the vapors in the tank expand or contract due to weather changes (i.e., an increase or decrease in atmospheric temperature).

[17] API Standard 2000, Venting Atmospheric and Low-Pressure Storage Tanks, 1998.

[18] A frangible roof is a weak roof-to-shell attachment that preferentially fails over other welded joints when subject to overpressure. Failure of the roof-to-shell joint provides a means to relieve overpressure and to avoid catastrophic failure of the tank and loss of contents.

[19] No emergency venting was provided in the original design because the emergency vent loading for fresh H_2SO_4 is relatively low given the extremely low volatility of acid, even when subject to an external fire scenario; in addition, tank 393 initially had no pressure control. Spent H_2SO_4 contains some hydrocarbons with a much higher volatility, which necessitates an emergency venting capability per API 2000. Also, with the addition of an inerting system, API 2000 recommends that emergency pressure relief be designed for the scenario in which the pressure regulator valve fails in the open position, causing excessive flow of inert gas into the tank.

3.2.2 Tank Inerting Design

When tanks 391 and 396 were converted to spent acid service in 1997, each tank was equipped with a pressure regulator valve to control CO_2 flow and two local pressure gauges. However, when the inerting system on tank 393 was installed in March 2000, it was set up in a different manner (Figure 9).

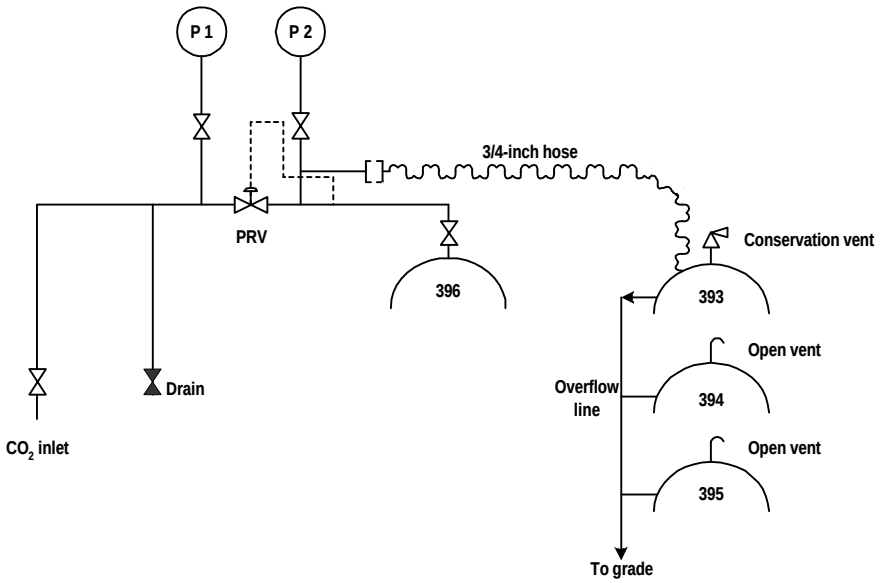


Figure 9. Inerting system schematic (CO_2 flow to tank 393 and overflow connection to 394/395).

Instead of having a dedicated pressure regulator valve, tank 393 was supplied with CO_2 from a ¾-inch flexible rubber hose connected to the piping on tank 396.

Instead of having a dedicated pressure regulator valve, tank 393 was supplied with CO_2 from a ¾-inch flexible rubber hose connected to the piping on tank 396. The hose ran along the catwalk between the two tanks and entered tank 393 through a hole in the roof (see Figure 8), which was created when a corroded nozzle fell off. The hose arrangement was considered temporary, but it remained in place for over a year and was never replaced with hard piping, as was done for the other spent acid tanks.

Motiva had no documentation of an engineering analysis to justify that piggybacking a small-diameter hose off an existing CO_2 piping system was sufficient to supply CO_2 to tank 393. In fact, there was no documentation showing the gas supply required to adequately inert any of the tanks.

Tank 393 received only a fraction of the inert gas that it required because the length and small diameter of the hose significantly restricted flow.[20] Furthermore, the control valve was not designed to regulate CO_2 flow to two tanks simultaneously, which placed an additional demand on the system.

Tank 393 received only a fraction of the inert gas that it required because the length and small diameter of the hose significantly restricted flow.

Inert gas preferentially flowed to tank 396 because it presented the path of least resistance. The pressure signal to the regulator valve did not actually sense the pressure in either tank 393 or 396, but rather measured the CO_2 pressure in the pipe immediately downstream of the regulator valve–which had the effect of further reducing the flow of CO_2 to tank 393.

A WGI instrument technician was responsible for maintaining equipment in the inerting system. This person set the pressure regulators to a positive pressure of 2 inches water column.[21] The local pressure gauges on three of the four spent acid tanks were the only indication that the CO_2 inerting system was performing properly. However, operators rarely went on the catwalk and were not required to monitor the pressure gauges as part of their daily rounds. With no pressure gauge on the CO_2 flow to tank 393, there was no way to determine if the tank was receiving CO_2 through the temporary hose.

With no pressure gauge on the CO_2 flow to tank 393, there was no way to determine if the tank was receiving CO_2 through the temporary hose.

The National Fire Protection Association (NFPA) states that purge gas[22] must be introduced and exhausted to ensure effective

[20] The valve itself, a 1-inch Fisher Rosemount Type 1190 gas-blanketing regulator, is rated for 57,700 standard cubic feet per hour (scfh) nitrogen at an inlet pressure of 80 psig, or 45,300 scfh CO_2. This does not account for restrictions due to downstream piping, valves, bends, or expansion. CSB calculations show that the CO_2 flow to tank 393 was in the range of 110 cubic feet per hour (cfh), significantly below that necessary to maintain an inert atmosphere. CSB calculations indicate that–at this flow rate–the tank would likely have contained about 16 percent oxygen, which is more than enough to sustain the combustion of flammable gas.

[21] This pressure is equivalent to the downward pressure exerted by a column of water 2 inches high.

[22] Purge gas refers to a gas that is continuously or intermittently added to a system to render the atmosphere nonignitable (NFPA 69).

distribution and to maintain the desired oxidant concentration reduction[23] throughout the system being protected.[24] Because tank 393 was continuously open to the atmosphere through holes in the roof and shell (Section 3.1), there was no way to ensure effective distribution of the inerting medium throughout the tank vapor space. Furthermore, an overflow pipe on tank 393 connected its vapor space to nearby tanks 394 and 395–both in fresh acid service–which had vents open to the atmosphere and no inerting system.

If an adequate inerting system had been installed with proper tank integrity, it is likely that there would have been no combustible fuel/air mixture in tank 393.

3.2.3 Secondary Containment Systems

The DCR acid tank farm contained six atmospheric storage tanks, each with a capacity of 415,000 gallons. Prior to the incident, these tanks contained an estimated combined total of 1.7 million gallons of fresh and spent H_2SO_4. The tanks were not individually diked; a single secondary-containment dike (180 feet long by 130 feet wide by 5 feet tall) surrounded the tank farm. A set of drains within the dike was designed to collect spills and route them to the acid plant neutralization system.

The July 17 incident resulted in the near-instantaneous release of the entire 264,000-gallon contents of tank 393. The forces created by this catastrophic failure caused the product withdrawal line on tank 396 to break, thereby also releasing its 352,000-gallon contents.

The July 17 incident resulted in the near-instantaneous release of the entire 264,000-gallon contents of tank 393. The forces created by this catastrophic failure caused the product withdrawal line on tank 396 to break, thereby also releasing its 352,000-gallon contents. The resulting fire engulfed the remaining tanks. After the fire was extinguished, acid continued to leak from tank 394 for several weeks.

The initial release of material was described as a large wave of black liquid that crashed over the dike wall. The acid overwhelmed the spill collection system inside the secondary containment dike and

[23] Oxidant concentration reduction refers to the technique of maintaining the concentration of the oxidant in a closed space below that required for ignition to occur. Oxygen in air is the most common oxidant (NFPA 69).

[24] NFPA 69, Standard on Explosion Prevention Systems, 1997.

flowed into the oily water and stormwater sewers. A total of 1.1 million gallons of acid was released during and subsequent to the incident.

The material in the oily water sewer flowed to the wastewater treatment plant, which may have contained or treated some of the acid before it was discharged to the Delaware River. From the stormwater sewer, the acid flowed untreated through a Delmarva Power & Light channel and then to the river. Acid that moved northwest from the tank farm flowed to a tributary of Red Lion Creek. A portion of the spilled acid was pumped into fly ash settling ponds. Motiva estimated that 99,000 gallons of acid reached the Delaware River, killing fish and other aquatic life.

