Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres

EIGHTH VOLUME

William T. Royals, Ting C. Chou, and
Theodore A. Steinberg, editors

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Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eighth Volume

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To make technical information available as quickly as possible, the peer-reviewed papers in this publication were printed "camera-ready" as submitted by the authors.

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

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Overview

This eighth Special Technical Publication (STP) from ASTM Committee G-4 on Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres shares the same objectives as previous STPs. In these past publications, the objectives were to:

- Provide a reference text on oxygen compatibility, which remains a subject not adequately addressed in accessible literature;
- Build a reference of risk management concepts and practices used in designing and using oxygen systems;
- Provide a database to support 1) the material taught in the Committee's very successful Technical and Professional Training Course *Fire Hazards in Oxygen Systems,* and 2) the use of the numerous ASTM Committee G-4 guides, practices, and test methods;
- Serve as a guide to Committee G-4 members in their future efforts addressing the problems of safely designing, fabricating, operating, maintaining, and cleaning oxygen systems and related devices; and
- Provide the data necessary to begin the complex task of modeling the ignition and combustion processes of metallic and nonmetallic materials in oxygen-enriched atmospheres.

This STP, however, differs somewhat in character from the previous seven since it does not share the same dependence upon the Eighth International Symposium on Flammability and Sensitivity of Materials in Oxygen-Enriched Environments as the first seven did on their related symposia. ASTM Special Technical Publications are not necessarily proceedings of symposia, they do not always contain every paper presented at a related symposium, and they welcome the inclusion of papers that are not presented at symposia. Despite this distinction, the past series of seven STPs from Committee G-4 were totally dependent on their related symposia. Only occasionally was a paper not in this category.

In an effort by Committee G-4 to revitalize this series of publications, two differences in the eighth volume as compared to the previous seven volumes are notable. A series of seminars was held in conjunction with the regular biannual Committee G-4 meetings. This began in 1995 and, as a result, eight of the 35 papers included in this volume originate from seminars given at those meetings. Footnotes on the first page of each paper indicate the date and location at which the associated presentation was made.

In addition, since the early 1990s, ASTM's Committee G-4 has been exploring modifications to its peer review procedures, both to expedite publication of the volume and to produce a more uniform quality review that is fair to all parties and consistent with the Committee's stated objectives. This effort further dissociates this volume from the Eighth International Symposium by treating it as an equal and simultaneous, rather than consequential, product. Rigid deadlines were enforced, and most authors were able to meet specified due dates.

The Committee modified its past procedures concerning peer reviews within the context of the prevailing ASTM procedures. This was done for the papers produced from seminars as well as those prepared for the symposium. This modification in the review procedure involved the encouragement of peer reviewers to rely more on the use of mandatory changes rather than the more severe rejection of manuscripts. This was done except in certain obvious cases involving commercialism, poor quality, or republication. The papers included in Committee G-4's eighth STP that were subject to these new procedures clearly benefited. These new procedures and practices are expected to remain in effect in the preparation of future STPs by this committee. Indeed, an even more vital seminar series is anticipated in the next publication cycle leading up to the 2000 symposium.

This eighth volume contains papers on topics that have dominated and become the mainstay of past volumes, including component design and development or evaluation of test methods, ignition and combustion of metals, ignition and combustion of nonmetals, and failure analysis and safety. This eighth volume contains the keynote address and five sections. The keynote address is given by Ulrich H. Koch, a senior engineer for a commercial valve and fitting manufacturer, who has personally been witness to the aftermath of many failures of components and systems in oxygen service. Mr. Koch discusses several of these oxygen incidents and goes on to make a strong case for the need to develop an "oxygen system piping code" that would mandate the safety features advocated by G-4 and also be enforceable by law when adopted by various municipalities, as is the piping code and the boiler code of the ASME.

Like the keynote address, the first section of this volume highlights the importance of safety in oxygen systems. Within this section, Failure Analysis and Safety, two incident investigations are presented by Rago. This committee highly encourages the writeup of such events since they represent the unacceptable failures the committee's guides, practices, and test methods specifically try to avoid. By recording the factors causing these failures it is hoped they can be avoided in the future. Beeson, et al. present and discuss fire suppression rates and their implications in the design of hypobaric chambers. McDaniels presents an overview of failure modes and analyses techniques used by Kennedy Space Center in the characterization of NASA and Air Force flight hardware. This section also includes two papers that look at the important issue of oxygen system safety. The paper by Starr presents and reviews a newly proposed curriculum for oxygen training courses within first aid programs, and the paper by Gabel and Janoff investigates the safe use of oxygen-enriched mixtures by the SCUBA diving community.

