

Nitrogen: A Security Blanket for the Chemical Industry

PAUL YANISKO AND SHIYING ZHENG
AIR PRODUCTS

JOE DUMOIT
CASHCO, INC.

BILL CARLSON,
NEUTRONICS INC.

The benefits of nitrogen blanketing include improved process safety, better product quality, and longer equipment life. Here's how to achieve the desired safety or quality results while minimizing costs.

Although nitrogen blanketing is a simple practice that is widely used in the chemical, pharmaceutical, food processing, and petroleum refining industries, its potential to improve productivity and safety is often overlooked. Blanketing is the process of applying a gas to the vapor space of a container or vessel in order to control its composition. It can be implemented during production, storage, transportation, and final packaging, and can be used in a wide variety of containers ranging in size from storage tanks with capacities of millions of gallons to quart-size or smaller bottles.

Nitrogen is the most commonly used gas for blanketing because it is inert, widely available, and relatively inexpensive on virtually any scale. Other gases, such as carbon dioxide or argon, are also occasionally used; however, carbon dioxide is more reactive, and argon is about five to ten times more expensive, depending on the volume, location, etc.

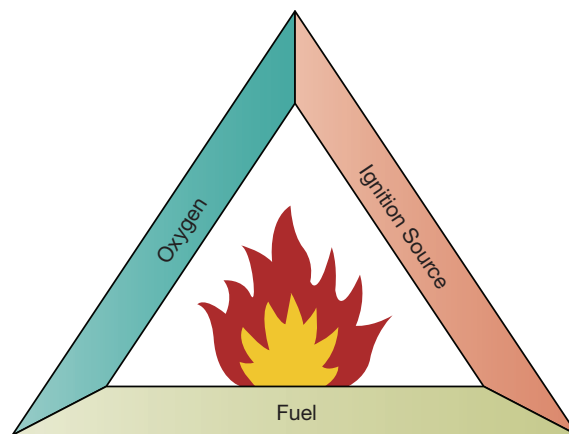
This article discusses the basics of nitrogen blanketing and explains how to implement it effectively and efficiently.

The benefits

Blanketing helps protect plant personnel, products, and plant assets by reducing the oxygen content in the vapor space of a storage tank or process vessel, making it inert. This eliminates the possibility of fire or explosion, decreases evaporation, and protects the tank from structural corrosion damage caused by air and moisture. It also prevents air, moisture, or other contaminants from entering the vapor space and causing product degradation.

Quality benefits. Some sensitive materials, especially in the food, pharmaceutical, and nutraceutical industries, may experience quality degradation when they come into contact with oxygen, moisture, or other contaminants. Blanketing creates a slight positive pressure inside storage containers, which prevents air and other contaminants from infiltrating and causing oxidative degradation and spoilage. The result is increased shelf life.

For example, oxygen and water vapor in the air cause undesirable reactions in edible oils, which are triglycerides. Water reacts with a triglyceride to form a diglyceride and a fatty acid. Oxygen reacts with the unsaturated fatty acids to form fat hydroperoxides (and other undesirable



▲ **Figure 1.** The fire triangle depicts the three elements needed for a fire: fuel, oxygen, and an ignition source.

products), which may further react to form undesirable polymers, acids, and aldehydes. Exposure to air reduces the oil's stability and alters the oil's color, flavor, and aroma. Nitrogen blanketing of edible-oil storage tanks, transfer lines, and railcars removes both oxygen and water vapor from these containers and prevents oxidation of the phospholipids, triglycerides, and free fatty acids — making this a simple and effective way to maintain the integrity of the oil.

Safety benefits. Tank blanketing provides the greatest benefit — safety — in industries where combustible, flammable, or explosive materials are processed, stored, or generated. Blanketing prevents these types of products from coming into contact with the oxygen in air, thereby creating a nonflammable environment that prevents fire and explosion.

A fire requires three elements (Figure 1): fuel, oxygen, and an ignition source. Removing any one of these three elements from the environment eliminates the possibility of fire.