The secondary containment dike was not designed to contain the instantaneous release of the contents of a storage tank. Although the dike had a hydrostatic design capacity of about 480,000 gallons,[25] it was not constructed to resist the dynamic tidal wave effect of such a rapid release. Noted process safety expert Frank Lees (1996) states: "It has been common to design bunds [i.e., dikes] for the hydrostatic load of the liquid in the tank, but not for the dynamic load." Although some advanced engineering techniques are available to address the issue of dynamic loading, no American Petroleum Institute (API), NFPA, or Center for Chemical Process Safety (CCPS) good practice guidelines recommend that such a sophisticated containment system be designed to contain a "tidal wave" of liquid flow.

3.3 Management of Change for Tank Conversion

When tank 393 was converted from fresh to spent acid service in 2000, several changes took place, including:

- Composition of the stored material
- Addition of tank ventilation control and flame arrester equipment
- Addition of an inert gas blanketing system.

[25] This capacity is equivalent to the contents of any single tank plus an additional safety margin.

Tanks 391 and 396 were the first two fresh acid tanks to be converted to spent acid service (in November 1997), and each had received a documented management of change (MOC) review for the flame arrester addition. However, no MOC documentation was produced for other work involved in the conversions, such as the addition of inerting systems.

API 750 states that changes in technology or facilities can introduce new hazards or compromise safeguards built into the original design.[26] It recommends that refiners review hazards that may be introduced as a result of changes in equipment and operating conditions. This procedure is known as "management of change."[27]

. . . there was no documented MOC review for any of the changes associated with the tank 393 conversion.

The Motiva MOC system was part of its process safety management program.[28] Although Motiva did not consider the acid tank farm to be covered by requirements of the OSHA Process Safety Management (PSM) Standard, MOC reviews were conducted when changes were made to some tank farm equipment (e.g., those detailed above on tanks 391 and 396); however, there was no documented MOC review for any of the changes associated with the tank 393 conversion.

An important step in the MOC process is management authorization and approval. This is an integral part of the OSHA PSM Standard, API 750, and the Chemical Manufacturers Association (CMA; now the American Chemistry Council [ACC]) guidelines. ACC states that the authorization review "should ensure that the actions required prior to the change, based on the hazard review step(s), are complete and properly documented" (CMA, 1993). The MOC associated with the tank 391 and 396 conversions was not reviewed and signed-off by other refinery departments, such as project engineering, maintenance, and inspection.

The MOC procedure used at Motiva included a checklist with 20 questions to identify potential hazards associated with the change.

[26] API RP 750, Management of Process Hazards, January 1990.

[27] MOC is a systematic method of reviewing the safety implications of modifications to process facilities, process material, organizations, and standard operating practices. Although API 750 applies to a limited range of potentially catastrophic hazards, it details the good practices and benefits of an MOC system.

[28] MOC is also a requirement under the OSHA PSM Standard, 29 CFR 1910.119, and the EPA Risk Management Program (RMP) regulation, 40 CFR 168.

However, CSB investigators determined that the checklist did not adequately address the hazards of changing atmospheric storage tanks from fresh to spent acid service, thus introducing flammable material into the tanks.

The checklist included several questions on the hazards of tank overpressure and failure of control systems, such as an inert gas blanketing system. For the tank 391 and 396 MOC checklist:

- The reviewer wrote "outside temperature" in response to: "What can cause much higher or lower than design pressure?"
- The reviewer indicated that there was no pressure relief valve to protect the equipment.
- There was no response to: "Is PSV capability adequate to relieve system?"[29]
- The reviewer answered "nothing" to: "What can happen if the control instrumentation fails?"

No concerns were documented about the possibility of tank overpressure due to nonroutine scenarios, such as an external fire. The checklist did not address the hazards of insufficient inerting of a tank containing hydrocarbons.

In 1993, CMA provided the following good practice guidance in Managing Process Changes: "For certain types of changes, plant management may determine that formal hazard evaluations are necessary. The MOC system should have formal criteria for initiating these analyses" (CMA, 1993).

The Motiva MOC procedure allowed the change initiator to request a process hazard analysis (PHA) from the site PSM coordinator. However, it provided no guidance on when to request a more comprehensive hazard analysis, such as a hazard and operability (HAZOP) study. The MOC for the tank conversion did not request a more thorough PHA.

Another aspect of MOC is the requirement for a prestartup safety review after the physical change is made, but before the revised equipment is used. Such a safety review would likely have identified

. . . CSB investigators determined that the [MOC] checklist did not adequately address the hazards of changing atmospheric storage tanks from fresh to spent acid service . . .

The Motiva MOC procedure allowed the change initiator to request a process hazard analysis . . . However, it provided no guidance on when to request a more comprehensive hazard analysis, such as a HAZOP study.

[29] PSV is an abbreviation for pressure safety valve; it is synonymous with pressure relief valve.

the temporary hose inserted into a hole on top of tank 393 as an unacceptable means of delivering inerting gas.

. . . a prestartup safety review . . . would likely have identified the temporary hose inserted into a hole on top of tank 393 as an unacceptable means of delivering inerting gas.

With a more comprehensive application of its MOC system prior to initiating the tank 393 conversion–including a review by a multidisciplinary team of refinery personnel–Motiva would likely have identified the inadequacy of the proposed inerting system, the lack of emergency pressure relief capability, and the need for engineering.

3.4 Management Practices–Tank 393

3.4.1 Lack of Recognition of Imminent Hazard Potential

Motiva management personnel did not recognize the imminent danger that tank 393 presented to people and the environment. This lack of recognition occurred despite:

- The history of leaks on tank 393.
- The pattern of corrosion reflected in the failure of other acid tanks.
- The repeated calls of Motiva inspectors for an internal inspection.
- The Unsafe Condition Report submitted by a unit operator on June 27, 2000, which noted holes in tanks 393 and 396.
- The supply of inerting gas to tank 393 via a temporary rubber hose dropped into a hole in the roof.

Unit managers believed that the repair of specific leaks would bring the tank back to a condition as good as or better than original.

Unit managers believed that the repair of specific leaks would bring the tank back to a condition as good as or better than original. In interviews, Motiva managers consistently told CSB that they did not perceive an imminent safety threat. At worst, managers believed there was a risk to the environment due to tank leaks. Supervision lowered the tank liquid level below the leak point; management believed that this action, in combination with the inerting system, would eliminate hazards.

It was believed that the tank inerting system was working properly and would prevent the accumulation of a flammable atmosphere in the tank vapor space. Managers maintained this assumption without any information to back it up:

- No adequate engineering resources were expended to properly design the system.
- No MOC procedures were followed when tank 393 was converted in 2000.
- No engineering or administrative controls were implemented (e.g., pressure or oxygen alarms, or flow or pressure readings) to ensure that the inerting system was functioning properly.

It was believed that the tank inerting system was working properly and would prevent the accumulation of a flammable atmosphere in the tank vapor space.

3.4.2 Deferral of Inspections

3.4.2.1 Operational and Inventory Constraints

Motiva missed several opportunities to inspect tank 393 when it was emptied in 2000 and 2001. Management stated that it was necessary to keep tank 393 in service to help handle high acid plant inventories because of operating problems in the acid regeneration unit that prevented it from operating at design rates. Excess spent acid was shipped to a contractor, who was also experiencing operating problems.

Motiva missed several opportunities to inspect tank 393 when it was emptied in 2000 and 2001.

In any case, in spite of the high inventory situation, Motiva switched the service of tank 393 between fresh and spent acid several times:

- In April 2000, from fresh to spent acid.
- In October 2000, from spent to fresh acid.
- In April 2001, from fresh to spent acid (until July 17, the day of the incident).

The tank was emptied to switch services. The switchover did not require a cleaning or draining, simply the removal of as much material as possible by pump. Each switchover represented an opportunity

around which Motiva could have planned its inventory and acid regeneration schedules to allow for inspection of tank 393.

Each switchover represented an opportunity around which Motiva could have planned its inventory and acid regeneration schedules to allow for inspection of tank 393.

Motiva estimated that a full internal inspection of one of the spent acid tanks required 3 months, including draining and cleaning; any necessary repairs lengthened the out-of-service time. To accommodate this time span, Motiva management could have considered:

- Converting another fresh acid tank to spent acid.
- Slowly reducing the inventory in tank 393 by increasing shipments of acid to the regeneration contractor.
- Emptying and inspecting the tank in winter, when the usage of spent acid was greatly reduced.

Motiva management did not pursue any of these alternatives.

3.4.2.2 EPA Inspection and Perceived Budget Constraints

In May 2000, EPA performed a Spill Prevention, Control, and Countermeasures (SPCC) inspection of DCR under the Federal Water Pollution Control Act, as amended by the Oil Pollution Act of 1990. The inspection findings and EPA response are outlined below and detailed in a Unilateral Administrative Order for Abatement of Endangerment, dated June 22, 2000:

- EPA identified three oil storage tanks that it believed presented "an imminent and substantial threat to the environment." These tanks, which showed significant corrosion, had not received an internal inspection since they were built in the late 1950s. Motiva was ordered to take the tanks out of service within 10 days.
- EPA identified 15 additional oil storage tanks either due for inspection or whose external condition suggested the need for an inspection.