The second section, Component Design and Development or Evaluation of Test Methods, contains four papers. The paper by Santay, et al. presents design strategies to help avoid the hazards associated with adiabatic compression in a polymer-lined flex-hose while the Newton, et al. paper presents a new test system used to evaluate materials' response to pneumatic impact with oxygen. Steinberg and Veidt present a new technique to accurately determine the regression rate of the melting interface that forms when cylindrical metal rods are burned in the configuration most common in promoted (ignition) combustion tests. Key, et al. present a discussion on what affects the reproducibility of the results obtained in these tests.

The third and largest section, Ignition and Combustion of Metals, contains twelve papers. Three papers by Wilson and Stoltzfus and Wilson, et al. take an important first step in modeling aspects of the ignition and combustion process for metals in oxygen. Equally important is their use of published ASTM data in their modeling efforts as they show the significance of these data to other, less typical, users. Six papers in this section present experimental results on the ignition and combustion characteristics of various alloys in oxygen. The data in these papers are presented and discussed, depending upon the authors, as they relate to sample configuration, oxidizer flow parameters, alloy type, burn criterion used, surface finish, and ignition resistance to particle impact. Wilson, et al. use the powdered oxide product produced when some metals burn to analyze the metal combustion process. Steinberg and Stoltzfus present results from long-duration reduced gravity tests conducted aboard the NASA KC-135 for nine metallic materials. The results are compared and shown to be consistent to results from short-duration drop-tower tests presented in earlier STPs. The results are also compared to normal gravity results and some interesting observations made. This section closes with a paper from Zawierucha and Million on their experiments to initiate burning on aluminum heat exchangers in liquid oxygen.

Ignition and Combustion of Nonmetals is the fourth section. Four of the seven papers in this section focus on the compatibility of various polymers/elastomers in oxygen environments. Williams and Faughnan present an article describing the methods used at Kennedy Space Center to characterize polymers found in oxygen environments. Steinberg presents the results of an experimental study on the flammability of several materials being considered for new rail transport carriages and some preliminary results on the burning of several endotracheal tube materials. Yentzen, et al. conclude this section with a presentation and discussion of the results of a dynamic O-ring seal tester for elastomeric materials in terms of both relative oxygen sensitivity and relative wearability.

The final section in this volume consists of five papers, a mix of interesting topics not easily classified under the other headings. With the recent increase in the use of composite materials, the paper by Beeson, et al. on the ignitibility of composites in liquid and gaseous oxygen is, perhaps, an indication of a new direction in testing for this committee. Castillo and Werley look at strategies for eliminating bypass valves in selected oxygen systems by first looking at what the bypass valve is accomplishing in the system. Egoshi, et al. present an interesting article on the migration of oil by evaporation and condensation in structured packings. These phase changes can occur during defrosting operations and results for two oils are presented and discussed. Newton, et al. present an important paper describing development, organization, and structure of data management systems for both metallic and nonmetallic materials' compatibility in oxygen-enriched environments. Development of such a database is very important as there is an enormous amount of data presently available on this topic that is not easily accessible. Sidebotham, et al. conclude the section with a discussion of the hazards associated with the burning of intestinal gas mixtures created during nitrous oxide anesthesia.

This eighth STP on the Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres, the most voluminous in the series, provides an excellent new source of information for practitioners of oxygen compatibility and clearly meets the stated objectives of the G-4 Committee.

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OXYGEN PIPING CODE—WHERE KNOWLEDGE BECOMES PRACTICE: KEYNOTE ADDRESS

REFERENCE: Koch, U.H., **"Oxygen Piping Code—Where Knowledge Becomes Practice: Keynote Address,"** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eighth Volume, ASTM STP 1319,* William T. Royals, Ting C. Chou, and Theodore A. Steinberg, Eds., American Society for Testing and Materials, 1997.

ABSTRACT: The principles of oxygen safety have been well known for many years, but oxygen fires—most having the same technical causes—continue to occur. This paper reviews several typical oxygen fire incidents. The author points out that, despite the best efforts of the ASTM G-4 Committee and others to inform and educate, existing knowledge about oxygen system safety does not reach the people who need it most, such as architects, engineers, contractors, building inspectors, and insurance underwriters. The author suggests that the ultimate solution is a national oxygen piping code and that the ASTM G-4 Committee should take an active role in its development.

