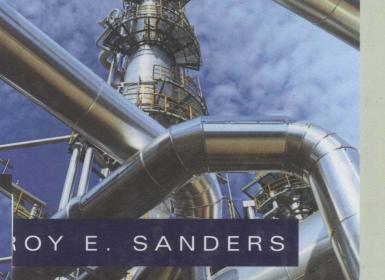




# Chemical Process Safety Learning from Case Histories

Third Edition



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# **Chemical Process Safety**

Learning from Case Histories

Roy E. Sanders



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## Preface

Look around the bookshelves for technical books. There are many good recent books and articles on Chemical Process Safety theory and procedures. These texts offer sound advice on identifying chemical process hazard analysis, training, audits, and guidelines books addressing the elements of U.S. Department of Labor's Occupation Safety and Health Administration's (OSHA's) Process Safety Management Law. However, only a few people, such as Trevor A. Kletz, offer many authentic case histories that provide opportunities to learn fundamentals in process safety.

Trevor Kletz encouraged me to write a book on plant modifications in 1989. At that time, we were working together teaching an American Institute of Chemical Engineers Continuing Education Course entitled "Chemical Plant Accidents—A Workshop on Causes and Preventions." I hope that my books in some way mimic Trevor Kletz's style of presenting clear, interesting anecdotes that illustrate process safety concepts. Hopefully, my recorded case histories can be shared with chemical process operators, operations supervisors, university professors studying chemical process safety, chemical plant pipefitters, welders, and maintenance supervisors.

The first book was a moderate success. The sequel received a new title, *Chemical Process Safety: Learning from Case Histories.* The second edition includes the best parts of the first book, two new chapters, new incidents, and plenty of additional vivid photos.

This third book offers major improvements. There are up-to-date statistics in chapter one. There is more on nitrogen asphyxiation and new case histories. There is also a completely new chapter on accidents involving compressors, hoses, and pumps. This book provides many new, useful references and many that can be found on websites.

The reader should be aware that all my experiences were within a major chemical plant with about \$2 billion replacement cost, 1500 employees, and over 600 acres of chemical plant. There are toxic gases, flammable gases, flashing flammable liquids, combustible liquids, and caustic materials, but there were no significant problems with combustible dusts and no significant problems with static electricity.

The information in this book came from a number of sources, including stories from my experiences in the now defunct Louisiana Loss Prevention Association; students in the AIChE's "Chemical Plant Accidents" course; members of the Lake Area Industries—McNeese State University Engineering Department's OSHA Support meetings; coworkers, friends, and the literature. I believe the case history stories are true, but some are hearsay and are not supported with any documentation. The approaches and recommendations made on each case seemed appropriate. However, the author, editor, and publisher specifically disclaim that compliance with any advice contained herein will make any premises or operations safe or healthful or in compliance with any law, rule, or regulation.

# Acknowledgments

#### **Third Edition**

I am appreciative of all the support I received to make this third edition a reality. I am grateful that my family and close friends understood that I had to make a few sacrifices and miss some activities to get this third edition completed.

Without the editor's support by Christine Kloiber and Phil Carmical of Elsevier Science, no words would have been written. But, once the words are written I continue to rely on the guidance and keenly developed proofreading skills, and candid critiques of Selina Cascio to convert my blemished sentences into free flowing, easily understood thoughts. Selina has helped me with nearly all of my technical writings over the past 20 years, and her input has really made a positive impact.

I am grateful for the additional material that appears in this third edition courtesy of David Chung of the U.S. Environmental Protection Agency, from Douglas S. Giles and Peter N. Lodal of Eastman Chemical Company, from Dr. Trevor A. Kletz, from Nir Keren of the Mary Kay O'Connor Process Safety Center, from Catherine Vickers of PPG, and countless others who are referenced throughout the text. I was also lucky to get talented drafting help from Manuel David. Manuel created easy-to-understand illustrations to support the narratives of the incidents.

I would be also be remiss if I did not thank the PPG Professionals in Monroeville, Pennsylvania for their technical and legal review. The Monroeville supporters include Jeff Solomon, David McKeough, and Maria Revetta.