EPA ordered Motiva to develop a tank inspection plan for these 18 tanks.

Motiva replied to the order with a response action plan on July 18, 2000, detailing a program to inspect all 18 tanks by September 2003.

While developing the response plan, Motiva took the opportunity to include the inspection of 26 other tanks. This effort resulted in a plan that would bring all Motiva tanks into inspection compliance by the end of 2005. Under this initial plan, tank 393 was scheduled for inspection in 2001.

In mid-2000, as the tank inspection schedules were being prepared, a team of representatives from all Motiva and Equilon refineries (jointly managed as the Equiva "Alliance") was investigating tank maintenance practices. The team identified potential savings through better management of tanks and the tank cleaning cycle. As Motiva entered the preparation period for its year 2001 budget, these potential savings were meted out to the individual refineries and resulted in reduction of the DCR tank maintenance budget.

In January 2001, as a result of this budget reduction, DCR managers re-examined the tank inspection program:

- Top priority went to two tanks that were considered imminent environmental dangers–one had a leak at the floor-to-shell weld, or "chime" area; and the second was a floating roof tank whose seal area was larger than allowed by air pollution regulations.
- Second priority went to the tanks identified by EPA in its unilateral order.

Additional tanks would be scheduled for inspection as the budget allowed.

To accommodate this budget reduction, it was decided to defer the inspection of nine tanks–including tank 393–which were not perceived by management to present safety or environmental concerns. Tank 393 was rescheduled for inspection from February 2001 to January 2002. Motiva corporate management was informed of the inspection deferral for the nine tanks at a DCR meeting in April 2001.

To accommodate [a] budget reduction, it was decided to defer the inspection of nine tanks–including tank 393–which were not perceived by management to present safety or environmental concerns. Tank 393 was rescheduled for inspection from February 2001 to January 2002.

3.5 Hot Work

Motiva allowed hot work to proceed in the vicinity of tanks known to have holes, which provided a pathway for sparks or slag to contact and ignite flammable vapors inside the tank.

The contract employees had worked the catwalk repair job four times during June and July 2001, prior to July 17. On at least two other occasions, they arrived at the job site but did not work because unit operators were unable to approve a hot work permit:

- Once because of high SO_2 levels in the work area.
- On a second occasion (June 27) because the operator obtained a 1 percent reading on a hand-held explosivity monitor in the area where the work was to be performed.

After rejecting the hot work permit on June 27, the operator submitted the Unsafe Condition Report, noted earlier, which described the holes in tanks 393 and 396.

On the day of the incident, neither the operators nor the supervisor who approved the hot work permit–nor the contract employees performing the work–were aware of the hazards posed by the holes in the roofs of the acid tanks. Additionally, the contract employees told CSB that they were not aware that spent H_2SO_4 contained flammable hydrocarbons or that there could be a flammable atmosphere in the vapor space of the spent acid storage tanks.

It is generally accepted good practice to retest the area around hot work after workers are away from the job for an extended period, such as a lunch break, or if conditions change. API 2009 states:

> For situations where the work is delayed or suspended in an area that has previously been pronounced gas-free, the permit system shall specify the length of time beyond which oxygen and flammability detector tests must be repeated or the permit reissued. . . . Periodic combustible gas and oxygen retests (or continuous monitoring) may be required while hot work is proceeding. . . . The permit should specify the monitoring frequency.[30]

Motiva allowed hot work to proceed in the vicinity of tanks known to have holes, which provided a pathway for sparks or slag to contact and ignite flammable vapors inside the tank.

Additionally, the contract employees told CSB that they were not aware that spent H_2SO_4 contained flammable hydrocarbons or that there could be a flammable atmosphere in the vapor space of the spent acid storage tanks.

It is generally accepted good practice to retest the area around hot work after workers are away from the job for an extended period, such as a lunch break, or if conditions change.

[30] API RP 2009, Safe Welding, Cutting and Hot Work Practices in the Petroleum and Petrochemical Industries, February 2002.

Several changes occurred on the day of the incident that should have triggered retesting or continuous monitoring:

- The ambient temperature rose from 71 degrees Fahrenheit (°F) at 8:00 am, when the initial testing was conducted, to 85°F at 1:00 pm, near the time of the incident. As the temperature increased, more hydrocarbons evaporated from the liquid in the tank and entered the vapor space. As the volume of vapors expanded, the temperature rise also increased the likelihood of flammable vapors being released from the tank and contacted by sparks from the hot work.

The ambient temperature rose from 71°F at 8:00 am, when the initial testing was conducted, to 85°F at 1:00 pm, near the time of the incident. . . . the temperature rise also increased the likelihood of flammable vapors being released from the tank . . .

- The contract employees switched from acetylene torch cutting to air carbon arc gouging because acetylene was not hot enough to cut through the rusted sections of the catwalk. Air carbon arc gouging generates significantly more sparks than oxy-acetylene cutting. Motiva Form R-241H, Instructions for Issuing Hot Work Permits, discusses air arc operations:

  > Air arcing involves the use of copper electrode for heating, and approximately 80 psi air pressure. Temperatures generated along with the air will gouge, cut or flush metal such as stainless steel and other hard metals. Since the air is used to blow away the melted metal, sparks and large pieces of molten metal are spread over a vast area which requires strict confinement of sparks. . . . All work requiring this type of hot work outside of vessels will be boxed in with suitable materials to assure absolute spark control.

- The repair work did not occur in one location, but moved from the catwalk area near tank 396 toward tank 393.

Motiva's "General Instructions for Issuing Safework, Hot Work, and Entry Permits" states: "Gas tests shall be for the time duration of the permit. If conditions may change, operations shall recommend use of a fixed gas monitor or a personal monitor for protection." Motiva employees stated that they would not typically retest an area unless requested by personnel doing the work.

There was no communication between WGI and Motiva when the contract employees switched from oxy-acetylene to air carbon arc gouging, and the Motiva requirement for spark control was not

There was no communication between WGI and Motiva when the contract employees switched from oxy-acetylene to air carbon arc gouging, and the Motiva requirement for spark control was not followed. Nonetheless, given the presence of a flammable atmosphere in tank 393 and the holes in the tank, any form of hot work could have resulted in the incident.

followed. Nonetheless, given the presence of a flammable atmosphere in tank 393 and the holes in the tank, any form of hot work could have resulted in the incident.

3.6 Unsafe Condition Report

The operator who denied the hot work permit on June 27, 2001, due to high flammable vapor readings wrote an Unsafe Condition Report. This report was a means by which a worker could bring to management and union attention safety and health issues that were not adequately addressed by the worker's immediate supervision.

Unsafe Condition Reports were rarely written and were considered to indicate an urgent problem. The operator reported:

> 393 TK is still being fed a blanket (CO_2) by a nitrogen hose from the regulator on 396 TK. This hose is shoved in a hole in the top of the 393. The hole came from a nozzle that fell off because it was corroded so bad. 396 TK also has a (1½) nozzle that fell off because it was corroded so bad. Now it's open to atmosphere. Note: The one regulator is working for both tanks.

This report was distributed to acid plant department supervision, the refinery safety department, and the joint [union/management] health and safety committee. A copy was placed in a book in the acid plant control room.

A safety department representative visited the area after receiving the report and noted: "Top platform walkway is a hazard, SO_2 and acid fumes. Don't allow access to area without air mask." The findings of the operator and the safety department were referred by unit supervision to a team that was formed to address safety and health issues in the acid plant area. However, in the 3 weeks between submission of the Unsafe Condition Report and the day of the incident, Motiva did not correct the deficiencies noted or implement temporary safeguards.

Unsafe Condition Reports were reviewed at monthly joint safety committee meetings. However, the June 27 report was received after the June meeting and had not yet been discussed at the time of the incident.

Although Unsafe Condition Reports were placed in the acid unit control room, there were no requirements to ensure that operators read the reports or were familiar with the issues. On the day of the incident, the operators and supervisor were not aware of the holes on the top of tanks 393 and 396.

The Unsafe Condition Report was one more factor indicating to Motiva management the imminent hazard posed by tank 393. With prompt attention to the report, it is likely that no work would have been authorized near the acid storage tanks, thus preventing the July 17 incident.

The Unsafe Condition Report was one more factor indicating to Motiva management the imminent hazard posed by tank 393. With prompt attention to the report, it is likely that no work would have been authorized near the acid storage tanks, thus preventing the July 17 incident.

3.7 Spent Sulfuric Acid Classification

The characterization of spent H_2SO_4 in oil industry material safety data sheets (MSDS) varies widely; for example, the NFPA flammability rating of spent acid varies from 0 to 3. However, several MSDSs from refiners contain the following flammability data:

- "Hydrocarbons in the acid may burn and flammable hydrocarbon gases may accumulate in the headspaces of tanks, truck trailers, and railcars."
- "OSHA Flammability Class–Flammable Liquid."