KEYWORDS: oxygen fires, regulator fires, oxygen system safety, piping codes, ball valves, diving, medical oxygen, standards, guides, practices, oxygen-enriched, nonmetals, metals, materials

Introduction

This is the eighth symposium the G-4 committee has sponsored since 1982; it could have been billed as the Centennial Symposium, because the air separation industry is about a hundred years old. In 1895, Karl von Linde, a German engineer, and William Hampton, a British physician, simultaneously developed the first process for continuous liquefaction of air. A few years later, in 1902, Linde patented his fractional distillation process for air separation and a new industry was born.

Other engineers and scientists developed similar processes and contributed to the development of this industry, but the name Linde is well known because he also established a company that still exists a century later.

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Oxygen Safety Principles Well Known Long Ago

This symposium is an opportunity to exchange new information and the agenda promises many interesting papers, but the principles for the safe use of oxygen were understood a long time ago. Rather than focus on what is new, I am going to adopt the opposite point of view as my theme: In the words of King Solomon, " . . . there is nothing new under the sun."

Bob Neary reminded us of that in his opening speech at the first G-4 symposium in 1982 [*1*]. He told us about a 1923 paper that identified many common causes of oxygen regulator fires—such as adiabatic compression as a source of ignition, autoignition of nonmetals, metals ignition, and others. These causes were recognized in that paper and many subsequent papers in the intervening years. That was 60-year-old knowledge when Bob gave his keynote speech; now it is three quarters of a century-old knowledge.

I suspect that it is, in fact, century-old knowledge. I believe that Linde, Hampton, and their peers understood the essentials of what would cause an oxygen fire. Why? Without that knowledge they might not have lived long enough to complete their developments.

Principles Well Known But Often Not Practiced

If it is true that the principles of oxygen fire are old and well known, then why do we continue to have such fires? Let me show you some examples of fires I have encountered. Perhaps they will lead us to an answer.

Navy Seal Training Facility

This fire—my first encounter with oxygen fires—occurred in 1970 at the Navy's Seal Team training facility in San Diego. The lines were small, three-eighths inch stainless steel tubing, with a manifold of tube fitting tees and quarter-inch quick-opening ball valves close-coupled to the tees, all mounted on a plywood panel (FIG. 1). The causes of the fire are obvious, even from this picture: adiabatic compression from a quick-opening valve; high velocity impact at a tee; high velocity, friction, and

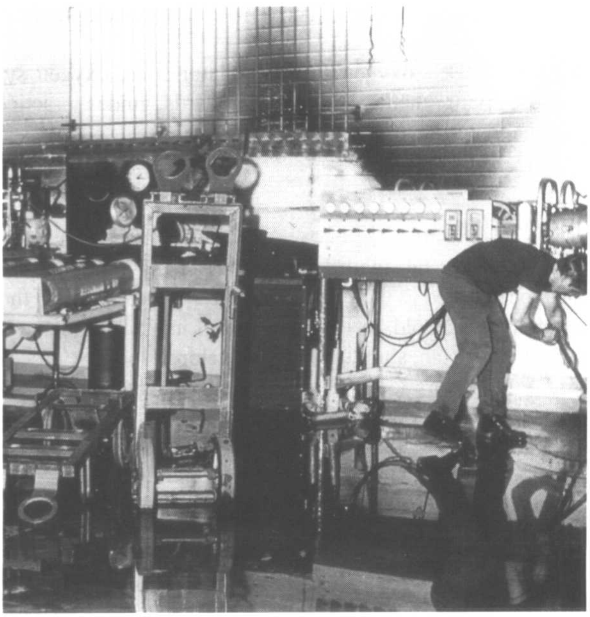

FIG. 1 — A cascade system used to fill SCUBA tanks ignited when a ball valve was opened at full pressure. The builders were experienced divers, but were not trained in oxygen system design.

particle impact at a large volume of TFE fluorocarbon inside the valve; and undoubtedly others.

There were ball valves throughout the system, but not one to serve as an emergency shutoff valve in case of fire. The fire was put out when someone climbed up on a platform and closed the valve on each individual oxygen cylinder that was feeding the fire, a risky action at best.

Why? Diving instructors built this system to refill scuba tanks. They knew how to use oxygen, but not how to design systems to handle it safely. They didn't even know how dangerous it could be or why. Neither did I. I had no idea that it was possible to create such a fire, let alone how. My hurried search for information on oxygen fires revealed nothing. The information to prevent that fire was known, but not to the people who needed it.