The headspace of a storage tank contains a mixture of air and the vapor of the flammable material being stored (e.g., a solvent). The mixture of solvent vapor and air may ignite and burn if the vapor mixture is within the solvent's flammability limits and an ignition source is present. Even if storage tanks are electrically grounded to reduce the probability of ignition, static charges can develop within the system or within the solvent itself and act as an ignition source. Since it is practically impossible to completely eliminate sources of static charge, and the fuel cannot be eliminated because it is the material being stored, oxygen is the only leg of the fire triangle that can be controlled.

A storage tank can be made inert by:

- reducing the oxygen content of the vapor space to a value that is less than the concentration that will support combustion, *i.e.*, the limiting oxygen concentration (LOC)
- reducing the fuel concentration in the vapor space to a value less than the minimum concentration that can sup-

Table 1. NFPA 69 (1) contains a full table of limiting oxygen concentrations (LOC), such as those listed here for some common materials at ambient temperature and pressure.

Material	LOC, vol. % O ₂
Propylene Oxide	5.8
Methanol	8.0
Ethanol	8.5
Acetone	9.5
Benzene	10.1
Vinyl Chloride	13.4

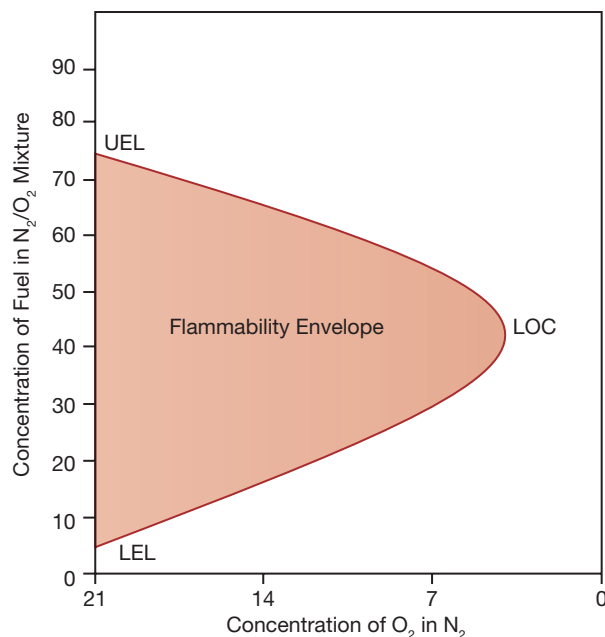
port combustion, *i.e.*, the lower explosive limit (LEL) or lower flammability limit (LFL)

- increasing the fuel concentration in the vapor space to a value greater than the maximum concentration that can support combustion, *i.e.*, the upper explosive limit (UEL) or upper flammability limit (UFL).

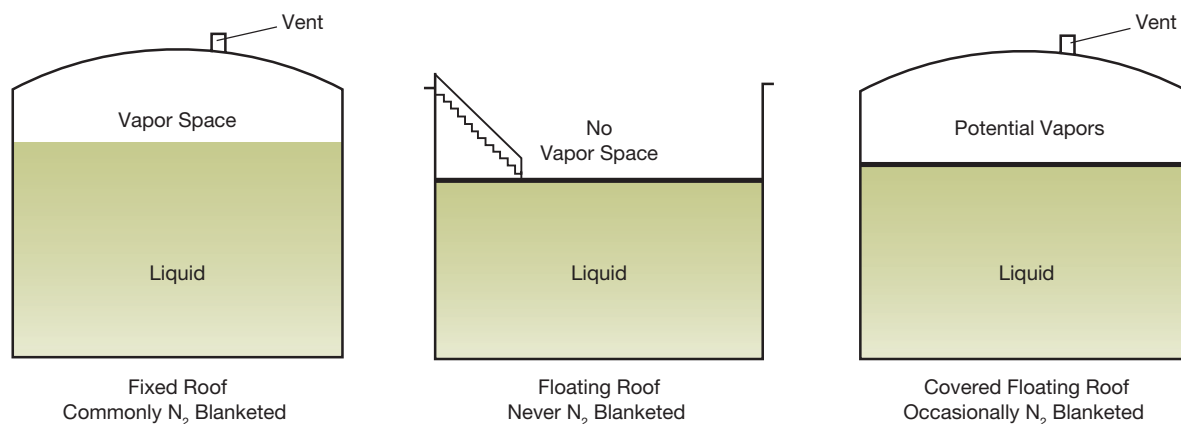
A material's LEL and UEL (Figure 2) can be found in the material safety data sheet (MSDS) provided by the manufacturer. LOC values for many chemicals (e.g., Table 1) can be found in chemical engineering and chemistry handbooks as well as in the National Fire Protection Association's *NFPA 69: Standard on Explosion Prevention Systems (1)*. Computational methods can be used to determine the flammability limits of mixtures of gases, fuels, and inert substances at elevated temperatures and pressures (2).