The Motiva MSDS for spent H_2SO_4 in effect at the time of the incident showed an NFPA fire rating of "0." Under "firefighting measures," the MSDS stated: "The product is not combustible."

The Motiva MSDS for spent H_2SO_4 . . . showed an NFPA fire rating of "0." Under "firefighting measures," the MSDS stated: "The product is not combustible."

There were sufficient hydrocarbons in the spent acid, in addition to those that vaporized to form the flammable atmosphere, to burn for one-half hour. Eyewitnesses stated that the surface of the liquid was burning as the spent acid flowed across and out of the diked area. The fact that Motiva installed inerting systems and flame arrestors on the H_2SO_4 tanks as they were converted from fresh to spent acid indicates that it was aware of the potential generation of flammable vapors and the need for protection.

The contract employees who had been working on the catwalk repair job were aware of the characteristic acid fumes from the storage tanks, for which they wore respirators with acid-gas cartridges. However,

The contract employees . . . were aware of the characteristic acid fumes from the storage tanks, for which they wore respirators with acid-gas cartridges. However, they were unaware of the potential flammability of the material in the tanks.

they were unaware of the potential flammability of the material in the tanks.

Based on CSB interviews with contractor personnel, it is likely that–had they known of the hazards–they would have taken additional precautions, such as using fire blankets to contain sparks from the hot work. However, given the fact that there were several openings in tank 393 and that fire blankets do not provide a barrier to flammable vapors exiting a tank, it is not certain that any precautions–short of banning hot work near the tanks–would have prevented the July 17 incident.

3.8 Review of Similar Incidents

3.8.1 Pennzoil, Rouseville

An October 16, 1995, incident at a Pennzoil refinery in Rouseville, Pennsylvania, is strikingly similar to the Motiva incident (USEPA, 1998). Welding was being conducted near a wastewater tank that contained a layer of flammable liquid. Sparks from the welding operation contacted flammable vapors at openings in the tank. An internal deflagration caused the tank to fail at the bottom seam and shoot into the air, releasing its contents, which subsequently caught fire. Five workers were killed.

In its investigation of this incident, EPA determined that:

- After initial flammability checks in the morning, hot work was allowed to continue as ambient temperatures rose. There were no rechecks for flammability after a morning work break and no use of continuous monitoring equipment.
- The tank that failed was not adequately protected from hot work. Openings in the tank allowed ignition sources to come into contact with flammable vapors.
- The tank did not have a frangible roof or other emergency venting.

3.8.2 ARCO, Channelview

Seventeen workers were killed on July 5, 1990, at the ARCO Chemical Company in Channelview, Texas, when a 900,000-gallon tank storing wastewater and hydrocarbons exploded. Although the tank had a nitrogen purge system and oxygen analyzers, the investigation determined that the nitrogen purge flow was insufficient to ensure a nonflammable atmosphere in the tank.

On the day of the incident, the oxygen analyzer–which would have provided warning of a flammable mixture–was malfunctioning. In addition, the tank contained significantly more hydrocarbons than specified in design documents. A number of possible ignition sources were identified.

3.9 Regulatory Issues

3.9.1 Process Safety Management Coverage

The DCR H_2SO_4 storage tanks were not covered under OSHA PSM, EPA RMP, or the Delaware Accidental Release Prevention Regulation.

3.9.1.1 OSHA Process Safety Management

The OSHA PSM Standard (29 CFR 1910.119) is a systematic approach to safety and the prevention of catastrophic incidents. It requires adherence to 14 elements of good safety management for processes containing specific chemicals or flammables if they are present in quantities of greater than 10,000 pounds. The PSM Standard does not cover H_2SO_4.

Although the amount of flammables in the spent acid storage tanks could not be conclusively determined, Motiva believed that the tanks were also exempt from PSM coverage under an exemption for

Although the amount of flammables in the spent acid storage tanks could not be conclusively determined, Motiva believed that the tanks were also exempt from PSM coverage under an exemption for "flammable liquids stored in atmospheric storage tanks . . . which are kept below their normal boiling point without benefit of chilling or refrigeration" . . .

"flammable liquids stored in atmospheric storage tanks . . . which are kept below their normal boiling point without benefit of chilling or refrigeration" (29 CFR 1910.119[a][1][b]). Based on these facts, Motiva did not cover its spent acid storage tanks under the PSM Standard.

. . . the DCR acid storage tanks were interconnected with the alkylation process, which was covered by the PSM Standard.

In 1995, an administrative law judge ruled that PSM coverage does not extend to stored flammables in atmospheric tanks even if connected to a process.[31] OSHA has not challenged this decision and did not cite Motiva for violations of the PSM Standard in its citations following the incident.

However, the DCR acid storage tanks were interconnected with the alkylation process, which was covered by the PSM Standard. The standard defines "process" as:

> . . . any activity involving a highly hazardous chemical including any use, storage, manufacturing, handling, or on-site movement of such chemicals, or combination of these activities. For the purposes of this definition, any group of vessels which are interconnected and separate vessels which are located such that a highly hazardous chemical could be involved in a potential release shall be considered a single process (29 CFR 1910.110[b]).

In addition, because the spent acid contained some light, flammable hydrocarbons–which are covered by the standard–there was a potential for a release involving a highly hazardous chemical.

3.9.1.2 EPA Risk Management Program

The EPA RMP contains process safety management requirements that are similar to those in the OSHA PSM Standard; however, the RMP list of covered chemicals is more restricted. Certain toxic substances are covered, as in PSM, but RMP covers only a specific list of extremely flammable materials. It does not cover the hydrocarbons in the spent acid storage tanks.

[31] U.S. Secretary of Labor v. Meer Corporation, OSHRC Docket No. 95-0341, 1995.

3.9.1.3 Delaware Accidental Release Prevention Regulation

Delaware has had a State regulation for the management of extremely hazardous substances since 1990–2 years before promulgation of the OSHA PSM Standard. Delaware adopted the EPA RMP program in 1999. However, the State regulation includes some chemicals not listed in RMP; and, for some substances, it specifes a lower threshold quantity above which companies must comply. Nonetheless, the Delaware regulation did not cover the DCR spent acid storage tanks.

[Although] Delaware has had a State regulation for the management of extremely hazardous substances since 1990–2 years before promulgation of the OSHA PSM Standard, . . . [it] did not cover the DCR spent acid storage tanks.

3.9.1.4 Motiva Acid Tank Farm PSM Activities

Motiva implemented some good process safety management practices based on elements of the OSHA PSM Standard, including a PHA for the tank farm and hot work permitting sitewide. However, Motiva did not implement, or inadequately implemented, other practices, such as:

- **Ensuring the mechanical integrity of equipment**–The OSHA PSM Standard requires facilities to correct deficiencies in equipment that are outside acceptable limits in a safe and timely manner. Motiva management did not respond to its inspectors' repeated calls for an internal inspection, nor did they repair the leak that occurred in May 2001.
- **Consistently applying MOC procedures**–Motiva's use of the MOC procedure when tanks 391 and 396 were converted from fresh to spent acid service (see Section 3.3) was inadequate, and no MOC was done when tank 393 was converted in 2000.

If Motiva had adequately applied good process safety management practices, as codified in the OSHA PSM Standard, it is likely that the July 17 incident would not have occurred.

If Motiva had adequately applied good process safety management practices, as codified in the OSHA PSM Standard, it is likely that the July 17 incident would not have occurred.

3.9.2 Jeffrey Davis Aboveground Storage Tank Act

As a result of the Motiva incident and other incidents that were not covered by State or Federal process safety regulations, the State of Delaware enacted legislation in July 2002 to control the installation, operation, maintenance, and repair of aboveground storage tanks.

The purpose of the Jeffrey Davis Aboveground Storage Tank Act–named in memory of the WGI worker killed in the Motiva incident–is to provide for the safe containment of petroleum and other regulated substances in aboveground storage tanks exceeding 12,499 gallons in capacity. The act mandates DNREC to develop regulations to address the maintenance, inspection, upgrade, and closure of such vessels, along with regulations for the cleanup of spills or releases to the environment.

The purpose of the Jeffrey Davis Aboveground Storage Tank Act . . . is to provide for the safe containment of petroleum and other regulated substances in aboveground storage tanks exceeding 12,499 gallons in capacity.

The legislation applies to substances covered under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, 42 USC 103), liquid petroleum products, and carcinogens, as well as any other substances that DNREC may add during its rulemaking. H_2SO_4 is a CERCLA hazardous substance subject to 40 CFR 302. Tanks subject to the Delaware Extremely Hazardous Substances Risk Management Act requirements are exempt from this legislation.