Fortunately, an auditor from Linde had visited our plant a couple of times to check how we were cleaning our valves ordered for oxygen service. He was a great help to me and even sent me a paper, but asked me not to circulate it because it had not been published. I read it for the first time on the plane to San Diego. It contained everything I needed to know to answer the Navy's questions and explain what caused the fire. They actually believed me! Of course, I didn't tell them how recently I had learned it and how little else I knew. The paper—undated—was written by W. E. Groves of Linde. I never met Mr. Groves, but always felt I owe him a thank-you.

Small Cylinder Filling Plant

This fire occurred when a ball valve was opened in a high-pressure line where it

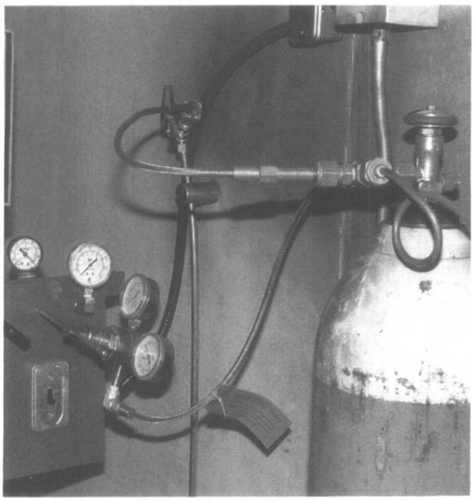

FIG. 2 — A ball valve was installed in a high-pressure oxygen line where it entered the building. It was intended to be an emergency isolation valve, but the owner did not know that. Instead, he used it as a vent valve and ignited the system.

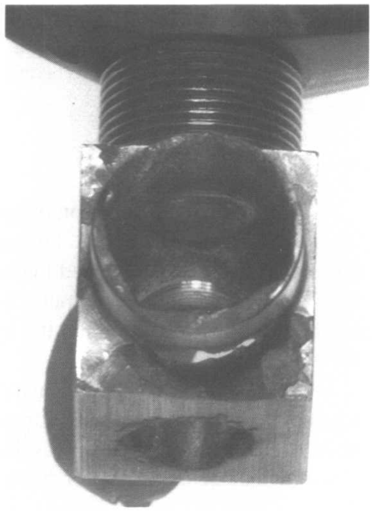

FIG. 3 — The TFE in the ball valve ignited, burned the valve, and ignited the TFE lining in the outlet hose.

entered the building (FIG. 2). The causes were the same as before: a quick-opening ball valve, high-velocity impact at TFE seats, TFE-lined hoses at the valve outlet, and so forth. Technically, nothing new (FIG. 3).

But what really caused this incident? The design guide, G-88, is supposed to be used by *qualified technical personnel,* persons with the necessary training and experience to apply the principles of chemistry and physics to oxygen systems. The two men who built this plant had years of experience from working in the industry, but neither had any formal training or experience in system design.

Nor did the person from the local jurisdiction who approved their design. He had correctly insisted on adding the ball valve where the line entered the building, obviously as an emergency shutoff valve. But no one had told the two builders why it was there, how to use it, or—most importantly—how to open it safely. After the plans were approved the builders moved their system from the center of the building to the wall, where it effectively blocked emergency access to the ball valve. Then they used the ball valve as a vent valve and started a fire.

What caused this fire? All the same causes as in the first example. Is it true that a little knowledge can be a dangerous thing?

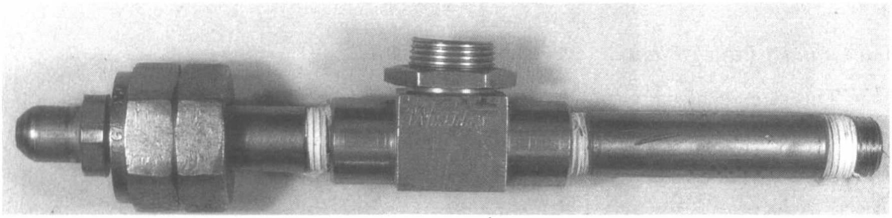

FIG. 4 — A ball valve was installed between the oxygen cylinder valve and the regulator to simplify purging.

Filling Plant Regulator Fire

One of the most common oxygen fires is a simple regulator fire. This one started when the operator opened the ball valve. But why would anyone put a ball valve between the regulator and the cylinder valve?