#### **Second Edition**

I am grateful for Michael Forster of Butterworth–Heinemann for encouraging a second edition of this book. He has been a steady support for this challenge for several years. Without his energy and support this second edition would not have happened.

The professional proofreading skills of my daughter Laura Sanders and her husband Morgan Grether have be instrumental in adding life and clarity to about one half of the chapters. And the project could not be finished without the guidance, keenly developed proofreading skills, and candid critiques of Selina Cascio. I would be also be remiss if I did not thank the PPG Professionals in Monroeville, Pennsylvania for their technical review. The Monroeville supporters include David McKeough, Maria Revetta, and Irwin Stein.

I am grateful to Dr. Mark Smith, of the Institution of Chemical Engineers, for extending the permission granted in the first edition to use a few sketches and photos to enhance several case histories.

Also a note of thanks to Manuel David and Warren Schindler, talented drafters, who provided several excellent sketches to add visual images to clarify important concepts. Naturally, I am very grateful and appreciate the continuing support of Dr. Trevor A. Kletz. He has never been too busy to provide guidance.

To my wife, Jill, and to Julie and Lisa, my two daughters who live with me, thanks for understanding. When you have a full-time job, a project like this requires sacrifice. I appreciate their patience as I had to avoid some family activities for over a year while I whittled away on this project.

#### **First Edition**

A number of people deserve thanks for encouraging me and helping me with this challenge. As an engineer within a chemical manufacturing facility, opportunities to write articles did not seem realistic to me. In the early 1980s after submitting a rather primitive proposed technical paper, Bill Bradford encouraged me to draft a manuscript. My first technical paper was on the subject of Plant Modifications and it was presented to the AIChE in 1982.

In 1983, Trevor A. Kletz asked me to help him teach an American Institute of Chemical Engineers Continuing Education Course. I was shocked and elated to be considered. It was such a great opportunity to learn from this living legend in Loss Prevention. It has been educational and enjoyable ever since; he has become my teacher, my coach, and my friend.

I assisted Trevor Kletz in teaching a two-day course entitled "Chemical Plant Accidents—A Workshop on Causes and Preventions." We periodically taught the course for six years, and then he encouraged me to consider writing this book on Plant Modifications. Jayne Holder, formerly of Butterworth, was extremely supportive with all my concerns and questions.

Before I got started, I was searching for help and William E. Cleary, Jack M. Jarnagin, Selina C. Cascio, and Trevor A. Kletz volunteered to support the project. Then the hard part came. Again, Trevor Kletz and Jayne Holder encouraged me to get started.

I am grateful to Bill Cleary for his technical and grammatical critique, and to Selina Cascio for her skill in manuscript preparation including endless suggestions on style and punctuation. Jack Jarnagin's drafting assistance provided the clear illustrations throughout the text, and to Trevor for his continuous support.

Also, thanks to my wife, Jill, for both her patience and her clerical help, to my daughter Laura for proofreading, and to Warren H. Woolfolk for his help on Chapter 8. Thanks to Bernard Hancock, of the Institution of Chemical Engineers (U.K.) for his generous permission to use a number of photos to enhance the text. I also thank the management of PPG Industries—Chemicals Group, my employer, for their support. Finally, I appreciate the many contributors of incidents and photographs who, because of the situation, wanted to remain anonymous.

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#### **CHAPTER 1**

# Perspective, Perspective, Perspective

#### Introduction

Perspective, perspective, perspective—chemical manufacturing industries are often the targets of misperceptions. In this opening chapter, be prepared to see a more accurate representation of the U.S. chemical industry, including its value to humanity, its history, and its high degree of safety. The first section is a brief review of the countless benefits of the chemical industries that surround us, increase our life span, and enhance our enjoyment of life. The second section is a glimpse of the history of the vital chemical manufacturing industry. However, the concept of comparative risks is the main emphasis of this chapter. The perceived risks of the chemical industry and its occupations are often misunderstood.