The Jeffrey Davis Aboveground Storage Tank Act directs DNREC to enact regulatory requirements for spill prevention and control, as summarized below:

- Product inventory or similar control system to adequately identify tank releases.
- Procedures to follow when systems indicate abnormal loss or gain of a substance that is not explainable by spillage, temperature variations, or other known causes.
- Corrective action in response to a tank release.
- Record of actions taken in accordance with the above items.
- Enforcement program.
- Standards to ensure against any future release from a tank being taken out of service or reintroduced into service.

There is also a requirement for regulations to be developed for "appropriate inspection, maintenance, monitoring, and repair of aboveground storage tanks . . ." The legislation further specifies that, at a minimum, an inspection report be developed whenever a tank is emptied for maintenance or repair or removed from service.

Inspection reports must describe the thickness of tanks and the repairs needed; a followup completion report is required. Newly constructed tanks require a report on welding certification, and nondestructive testing (NDT) prior to placing the tank in-service. In addition to submitting a copy to DNREC, all reports are to be kept on file for the life of the tank.

DNREC was given the authority to promulgate additional regulatory requirements consistent with the directives of the legislation. The legislature directed DNREC to "consider" the standards and recommended practices of NFPA, API, the National Association of Corrosion Engineers (NACE) International, American Society for Testing and Materials (ASTM), Underwriters Laboratories (UL), Petroleum Equipment Institute (PEI), and Steel Tank Institute (STI). Current Delaware State regulations for underground storage tanks establish inspection and maintenance requirements through "incorporation by reference" from several of these organizations.

With regard to tank inspection, maintenance, and repair, the legislation provides only the general requirements noted above. It does not directly impose new requirements for periodic internal and external tank inspections at defined intervals, such as contained in API 653,[32] nor does it specify the timeframe for repairs to be completed. For existing tanks, it requires inspection only when tanks are removed from service or emptied for maintenance or repair. However, the legislation does enable DNREC to promulgate more detailed requirements, including those from API and NACE International.

The legislation provides DNREC with the authority to inspect and monitor tanks at all reasonable times as well as to obtain copies of all records related to a regulated tank. As of July 2002, DNREC is in the initial stages of assembling a technical advisory workgroup to provide input on the specific regulatory requirements. It has a goal of completing the regulation within 24 months.

[32] API Standard 653, Tank Inspection, Repair, Alteration, and Reconstruction, December 1995.

4.0 Root and Contributing Causes

4.1 Root Causes

1. **Motiva did not have an adequate mechanical integrity management system to prevent and address safety and environmental hazards from the deterioration of H_2SO_4 storage tanks.**
   - The repeated recommendations of the tank inspectors that tank 393 be taken out of service "as soon as possible" for an internal inspection were unheeded.
   - A leak in the shell of tank 393, observed in May 2001, was not repaired. Instead, the tank liquid level was lowered below the leak point and the tank remained in service.
   - Management failed to recognize the imminent hazard posed by the holes in tank 393 and did not promptly initiate repairs or take the tank out of service
2. **Motiva engineering management and MOC systems inadequately addressed conversion of the tanks from fresh to spent acid service.**
   - The CO_2 inerting supply to tank 393, installed in 2000, was incapable of maintaining a nonflammable atmosphere.
   - CO_2 was supplied to tank 393 via a temporary hose run off the inerting system of an adjacent tank. The hose was dropped into a hole in the roof of tank 393.
   - No engineering calculations were made to determine proper sizing for the inerting system.
   - The tank conversion was completed without review of changes by technical experts, process hazard analyses, or prestartup safety reviews–all elements of a proper MOC program.
3. **The Motiva hot work program was inadequate.**
   - Motiva scheduled and permitted hot work to be conducted above and around tanks that contained flammable vapors and had known holes; tank 393 had a leak in its shell and open holes in its roof, and tank 396 also had an open hole in its roof.

- After authorizing the hot work, Motiva management did not institute adequate precautions to ensure worker safety, such as continuous monitoring.

4.2 Contributing Causes

1. **The Motiva refinery system for investigating Unsafe Condition Reports, informing workers about such reports, and tracking the satisfactory resolution of issues was inadequate.**
   - In the 3 weeks between submittal of the Unsafe Condition Report on June 27 and the day of the incident, management did not correct the reported deficiencies or implement temporary safeguards.
   - Motiva operators would likely not have authorized hot work in the vicinity of the tank if they had understood the hazards, nor would contract employees have conducted the work.
2. **The Motiva Enterprises LLC management oversight system failed to detect and hold Motiva refinery management accountable for deficiencies in the refinery's mechanical integrity, engineering management, and MOC systems.**

5.0 Recommendations

Occupational Safety and Health Administration

Ensure coverage under the Process Safety Management Standard (29 CFR 1910.119) of atmospheric storage tanks that could be involved in a potential catastrophic release as a result of being interconnected to a covered process with 10,000 pounds of a flammable substance. (2001-05-I-DE-R1)

Delaware Department of Natural Resources and Environmental Control

Ensure that regulations developed for the recently enacted Jeffrey Davis Aboveground Storage Tank Act require that facility management take prompt action in response to evidence of tank corrosion that presents hazards to people or the environment. (2001-05-I-DE-R2)

Motiva Enterprises–Delaware City Refinery

1. Implement a system to ensure accountability for mechanical integrity decision making. (2001-05-I-DE-R3) Include the following specific items:

   - Review of inspection reports by subject area experts, such as metallurgists or equipment design engineers, to ensure adequate analysis of failure trends and suitability for intended service.
   - Establishment of a planning system to ensure the timely repair of equipment.

   The Center for Chemical Process Safety (CCPS) publication, Plant Guidelines for Technical Management of Chemical Process Safety, Chapter 3, "Accountability Objectives and Goals," presents a model for such a system.

2. Review the design of existing tankage that contains or has the potential to contain flammables to ensure that, at a minimum (2001-05-I-DE-R4):

   - Inerting systems are installed where appropriate and are adequately sized and constructed.
   - Emergency venting is provided.

3. Ensure that management of change reviews are conducted for changes to tank equipment and operating conditions, such as (2001-05-I-DE-R5):

   - Tank service and contents
   - Tank peripherals, such as inerting and venting systems.

4 Revise the refinery hot work program to address the circumstances that require use of continuous or periodic monitoring for flammables. (2001-05-I-DE-R6)

5. Upgrade the refinery Unsafe Condition Report system to include the following (2001-05-I-DE-R7):

   - Designation of a specific manager with decision-making authority to resolve issues.
   - Establishment of a mechanism to elevate attention to higher levels of management if issues are not resolved in a timely manner.
   - Identification of a means to ensure communication of hazards to all potentially affected personnel.

   Work with the Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE) Local 2-898 to design and implement the improved system.

Motiva Enterprises LLC

1. In light of the findings of this report, conduct periodic audits of storage tank mechanical integrity and design, Unsafe Condition Reports, hot work, management of change, and accountability systems at Motiva oil refineries. Ensure that the audit recommendations are tracked and implemented. Share the findings with the workforce. (2001-05-I-DE-R8)

2. Communicate the findings and recommendations of this report to the workforce and contractors at all Motiva refineries. (2001-05-I-DE-R9)

American Petroleum Institute (API)

1. Work with NACE International (National Association of Corrosion Engineers) to develop API guidelines to inspect storage tanks containing fresh or spent H_2SO_4 at frequencies at least as often as those recommended in the latest edition of NACE Standard RP 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures. (2001-05-I-DE-R10)
2. Revise API tank inspection standards to emphasize that storage tanks with wall or roof holes or thinning beyond minimum acceptable thickness that may contain a flammable vapor are an imminent hazard and require immediate repair or removal from service. (2001-05-I-DE-R11)
3. Ensure that API recommended practices address the inerting of flammable storage tanks, such as spent H_2SO_4 tanks. Include the following (2001-05-I-DE-R12):
   - Circumstances when inerting is recommended.
   - Design of inerting systems, such as proper sizing of inerting equipment, appropriate inerting medium, and instrumentation, including alarms.
4. Communicate the findings and recommendations of this report to your membership. (2001-05-I-DE-R13)

NACE International (National Association of Corrosion Engineers)

1. Work with the American Petroleum Institute to develop API guidelines to ensure that storage tanks containing fresh or spent H_2SO_4 are inspected at frequencies at least as often as those recommended in the latest edition of NACE Standard RP 0294-94, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures. (2001-05-I-DE-R14)
2. Communicate the findings and recommendations of this report to your membership. (2001-05-I-DE-R15)

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE) Local 2-898	Work with Motiva management on the design and implementation of an improved Unsafe Condition Report program. (2001-05-I-DE-R16)
Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)	Communicate the findings and recommendations of this report to your membership. (2001-05-I-DE-R17)
National Petrochemical and Refiners Association (NPRA)	Communicate the findings and recommendations of this report to your membership. (2001-05-I-DE-R18)
Building and Construction Trades Department–AFL-CIO	Communicate the findings and recommendations of this report to your membership. (2001-05-I-DE-R19)

By the

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

Carolyn W. Merritt
Chair

John S. Bresland
Member

Gerald V. Poje, Ph.D.
Member

Isadore Rosenthal, Ph.D.
Member

Andrea Kidd Taylor, Dr. P.H.
Member

August 28, 2002

6.0 References

Albright, Lyle F., 2002. Report to U.S. Chemical Safety and Hazard Investigation Board.