The regulator, which was on a gas chromatograph, was purged with nitrogen when not in use. The ball valve was there to keep air out of the regulator while it was being connected to a gas cylinder (FIG. 4). After it was connected, the operator quickly purged the short connection between the cylinder valve and the

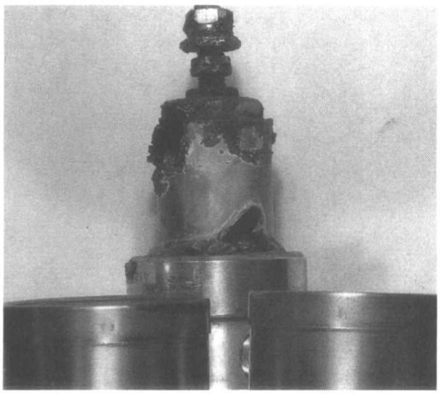

FIG. 5 — The regulator ignited when the ball valve was opened after the cylinder valve had been turned on.

ball valve by filling with cylinder gas and venting a few times through the CGA connection on the cylinder.

This time he forgot to vent before he opened the ball valve. The regulator caught fire (FIG. 5) and so did his shirt. Each time he opened the CGA connection, he sprayed his shirt with oxygen. His shirt burned violently, and he spent a couple of months in the hospital and a year off work.

The plant was a cylinder filling plant operated by a major gas company with plenty of technical experts. But where were the "qualified technical personnel" in this situation? At the home office, a thousand miles away. The operator was a young chemical engineering graduate, as was his manager. Both had ample education, but little training and even less experience. And they did not design this apparatus; their predecessors had used it for years. They were the innocent victims of a dangerous design. Once again, the need to know didn't connect with the information available.

Commercial Filling Plant

This ball valve was on a half-inch supply line, also in a cylinder filling plant owned and operated by a major gas company (FIG. 6). The operator simply opened the valve too quickly. He had been reprimanded in the past for "snapping" ball valves open. About a year before, he had attended a safety training session in which the ASTM video on oxygen fires was the training material.

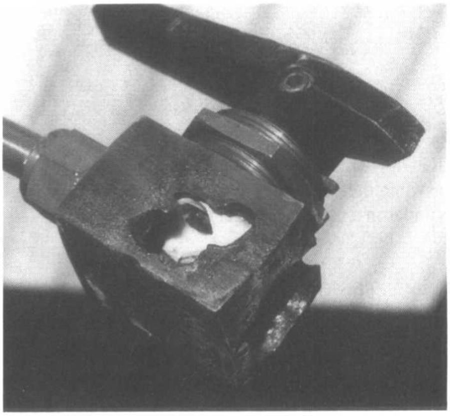

FIG. 6 — This ball valve ignited when it was opened on a high-pressure oxygen line in a cylinder filling plant. It was one of many ball valves used throughout the plant on all gases, including many oxygen lines.

The plant was loaded with ball valves in all systems, oxygen and all other gases. The plant manager argued firmly that there was nothing wrong with that. All his people were carefully trained to crack the ball valve open and listen to the sound it made. That way they could be sure to not pressurize a system too quickly. The manager made no changes after this incident.

Education, training, management, technical support resources—all the ingredients needed to do the job safely—were in place. What was the missing link? Enforcement, perhaps?

Eye Clinic

A medical clinic that did eye surgery had a small in-house oxygen supply system consisting of two cylinders, one in service and one on standby. This ball valve was on a pressure sensor that signaled when the cylinder in service was getting low (FIG. 7). It was opened when the cylinders were switched. This time the cylinder pressure entering the small volume of the sensor raised the temperature of the TFE valve seat enough to destroy it (FIG.

8). The fumes went into the oxygen system and affected the two patients in surgery—fortunately not critically.

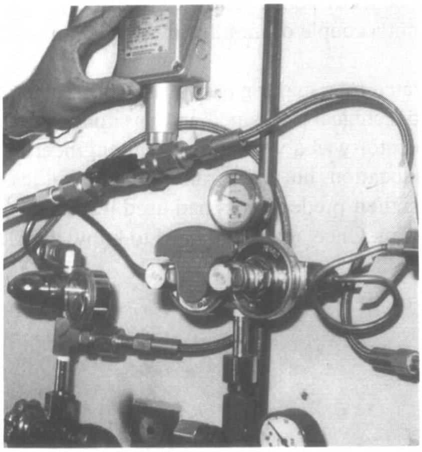

FIG. 7 — This three-way brass ball valve was used to switch the pressure sensor to the operating cylinder in a medical oxygen system.