Working in the chemical industry is safer than most individuals realize. We shall provide a perspective of the risks of working within this industry by comparing that risk with actual statistical dangers encountered with other well-understood occupations, commonplace activities, and life-styles. Later chapters will focus on costly errors in the chemical industry along with practices and procedures to reduce the occurrence and severity of such incidents. Viewed in isolation, case histories alone could easily lead to the inaccurate picture that the chemical industry is dangerous. In fact, the chemical industry has an impressive safety record that is considerably better than most occupations. The news media does not often speak of the safety of the chemical plants because these passive truths lack news-selling sizzle.

# The Media Rarely Focuses on the Benefits of the Chemical Industry

Chemical manufacturing and petroleum refining have enriched our lives. Few individuals in the developed world stop to realize how the chemical industry has improved every minute of their day. The benefits of the industries are apparent from the time our plastic alarm clock tells us to wake up from a pleasant sleep on our polyester sheets and our polyurethane foam mattresses. As our feet touch the nylon carpet, we walk a few steps to turn on a phenolic light switch that allows electrical current to safely pass through polyvinyl chloride insulated wires. At the bathroom sink, we wash our face in chemically sanitized water using a chemically produced soap.

#### 2 Chemical Process Safety

We enter the kitchen and open the plastic-lined refrigerator cooled by fluorochlorohydrocarbon chemicals and reach for the orange juice, which came from chemically fertilized orange groves. Many of us bring in the morning newspaper and take a quick look at the news without thinking that the printing inks and the paper itself are chemical products. Likewise, other individuals choose to turn on the morning news and do not think twice that practically every component within the television or radio was made of products produced by the chemical industry. In short, we just do not think we are surrounded by the benefits created from chemicals and fail to recognize how the industries have enriched our lives.

A recent publication distributed by the American Chemical Society states:

The chemical industry is more diverse than virtually any other U.S. industry. Its products are omnipresent. Chemicals are the building blocks for products that meet our most fundamental needs for food, shelter, and health, as well as products vital to the high technology world of computing, telecommunications, and biotechnology. Chemicals are a keystone of U.S. manufacturing, essential to the entire range of industries, such as pharmaceuticals, automobiles, textiles, furniture, paint, paper, electronics, agriculture, construction, appliances and services. It is difficult to fully enumerate the uses of chemical products and processes. . . . A world without the chemical industry would lack modern medicine, transportation, communications, and consumer products. [1]

# A Glance at the History of Chemical Manufacturing before the Industrial Revolution

Humanity has always been devising ways of trying to make life a little better or easier. In the broad sense, prehistoric people practiced chemistry beginning with the use of fire to produce chemical changes like burning wood, cooking food, and firing pottery and bricks. Clay was shaped into useful utensils and baked to form water-resistive hard forms as crude jars, pitchers, and pots at least as far back as 5000 B.C. [2]

The oldest of the major industrial chemicals in use today is soda ash. It seems to date back to 3000 to 4000 B.C. because beads and other ornaments of glass, presumably made with soda ash, were found in Egyptian tombs. It seems a natural soda ash was used as an article of trade in ancient Lower Egypt. [3]

From what we know today, even the earliest civilized man was aware of the practical use of alcoholic fermentation. The Egyptians and Sumerians made a type of ale before 3000 B.C., and the practice may have originated much earlier. Wine was also made in ancient Egypt before 3000 B.C. by treading the grapes, squeezing the juice of the crushed grapes, and allowing the juice to ferment in jars. In addition to the ale and grape-wine, the ancients drank date-wine, palm-wine, and cider. [4]

The Romans and Greeks before the Christian era seem to have been without soap as we know it, and to some of us today their cleaning methods seem unrefined. The Greeks used oil for cleansing the skin, and supplemented it with abrasives such as bran, sand, ashes, and pumice-stone. Clothes and woolen textiles were cleaned by treading the material or beating the fabric with stones or a wooden mallet in the presence of fuller's earth together with alkali, lye, or more usually ammonia in the form of stale urine. Roman fullers put out pitchers at the street corners to collect urine. As repugnant as it seems to many, it should

be noted that stale urine was used for cleaning clothes from Roman times up to the nineteenth century, when it was still in use on sailing ships. [5]