American Petroleum Institute (API), 2002. Safe Welding, Cutting, and Hot Work Practices in the Petroleum and Petrochemical Industries, API Publication 2009, Seventh Edition, February 2002.

API, 1998. Venting Atmospheric and Low-Pressure Storage Tanks, API Standard 2000, Fifth Edition, April 1998.

API, 1998. Welded Steel Tanks for Oil Storage, API Standard 650, Tenth Edition.

API, 1995. Tank Inspection, Repair, Alteration, and Reconstruction, API Standard 653, Second Edition, December 1995.

API, 1990. Management of Process Hazards, API RP 750, January 1990.

American Welding Society (AWS), 2000. Recommended Practices for Air Carbon Arc Gouging and Cutting, AWS C5.3:2000.

Center for Chemical Process Safety (CCPS), 1995. Plant Guidelines for Technical Management of Chemical Process Safety, American Institute of Chemical Engineers (AIChE).

Chemical Manufacturers Association (CMA), 1993. Managing Process Changes: A Manager's Guide to Implementing and Improving Management of Change Systems.

Dean, S., and G. Grab, 1986. "Corrosion of Carbon Steel Tanks in Concentrated Sulfuric Acid Service," Materials Performance, July 1986, pp. 48-52.

Dillon, C.P., 1977. Materials Selector for Hazardous Chemicals, Vol. 1: Concentrated Sulfuric Acid and Oleum, Materials Technology Institute of Chemical Process Industries, Inc.

Engineering Systems Inc., 2002. Motiva Refinery Sulfuric Acid Tank Collapse Consulting, prepared for U.S. Chemical Safety and Hazard Investigation Board.

Fyfe, D., R. Vanderland, and J. Rodda, 1977. "Corrosion in Sulfuric Acid Storage Tanks," Chemical Engineering Progress, March 1977, pp. 65-69.

Lees, Frank P., 1966. Loss Prevention in the Process Industries, Oxford: Butterworth-Heinemann, pp. 22-63.

McKetta, John J., ed., 1995. Encyclopedia of Chemical Processing and Design, Marcel Dekker, Inc., p. 459.

NACE International (National Association of Corrosion Engineers), 1994. Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures, NACE Standard RP 0294-94.

NACE International, 1991. Materials for the Handling and Storage of Commercial Concentrated (90 to 100%) Sulfuric Acid at Ambient Temperatures, NACE Standard RP 0391-01.

National Fire Protection Association, (NFPA), 1997. Standard on Explosion Prevention Systems, NFPA 69.

U.S. Environmental Protection Agency (USEPA), 1998. EPA Chemical Accident Investigation Report, Pennzoil Product Company Refinery, Rouseville, Pennsylvania.

APPENDIX A: Tank 393 History

A.1 1992– Thickness Readings

In 1992, in response to inspections of tanks 394 and 395 that noted corrosion, thickness measurements were taken on a section of the tank 393 shell. This inspection noted: "Approximately half of the corrosion allowance is used up in large sections of the entire exposed area." The inspectors' recommendation at this time was to conduct an internal inspection of tank 393 within 2 years.[1]

A.2 1994– Internal Inspection

In 1994, the Star Enterprise inspection department conducted a complete internal/external inspection of tank 393. There were two key findings:

- Thickness readings of the shell indicated that general corrosion was ongoing; however, thickness readings of the roof did not show significant metal loss.
- The inspectors detailed:

> . . . a severe corrosion groove inside the bottom shell course approx. 4 [inches] above floor plate. Groove is approx. ¾ [inch] wide and up to 7/16 [inch] deep and approx. 270 degrees around tank diameter.[2]

The corrosion groove was repaired using a buildup of weld metal. It should be noted that this repaired area was observed to be intact after the July 17, 2001, incident and did not contribute to the tank failure.

In 1995, in a final report on the repairs made as a result of the 1994 inspection, the inspection department noted: "At the present rate of corrosion this tank will have used up all of the corrosion allowance for the bottom two (2) shell courses in approx. four (4) years." It was recommended that the inspection department sonoray[3] in 2 years to

[1] Star Enterprise Inspection Dept., Delaware City Plant, No. 92-662, 393-TC-9 (99% Acid Storage), September 23, 1992.

[2] Star Enterprise Inspection Dept., Delaware City Plant, No. 94-485, 393-TC-9, Internal/External Inspection, July 21, 1994.

[3] Sonoray refers to ultrasonic thickness testing of tank walls and roofs using high frequency sound waves.

monitor corrosion and calculate for continued service.[4] However, no thickness measurements were taken until 4 years later (see Section A.3).

A.3 1998– Shell Leak

In June 1998, a leak was reported in tank 393. The leak was ¾ inch long and 3/32 inch wide, located 24 inches above the course 2-to-course 3 weld seam, or 18 feet above the bottom of the tank. The inspection report noted:[5]

- Ultrasonic thickness measurements (UTM) indicate a continuing general metal loss as compared to 1992 readings.
- The exposed sections of courses 2 and 3 are still within the 1/8-inch corrosion allowance and above the API 653 minimum thickness as calculated by the updated 1997 formula.
- The tank is overdue for an external sonoray survey as recommended in IR 95-031.

One month later, the inspection department did a followup inspection of the repairs. The inspection report noted:[6]

- Tank shell was power wire brushed per IR 98-416 [see above] in the repair area. Low UTMs were found. Therefore, the final repair was a 6-inch-diameter by 3/8-inch-thick carbon steel (CS) plate welded to the shell with a 2-inch 6000# CS half-coupling welded to the plate to cover the temporary plug repair. A screwed plug was installed in the coupling as final closure.
- A 5-foot-wide section of courses 1 and 2 [was] stripped of insulation for additional sonoray. This is the same area on the west side of the tank that was stripped in 1992 per IR 92-662

[4] Star Enterprise Inspection Dept., Delaware City Plant, No. 95-031, 393-TC-9 Sulfuric Acid Storage, Final Report, January 16, 1995.

[5] Star Enterprise Inspection Dept., Delaware City Plant, No. 98-416, 393-TC-9 Sulfuric Acid Storage, Shell Leak, June 23, 1998.

[6] Star Enterprise Inspection Dept., Delaware City Plant, No. 98-454, 393-TC-9, Sulfuric Acid Storage, Follow Up to IR 98-416, Final Shell Repair and Additional Sonoray, July 2, 1998.

[see above]. Comparison to 1992 readings indicates a continued metal loss averaging 0.02 to 0.03 inch in this area.

- Remove this insulation again in 2 years to sonoray shell.

A.4 1999–Shell Leaks

In April 1999, another leak occurred on tank 393. This leak was a 1/8-inch-diameter hole, located 18 inches above the repair made in 1998. The hole was plugged and a 12-inch-diameter CS plate was welded over the leak area. Thickness readings were taken in the vicinity of the leak. One reading of 0.13 inch was noted; this point was close enough to the leak to be covered by the plate. Another area of low thickness readings was observed directly above the area with the hole, and an 8-inch-diameter patch was welded to the shell to cover this thin area. The readings in the second area ranged from 0.24 to 0.15 inch. The nominal thickness for this, the third course, was 0.312 inch.[7]

Another leak occurred in September 1999. This leak, a hole 1 inch long by 3/16 inch wide, was located 12 inches below the course 3-to-course 4 weld seam and directly above the previous leaks. Thickness readings around the hole indicated a 30-inch-long horizontal groove inside the tank. The repair for this leak and the groove finding was to install a 35-inch-long by 11-inch-wide by 5/16-inch-thick CS patch.

A further recommendation in this inspection report stated: "Due to recent tank failures it is recommended that this tank be taken out of service as soon as possible for an internal inspection and sonoray survey."[8]

[7] Motiva Enterprises LLC, 393-TC-9, Sulfuric Acid Storage Tank, Leak at West Side, No. 99-352, April 29, 1999.

[8] Motiva Enterprises LLC, Delaware City Refinery Inspection Department, 393-TC-9, Sulfuric Acid Storage Tank, Shell Leak, No. 99-819, September 14, 1999.

A.5 2000–Shell Leaks

In April 2000, horizontal leaks were observed in tank 393. These leaks appeared to be the result of horizontal grooves extending through the shell wall. The inspection report noted:

> UT [ultrasonic thickness] readings revealed there is a thin horizontal groove on the ID of the shell approximately 1/8 [inch] wide by 20 [inches] long. Readings on the grooved area were between [0].10–[0].16 [inch] thick. The areas adjacent to the grooved area were between [0].23–[0].27 [inch thick]. Nominal thickness of this shell course is [0].312 [inch].