The safety implications of improper handling of flammable or combustible materials are severe. Yet, at some manufacturing plants, there is a false sense of security and a general belief that "it can't happen here." Consequently, inerting and blanketing are often overlooked during safety reviews, maintenance turnarounds, or upgrade projects. The lack of blanketing or inadequate blanketing of flammable products has resulted in serious fires and explosions.

In one incident, explosions and fire erupted at the Barton Solvents facility in Valley Center, KS, on July 17, 2007. The accident led to the evacuation of thousands



▲ Figure 2. A flammability diagram illustrates the material's flammability envelope, which is bounded by the lower and upper explosive limits (LEL and UEL) and the limiting oxygen concentration (LOC). This diagram is for hydrogen in air at standard temperature and pressure, for which LEL = 4.0%, UEL = 75.0%, and LOC = 5.0%.



▲ **Figure 3.** The type of vessel is an important consideration when designing a new or retrofit tank blanketing system.

of residents and resulted in projectile damage offsite, as well as extensive damage to the facility. The U.S. Chemical Safety and Hazard Review Board (CSB) conducted a thorough investigation (3) to identify the root cause and recommend preventive actions. The key findings were that static electricity, which accumulated in storage tanks during the transfer and storage of a nonconductive flammable liquid, ignited flammable vapor-air mixtures inside the storage tanks. An important recommendation from the investigation was to add inert-gas blanketing to the tank to reduce the concentration of oxygen in the headspace.

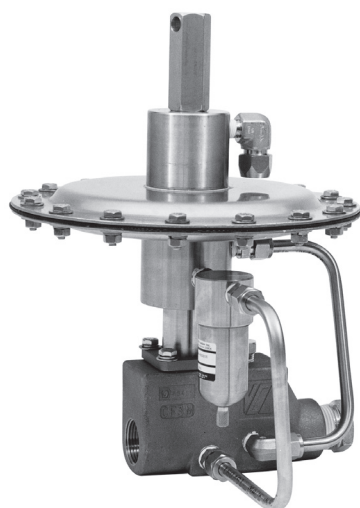
Types of vessels

When considering a new blanketing design or an upgrade to an existing installation, the first factor to consider is the type of vessel. This will determine whether

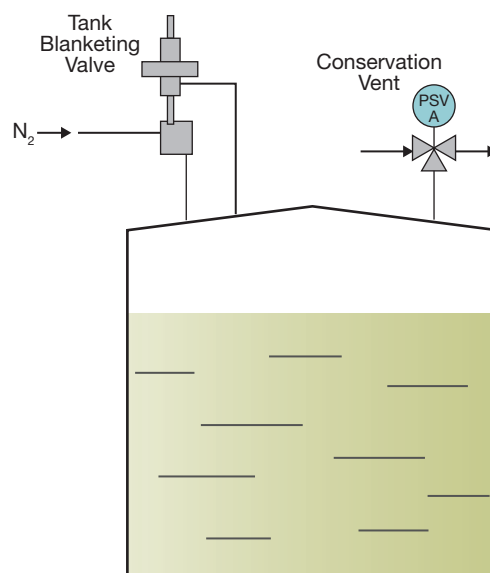
blanketing is needed and, if so, the appropriate means of control (pressure or concentration).

The most common type of tank (Figure 3) is the fixed-roof tank. When flammable or sensitive materials are stored in fixed-roof tanks, nitrogen blanketing is highly recommended. Floating-roof tanks usually are not blanketed because there is no headspace where vapor could build up. The headspace above the internal roof of a covered floating-roof tank (or internal-floating-roof tank) is occasionally blanketed.