During the 900s, Europeans only lived for about 30 years, and life was a matter of much toil for very little rewards. Food was scarce, monotonous, often stale or spoiled. Homes offered minimal protection from the elements and clothing was coarse and rough. War, disease, famine, and a low birth rate were ever present. Fewer than 20 percent of the Europeans during the Middle Ages ever traveled more than 10 miles (16 km) from the place they were born. The age that followed these bleak years brought forth a burst of inventiveness as mankind began to understand how science could take over some of their burdens. [6, 7]

In Europe, the harvesting and burning of various seaweeds and vegetation along the seashore to create a type of soda ash product is one of the earliest examples of recorded industrial chemical manufacturing. No one is sure when this type of chemical processing began, but it was fairly widespread before modern recorded history. In fact, the Arabic name for soda, *al kali*, comes from the word *kali*, which is one of the types of plants harvested for this early industrial chemical producing activity. The desired product of this burned vegetation was extracted with hot water to form brown colored lye. The process yielded primarily sodium carbonate (or by its common name, soda ash), which was used to manufacture soap and glass. Soda ash is by far the oldest of the major industrial chemicals used today. [3]

During the 1600s and 1700s, scientists laid the foundations for the modern chemical industry. Germany, France, and England initially manufactured inorganic chemicals to preserve meat and other foods, make gunpowder, dye fabrics, and produce soap. In 1635, the first American chemical plant started up in Boston to make saltpeter for gunpowder and for the tanning of hides. [8]

The chemical industry was being formed as the Industrial Revolution began, but as late as 1700, only 14 elements had been identified. The early chemical manufacturing process development can be accredited to Nicolas LeBlanc, a physician to the Duke of Orleans, who outlined a method of making soda ash starting with common table salt. The Duke of Orleans gave Dr. LeBlanc sufficient funds to build such a plant not far from Paris in the 1790s. [9] Other soda plants sprang up in France, England, Scotland, Austria, and Germany. [10]

The LeBlanc Process was the first large-scale industrial chemical process. The process produced large quantities of gaseous hydrochloric acid as a by-product that released into the air and caused what was probably the first large-scale industrial pollution. It was later found that this waste gas could be captured and reacted with manganese dioxide to produce gaseous chlorine. The LeBlanc Process was used until about 1861, after which it began to be replaced by the more efficient Solvay Process. [7]

# The Modern Industrial Chemical Industry Modifies Our Way of Living

During the 1800s, chemists discovered about half of the 100 known elements. After 1850, organic chemicals, such as coal-tar dyes, drugs, nitroglycerin explosives, and celluloid plastics were developed and manufactured. The two World Wars created needs for new and improved chemical processes for munitions, fiber, light-weight metals, synthetic rubber,

and fuels. [8] The 1930s witnessed the production of neoprene (1930), polyethylene (1933), nylon (1937), and fiberglass (1938), which signaled the beginning of an era that would see plastics replace natural materials. These "plastics" would radically influence how things were designed, constructed, and packaged. [11]

After the Second World War, the expansion of the petroleum refining and chemical process industries far outstripped that of the rest of the manufacturing industries. The chemical industry also was different than the older established industries due to the nature of toxic and flammable liquids and gases. [12] Naturally, the handling and storage of hazardous materials presented a potential peril that was often far greater than those posed by the traditional industries.

By the 1950s and 1960s chemical processing became more and more sophisticated, with larger inventories of corrosive, toxic, and flammable chemicals, higher temperatures, and higher pressures. It became no longer acceptable for a single well-meaning individual to quickly change the design or operation of a chemical or petrochemical plant without reviewing the side effects of these modifications. Many case histories of significant process accidents vividly show examples of narrowly focused, resourceful individuals who cleverly solved a specific, troubling problem without examining other possible undesired consequences. [13–21]

This book will focus on a large number of near misses, damaging fires, explosions, leaks, physical injuries, and bruised egos. A flawed "plant modification," improper maintenance, poor operating practice, or failure to follow procedures was determined to be at least a contributory cause in many case histories cited in the chapters that follow. Strangers to the chemical industry might be tempted to think that it is one of the most hazardous of industries; the opposite is true. The U.S. Chemical Industries (and most European Chemical Industries) are among the safest of all industries. The facts show that it requires a high degree of discipline to handle large quantities of flammable, combustible, toxic, or otherwise hazardous materials.