The recommended repair was to install a 12-inch-wide by 29-inch-long CS patch. This inspection report also repeated the previous recommendation for a tank inspection: "Due to the recent leaks on this tank it is recommended to remove this tank from service for an internal inspection as soon as possible."[9]

In July 2000, an epoxy patch–which was installed on tank 393 instead of the CS patch recommended in April–was found to be leaking. On this occasion, the CS patch originally recommended was finally installed. The inspection report again recommended: "This tank to be taken out of service as soon as possible for an internal inspection due to the corrosion on the shell."[10]

A.6 2001–Shell Leak

The final leak prior to the incident was first noted in the operators' logbook on May 5, 2001. In response to this leak, the area supervisor advised the operators to maintain the tank level at 21 feet, or approximately 1 foot below the leak point, to prevent the release of acid.

[9] Motiva Enterprises LLC, 393-TC-9, Sulfuric Acid Storage Tank, Refer to IR#99-819, No. 00-326, April 6, 2000.

[10] Motiva Enterprises LLC, 393-TC-9, Sulfuric Acid Storage Tank, Refer to IR#99-818 & IR#00-325, No. 00-508, July 3, 2000.

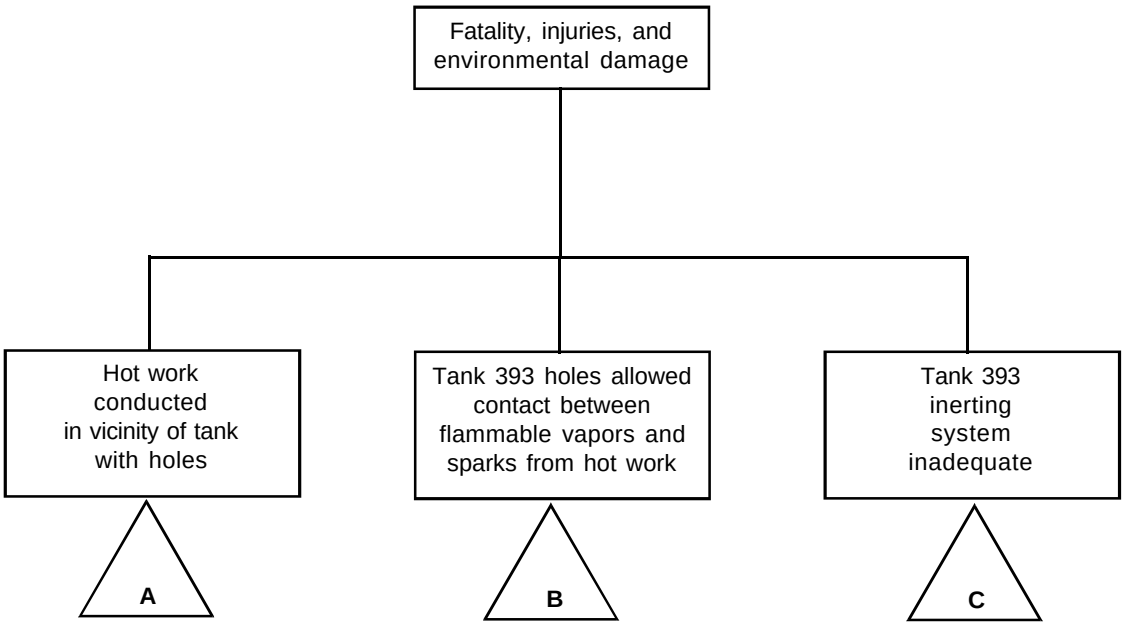
The inspection report for this leak was dated June 26, 2001[11]; the inspectors noted:

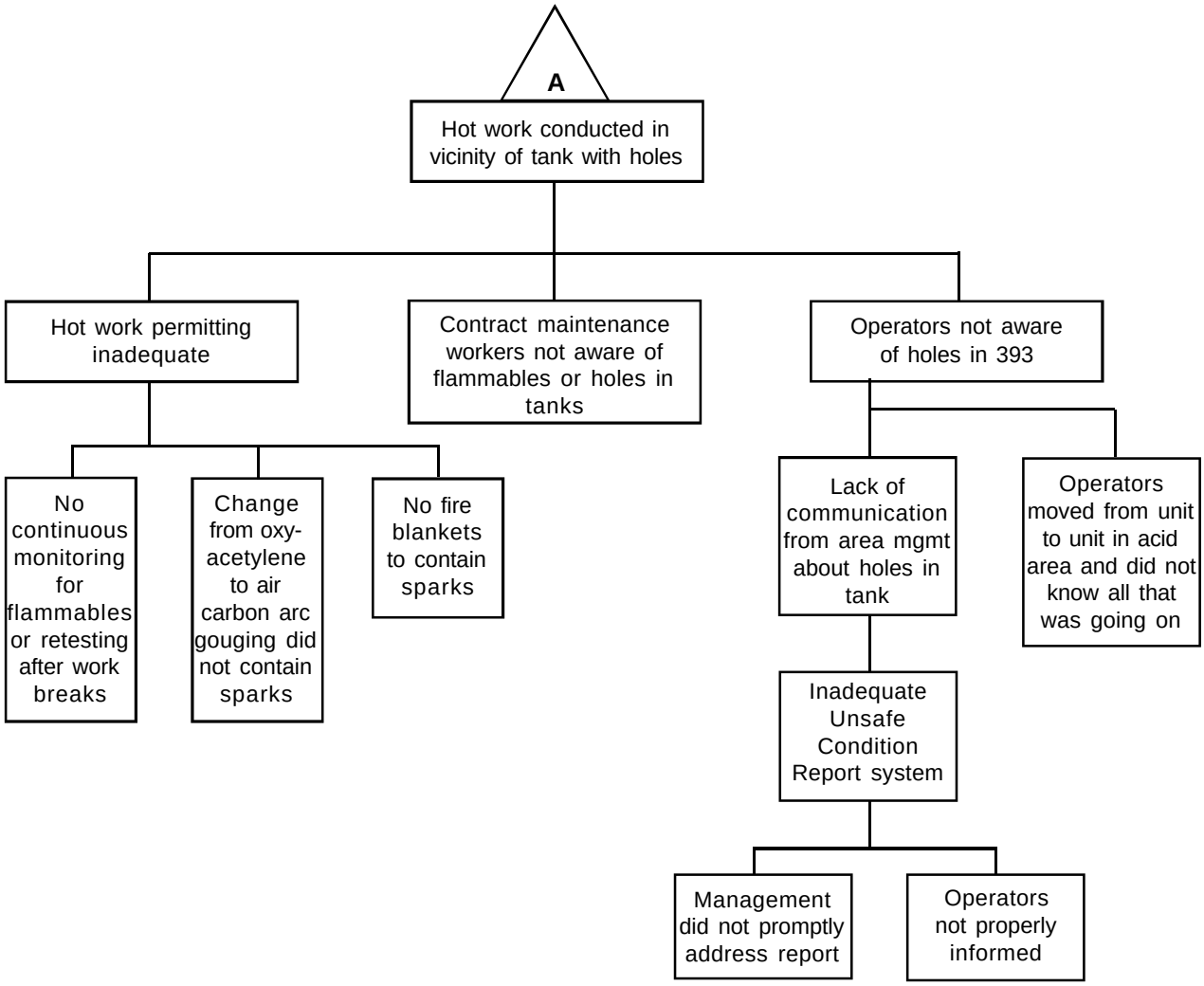
- A visual and UT inspection revealed a 3-inch-long by 1/8-inch-wide horizontal hole in the tank. The hole is approximately 1 inch above a previously installed lap patch.
- This tank has a history of leaks and internal corrosion.