Some enclosed spaces that do not hold pressure, such as pneumatic conveyors, hoppers that contain powders and dust, or controlled-atmosphere containers, may also



▲ **Figure 4.** A self-contained, pilot-operated tank blanketing valve controls the flowrate of nitrogen based on pressure. Photo courtesy of Cashco, Inc.



▲ **Figure 5.** A tank equipped with pressure-controlled blanketing adds nitrogen via the tank blanketing valve when the liquid level drops, and vents nitrogen through the conservation vent when the liquid level rises.

require blanketing. Nitrogen blanketing systems are essential in spaces that are not sealed tight enough to hold a slight positive pressure.

Nitrogen control by continuous purge

Three methods are commonly used for nitrogen control: continuous purge, pressure control, and concentration control.

Continuous purge systems employ a constant flow of nitrogen. This approach, while simple, has several disadvantages. First, its nitrogen consumption rate is high. In addition, the flowing nitrogen may strip the vapors in the headspace and place an additional load on the plant's air-emission control system. And, air can infiltrate the headspace if the tank discharges too quickly and the liquid level drops too fast.

Despite these shortcomings, however, continuous purge systems remain in use because they can be implemented quickly and easily. Retrofitting existing continuous-purge blanketing systems with pressure or concentration controls (discussed in the next two sections) will usually reduce costs.

Pressure control

Pressure-control systems are employed for sealed tanks, which hold pressure. A valve (Figure 4) senses the pressure in the headspace of the tank and delivers nitrogen accordingly. The headspace pressure can be set quite low — less than 1 in. w.c. is sufficient. As the tank discharges, the liquid level falls, the pressure drops, and nitrogen is added; as the tank is filling, the pressure rises, and nitrogen exits through a vent valve (Figure 5). Several pressure-control systems are available in the marketplace.

The amount of nitrogen required to blanket a tank under pressure control is the sum of the nitrogen required based on the tank's working throughput (N_w) and the nitrogen required by thermal breathing, *i.e.*, the rise and fall of the liquid level due to the external temperature changes (N_{TB}). The total volume of nitrogen needed can be calculated by the following simplified equations:

$$N_T = N_w + N_{TB} \quad (1)$$

$$N_w = \frac{V_T}{7.48} \quad (2)$$

$$N_{TB} = V_{HS} \left(\frac{T_{max} - T_{min}}{555} \right) \left(\frac{1}{7.48} \right) F \quad (3)$$

where N_T = total volume of nitrogen required per month, ft³; N_w = nitrogen required by the material flow through the tank, ft³; N_{TB} = nitrogen required by thermal breathing, ft³; V_T = total volume of material discharged from the tank per month, gal; V_{HS} = average empty headspace, gal;

T_{max} = maximum temperature in the tank, °F; T_{min} = minimum temperature in the tank, °F; F = estimated number of temperature swings per month; 7.48 is the factor to convert gallons to cubic feet; and 555 is a constant related to the vapor space expansion factor, °R.

The working-throughput component, N_w , can be calculated easily from the total volume of liquid discharged from each tank per month. The thermal breathing component, N_{TB} , is a function of the size of the tank, the average liquid level in the tank, and atmospheric conditions affecting the temperature in the tank (which vary due to changing weather). Furthermore, the actual temperature in the headspace of the tank is not always the same as the ambient air temperature — on sunny days, it is much higher, which in turn causes larger temperature swings and increases nitrogen consumption. But because thermal breathing is usually much smaller than the working throughput, the uncertainties associated with calculating N_{TB} result in relatively small errors in estimating total nitrogen usage per month.

The peak nitrogen usage, however, can be surprisingly

Table 2. For nonrefrigerated, uninsulated aboveground tanks larger than 840,000 gal, peak nitrogen requirements due to thermal breathing are specified in API Standard 2000 (3) and ISO 28300 (4).