The chemical industry generally handles business so well that it is difficult to find large numbers of recent incidents for examples. Many of the featured case histories in this book occurred over 20 years ago; however, the lessons that can be learned will be appropriate into the twenty-first century. Tanks can fail from the effects of overpressure and underpressure in 2010 just as well as they failed in the 1980s. Incompatible chemicals are incompatible in any decade and humans can be forgetful at any time. Before we review a single case history, it is time to boast about the safety record of the chemical industry.

#### Risks Are Not Necessarily How They Are Perceived

True risks are often different than perceived risks. Due to human curiosity, the desire to sell news, 24-hour-a-day news blitz, and current trends, some folks have a distorted sense of risks. Most often, people fear the lesser or trivial risks and fail to respect the significant dangers faced every day.

Two directors with the Harvard Center of Risk published (2002) a family reference to help the reader understand worrisome risks, how to stay safe, and how to keep the risk in perspective. This fascinating book filled with facts and figures is entitled Risk—A Practical Guide for Deciding What's Really Safe and What's Really Dangerous in the World Around You. [22]

The Introduction to Risk—A Practical Guide . . . starts with these words:

We live in a dangerous world. Yet it is also a world safer in many ways than it has ever been. Life expectancy is up. Infant mortality is down. Diseases that only recently were mass killers have been all but eradicated. Advances in public health, medicine, environmental regulation, food safety, and worker protection have dramatically reduced many of the major risks we faced just a few decades ago. [22]

The introduction continues with this powerful paragraph:

Risk issues are often emotional. They are contentious. Disagreement is often deep and fierce. This is not surprising, given that how we perceive and respond to risk is, at its core, nothing less than survival. The perception of and response to danger is a powerful and fundamental driver of human behavior, thought, and emotion. [22]

A number of thoughts on risk and the perception of risk are provided by a variety of authors. [22-29]

#### Splashy and Dreadful versus the Ordinary

In his 1995 article, John F. Ross states the public tends to overestimate the probability of splashy and dreadful deaths and underestimates common but far more deadly risks. [23] The Smithsonian article says that individuals tend to overestimate the risk of death by tornado but underestimate the much more widespread probability of stroke and heart attack. Ross further states that the general public ranks disease and accidents on an equal footing, although disease takes about 15 times more lives. About 400,000 individuals perish each year from smokingrelated deaths. Another 40,000 people per year die on American highways, yet a single airline crash with 300 deaths draws far more attention over a long period of time. Spectacular deaths make the front page; many ordinary deaths are mentioned only on the obituary page.

The authors of Risk—A Practical Guide . . . reinforce that fear pattern with this quote in the introduction, "Most people are more afraid of risks that can kill them in particularly awful ways, like being eaten by a shark, than they are of the risk of dying in less awful ways, like heart disease—the leading killer in America." [22] The appendix of this guide contains lots of supporting data. It reads that in 2001, two U.S. citizens died from shark attacks, and 934,110 citizens (1999) died of heart disease. Which one generally appears as a headline news article?

A tragic story of a 3-year-old boy in Florida (1997) illustrates this point. This young boy was in knee-deep water picking water lilies when he was attacked and killed by an 11-foot alligator. The heart-wrenching story was covered on television and in many newspapers around the nation. The Florida Game Commission has kept records of alligator attacks since 1948, and this was only the seventh fatality.

Many loving parents probably instantly felt that alligators are a major concern. However, it could be that the real hazard was minimum supervision and shallow water. Countless young children unceremoniously drown, and little is said of that often preventable possibility. The National Safety Council stated that in 2000, 900 people drowned on home premises in swimming pools and in bathtubs. Of that number, 350 were children between newborn and 5 years old. [24] ABC News estimated that 50 young children drown in buckets each year, but we are familiar with buckets and do not see them as hazards. [25]