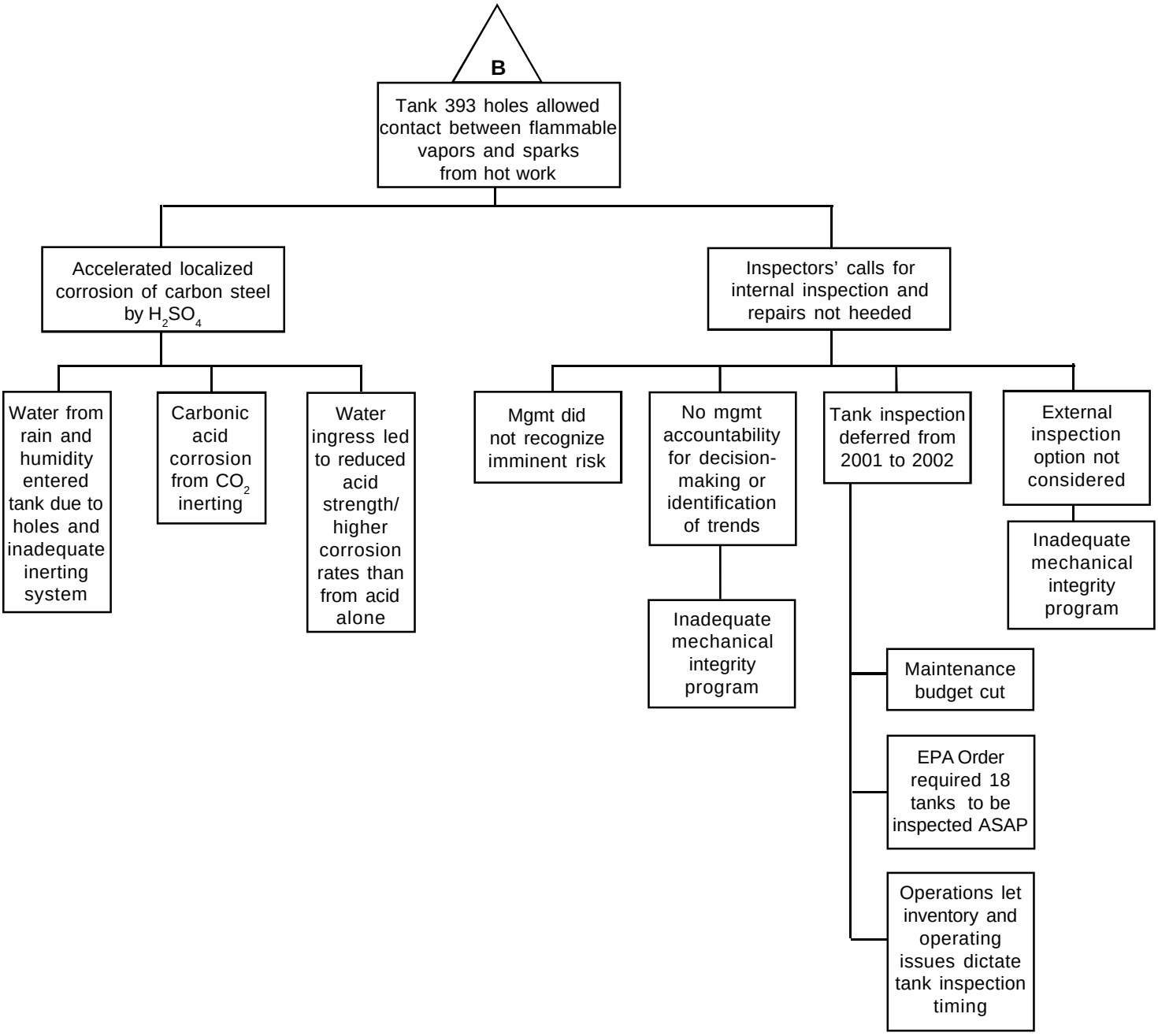
The recommended 22- by 22-inch repair patch was not installed. The inspectors also wrote: "This tank should be taken out of service asap [as soon as possible] for an internal inspection and permanent repair."

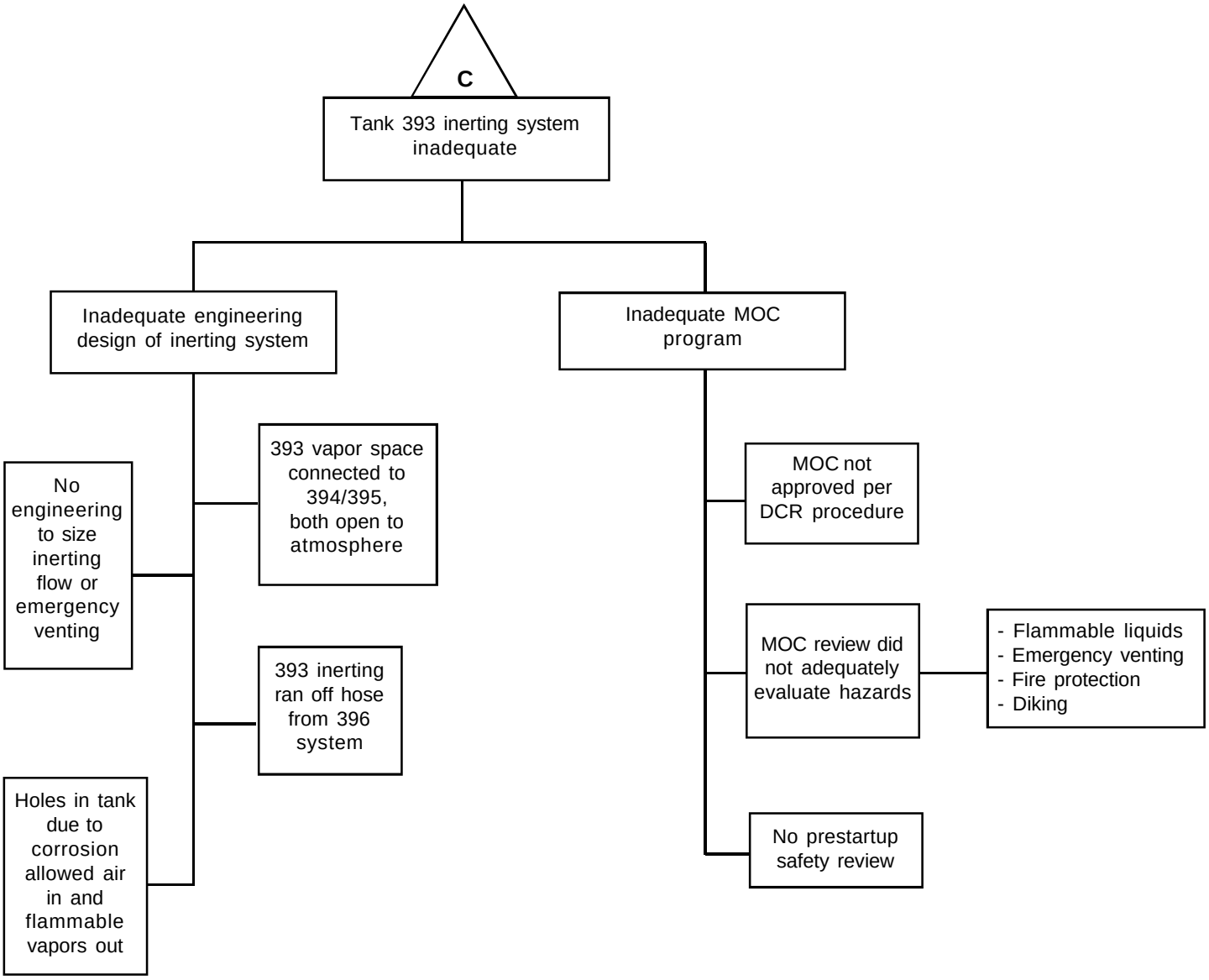
[11] Motiva Enterprises LLC, 393-TC-9, Sulfuric Acid Storage, No. 01-450, June 26, 2001.

APPENDIX B: Logic Diagram




A
Hot work conducted in vicinity of tank with holes
Hot work permitting inadequate
Contract maintenance workers not aware of flammables or holes in tanks
Operators not aware of holes in 393
No continuous monitoring for flammables or retesting after work breaks
Change from oxy-acetylene to air carbon arc gouging did not contain sparks
No fire blankets to contain sparks
Lack of communication from area mgmt about holes in tank
Operators moved from unit to unit in acid area and did not know all that was going on
Inadequate Unsafe Condition Report system
Management did not promptly address report
Operators not properly informed


B
Tank 393 holes allowed contact between flammable vapors and sparks from hot work
Accelerated localized corrosion of carbon steel by H_2SO_4
Inspectors' calls for internal inspection and repairs not heeded
Water from rain and humidity entered tank due to holes and inadequate inerting system
Carbonic acid corrosion from CO_2 inerting
Water ingress led to reduced acid strength/ higher corrosion rates than from acid alone
Mgmt did not recognize imminent risk
No mgmt accountability for decision-making or identification of trends
Tank inspection deferred from 2001 to 2002
External inspection option not considered
Inadequate mechanical integrity program
Inadequate mechanical integrity program
Maintenance budget cut
EPA Order required 18 tanks to be inspected ASAP
Operations let inventory and operating issues dictate tank inspection timing


C
Tank 393 inerting system inadequate
Inadequate engineering design of inerting system
Inadequate MOC program
No engineering to size inerting flow or emergency venting
393 vapor space connected to 394/395, both open to atmosphere
393 inerting ran off hose from 396 system
Holes in tank due to corrosion allowed air in and flammable vapors out
MOC not approved per DCR procedure
MOC review did not adequately evaluate hazards
- Flammable liquids
- Emergency venting
- Fire protection
- Diking
No prestartup safety review