Tank Capacity		N ₂ Inbreathing Requirement, scfh
bbl	gal	
20,000	840,000	20,000
25,000	1,050,000	24,000
30,000	1,260,000	28,000
35,000	1,470,000	31,000
40,000	1,690,000	34,000
45,000	1,890,000	37,000
50,000	2,100,000	40,000
60,000	2,520,000	44,000
70,000	2,940,000	48,000
80,000	3,360,000	52,000
90,000	3,790,000	56,000
100,000	4,200,000	60,000
120,000	5,040,000	68,000
140,000	5,880,000	75,000
160,000	6,720,000	82,000
180,000	7,560,000	90,000

Note: API 2000 includes tanks smaller than 20,000 bbl (840,000 gal). The absence of such tanks here does not imply that smaller tanks do not experience thermal breathing. Rather, for smaller tanks, the nitrogen blanketing requirements due to thermal breathing are calculated using Eq. 4, which does not include the G term of Eq. 5.

Fluids and Solids Handling

large due to rapid temperature changes. The peak nitrogen requirement and its frequency of occurrence are important for selecting and sizing the nitrogen supply system.

The peak usage can be estimated by the following simplified equations:

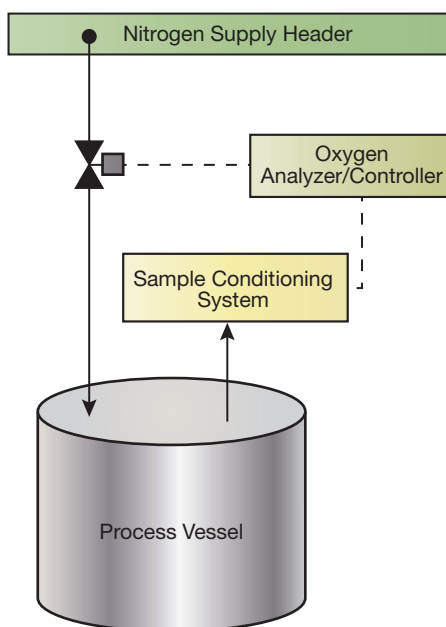
$$N_{max} = 8.021P + 0.02382C \quad \text{for tanks up to 840,000 gal (4)}$$

$$N_{max} = 8.021P + G \quad \text{for tanks larger than 840,000 gal (5)}$$

where N_{max} = maximum nitrogen flowrate, scfh; P = pump-out rate, gpm; C = total tank capacity, gal; 8.021 is the factor to convert from gpm to scfh; 0.02382 is a factor based on cooling an empty tank from a high of 120°F at rate of change of 100°R/h; and G is the nitrogen breathing requirement, scfh, obtained from Table 2.

Concentration control

Concentration control is suitable for unsealed tanks, which cannot hold pressure. It is very efficient — nitrogen usage is optimized because it is only added when it is needed. An oxygen analyzer (Figure 6) directly measures the actual oxygen concentration in the headspace vapor and uses it to control the flow of nitrogen to the tank. The conditions of most processes are much too harsh to permit the use of an *in situ* oxygen sensor. Thus, the sample-conditioning equipment (Figure 7) is an integral part of the analyzer system. A properly designed sample-conditioning



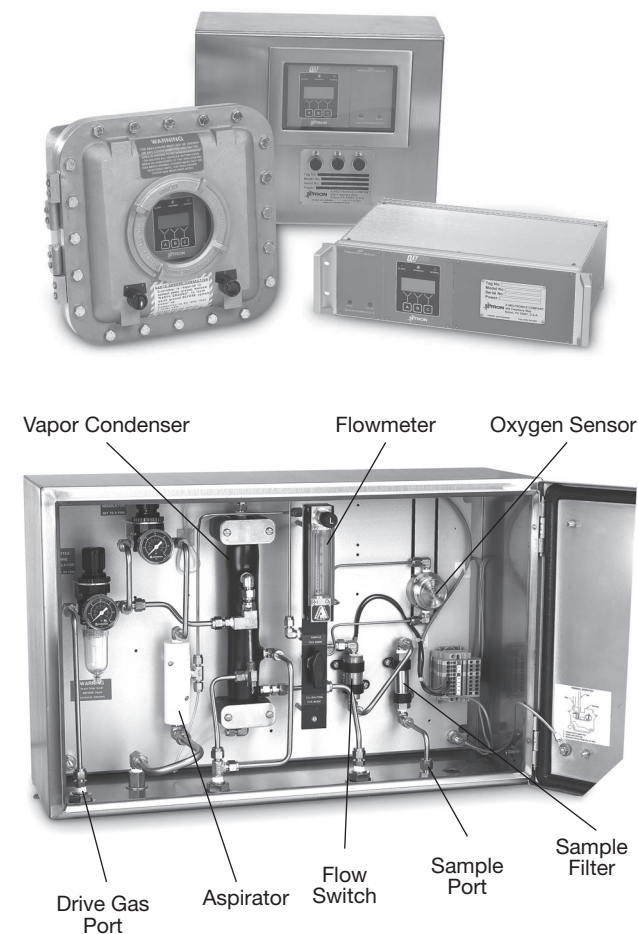
▲ **Figure 6.** A concentration-control system directly measures the oxygen in the headspace and meters nitrogen to the tank to maintain the desired setpoint.