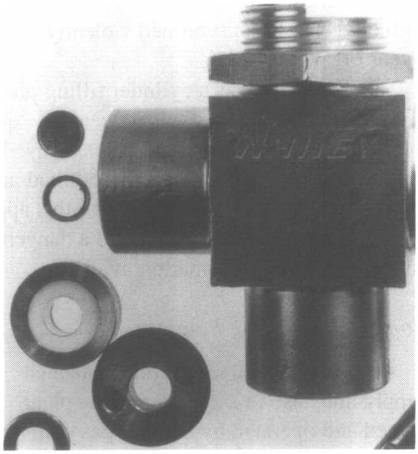

FIG. 8 — Compression heating in the ball valve burned all the TFE seats and contaminated the oxygen as it was being supplied to the patients.

The oxygen system was built by one local gas distributor and later modified by another. The person who designed the modifications was a young engineering graduate with a specialty in medical engineering. Even though his employer built such systems and sold gases to clinics in the area, he had not had any specific training on oxygen safety or system design. He had never heard of ASTM and had no idea where to get such information—or even that he needed it.

Semiconductor Plant

Modern technology is no cure for a lack of knowledge. This was in a small new semiconductor plant. An oxygen manifold for three cylinders had been fabricated out of copper tubing and three brass ball valves (FIG. 9). A sign on the wall read: "Open valves slowly." So the operator opened the cylinder valve slowly—first—and then the ball valve. The TFE in the valve at the end of the manifold burned up. Fortunately the valve was brass and did not burn.

Their solution was obvious: "The valve was defective." So the plant replaced it with an identical valve, every month for four months. Finally, the managers asked the manufacturer for help. After I explained what had happened, they realized that the fluorine from the burned TFE had caused them to make defective chips after each incident—but they had never related their problems with the oxygen system to their problems with product quality.

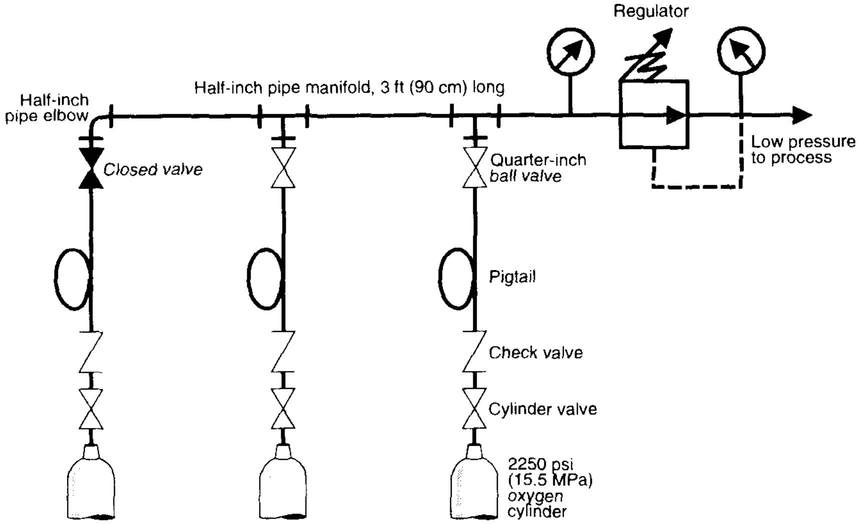

FIG. 9 — Three cylinders were connected by ball valves to a manifold to provide oxygen to a semiconductor production process. When a ball valve was opened to turn on a cylinder, compression heating burned the TFE in the ball valve at the end of the manifold.

Causes

What caused these incidents? The technical causes are all the same and you know them well: high velocity, compression heating, friction, particle impact, contamination, system design, component selection, operating procedures, and all the other reasons described in the many G-4 standards. Solomon was right; there really is nothing new under the sun.

Those are technical causes. But what about lack of education, training, and experience? The lack of awareness of the hazards and the information resources that were available? The lack of enforcement? Those are not technical causes; they are management issues. How do we manage safety at the plant level, the operating level, the corporate level, or at the community level?

A wealth of knowledge exists, more than enough to prevent accidents such as these. It simply does not get to the individuals who need to know. Rudolf Flesch described thinking as " . . . simply the manipulation of memories"[2]. If it is not in your memory, it doesn't exist and you can't use it.

Education

Is education the solution? Not by itself.

Plato's view was that education does not consist of telling people new things; it consists of extracting from their memories what they already knew. That was some 24 centuries ago, when an educated person could embrace civilization's whole body of