system allows the analyzer to measure reliably over a wide range of process conditions, including extremes in pressure, vacuum, and temperature, as well as in heavy-particulate and high-moisture environments.

The advantage of continuous concentration monitoring and control is that it conserves nitrogen by optimizing nitrogen usage. The savings can provide an accelerated payback on the cost of the monitoring and control equipment. Several commercially available systems are on the market, with varying degrees of complexity and in various price ranges.

Nitrogen supply

Nitrogen supply options include delivered liquid nitrogen stored in bulk or microbulk tanks or dewars, as well as delivered gaseous nitrogen stored in large tubes, cylinder banks, or cylinders. In addition, nitrogen can be generated



▲ **Figure 7.** A concentration-control system relies on oxygen analyzers (above top) and a sample conditioning system (above bottom). The latter enables the analyzer to provide reliable measurement even at extreme conditions of temperature, pressure, particulate loading, or moisture level. Photos courtesy of Neutronics, Inc.

onsite by a cryogenic plant, or by pressure-swing adsorption (PSA) or membrane units.

The choice of delivery method depends on the application's requirements for purity, usage pattern, volume, portability, footprint, and local power cost. New blanketing applications require calculations of nitrogen consumption based on tank volumes and throughputs, as discussed previously. When optimizing existing installations, the result of these calculations should also be compared with actual flow data taken from the plant's existing nitrogen lines over a period of time, usually about a week.

Nitrogen costs can be reduced if a lower purity can be accepted. A PSA or membrane nitrogen generator can produce nitrogen at any purity, and the lower the purity, the lower the unit cost. NFPA 69 requires operating at 60% of the LOC, which for many flammable materials is in the neighborhood of 10%. Thus, operating at 94% nitrogen would meet NFPA guidelines, although a more conservative 25% of the LOC, or 97.5%, adds a larger safety buffer.

A purity of 94–97.5% can be inexpensively supplied by a membrane or PSA unit. Applications that use blanketing primarily for quality benefits may be able to use lower-purity nitrogen. For example, certain edible oils may be blanketed with nitrogen in this purity range depending on the desired oil quality, shelf life, and prevailing storage conditions such as temperature and materials of construction.

Usage pattern is another important parameter that determines the appropriate delivery method. A plant's usage pattern can be determined by measuring the nitrogen flowrate over time, typically one week. There are three basic usage patterns:

- *constant baseline* — the flow is constant, such as the blanketing of a large tank farm. Onsite generation is an excellent choice for this pattern.

- *erratic* — the flows are inconsistent and unpredictable, often due to transfer or purging. Liquid nitrogen is often preferred to match the variable flow requirements.

- *periodic* — nitrogen consumption is predictable, but not constant. A gas-generation plant backed up by liquid nitrogen may be optimal.

Many plants exhibit a combination of usage patterns.

Closing thoughts

Nitrogen blanketing offers significant benefits in terms of product quality and process safety, and when implemented properly, pays dividends in terms of efficiency, effectiveness, and cost. Choosing the appropriate method of nitrogen supply and nitrogen control system based on the vessel design and the application can maximize the desired safety and quality results while minimizing capital and operating expenses.

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LITERATURE CITED

1. **National Fire Protection Association**, "NFPA 69: Standard on Explosion Prevention Systems," NFPA, Quincy, MA (2008).
2. **Melhem, G. A.**, "A Detailed Method for Estimating Mixture Flammability Using Chemical Equilibrium," *Process Safety Progress*, **16** (4), pp. 203–218 (1997).
3. **U.S. Chemical Safety and Hazard Investigation Board**, "CSB Issues Final Report on Barton Solvents Explosion . . .," www.csb.gov/newsroom/detail.aspx?nid=36, CSB, Washington, DC (2008).
4. **American Petroleum Institute**, "API 2000: Venting Atmospheric and Low-Pressure Storage Tanks," 6th ed., API, Washington, DC (2009).
5. **International Organization for Standardization**, "ISO 28300:2008 — Petroleum, Petrochemical and Natural Gas Industries — Venting of Atmospheric and Low-Pressure Storage Tanks," ISO, Geneva (2008).

PAUL YANISKO is the Process Industries Segment Leader in the International Commercial Technology Group at Air Products (7201 Hamilton Blvd., Allentown, PA 18195-1501; Phone: (610) 481-8728; Fax: (610) 481-5431; Email: yaniskpj@airproducts.com), where he is responsible for delivering industrial-gas-related solutions to customers in various industries, including the refinery, petrochemical, chemical, and pharmaceutical sectors. His main areas of focus are Asia and Latin America. Yanisko holds BS and MS degrees in chemical engineering from Lafayette College and the Univ. of Connecticut, respectively.

SHIYING ZHENG is a research associate at Air Products (7201 Hamilton Blvd., Allentown, PA 18195-1501; Phone: (610) 481-3027; Fax: (610) 706-5704; Email: zhengs2@airproducts.com). She has more than 14 years of industrial experience in technology R&D, inventing and developing new materials for a broad range of applications that include gas separation, personal care, digital printing, medical imaging, and electronic display. Her experience also includes evaluating technologies and developing new opportunities for the gas separation, electronics, and performance-materials businesses. In addition, she has extensive experience in patent law and is a registered patent agent. Before joining Air Products, she was a research associate at Eastman Kodak Co. The holder of an MS and a PhD in polymer science from Cornell Univ., Zheng is an inventor or co-inventor on 38 U.S. patents, and the author of seven peer-reviewed journal articles and two book chapters.

JOE DUMOIT is a regional sales manager for the VCI product line at Cashco, Inc. (607 W. 15th St., Ellsworth, KS 67439; Phone: (785) 472-4461; Fax: (785) 472-3539; Email: joed@cashco.com). He began his career in sales at Leeds & Northrup, followed by stints at Varec and at L & J Technologies. After several years, he moved to Durlam Associates, where he sold Cashco's Valve Concepts line; he became a co-owner of the firm in 1988 and continued to work in sales until the company was sold in 2000. He was then hired by Cashco as a regional sales manager and has continued selling and developing the VCI product line. Dumoit holds a BS degree in electrical engineering from the Univ. of Houston.

BILL CARLSON is the product line manager of the Ntron gas analysis division of Neutronics Inc. (456 Creamery Way, Exton, PA 19341; Phone: (610) 524-8800 x147; Fax: (610) 524-8807; Email: bill.carlson@neutronicsinc.com). He has dedicated the majority of his 21-year tenure to the design and development of oxygen-based Ntron ICS inert gas control systems for the pharmaceutical, chemical, and paint and coatings industries. He is a member of the International Society of Automation (ISA).

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**For more information,
please contact us at:**

Corporate Headquarters

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501
T 800-654-4567 or 610-706-4730
F 800-272-4449
gigmrktg@airproducts.com

Asia

Air Products Asia, Inc.
1001, 10/F, Sunning Plaza
10 Hysan Avenue, Causeway Bay
Hong Kong
T 852-2527-1922
F 852-2527-1827

China

Air Products and Chemicals
Investment Co., Ltd.
5/F, Building 72
887 Zu Chong Zhi Road
Zhangjiang Hi-Tech Park
Shanghai 201203
T +86-21-3896 2000
F +86-21-5080 7525

Europe

Air Products PLC
2 Millennium Gate
Westmere Drive
Crewe CW1 6AP
United Kingdom
T +44(0)800 389 0202
F +44(0)1932 258652
apbulkuk@airproducts.com



www.airproducts.com