The specialty gases business in 2013...

What are the specialty gases of today, and what are the trends that are shaping the market as we know it? *Specialty Gas Report* interviewed a number of companies in the specialty gases business to gauge their views on the market they operate in. Over the next six pages, see what they all had to say about the industry you do business in.

Specialty gases has become something of a traditional market, serving traditional applications. Life sciences, analytical instrumentation support, electronics, refining and chemical, lighting and even environmental are all established areas.

While new gas applications may have peaked around 20 years ago, today's increasingly high-tech industrial processes demand specialty gases with higher and higher levels of purity and more precise accuracies than ever before. So what are today's specialty gases?

Specialty gases would typically be high purity gases, exotic chemicals or high precision gas mixtures, with typical examples being gases such as helium, rare gases, packaged chemical gases, high purity air gases, calibration gas mixtures and laser gas mixtures. These products are principally supplied in cylinders, similar to the cylinders used for other industrial gases product groups of industrial welding and medical gases for healthcare.

As Gasco Affiliates, LLC explains, "Specialty gases is very much a 'catch-all' term for most people. A common definition is a pure gas at the upper end of its purity, sometimes 99.999 percent+ purity, or a mixture that is comprised of multiple components in very exact amounts and blend tolerances."

"Given the above definitions," the Florida-based company continues, "we can say that 'research grade' gases are definitely specialty gases such as hydrogen, helium, oxygen. Additionally, using the mixture definition, we can also include laser gases, some medical gases, EPA Protocol Gases and even portable calibration gases."

This latter point, concerning EPA Protocol Gases, is something that fellow company Norco, Inc. appears to confirm too. Keith Partch, Norlab sales manager at Norco, told *SGR*, "In our market here in the Northwest, we have found that we are finding opportunities in the EPA Protocol, medical, and environmental markets, as well as in our Industrial Hygiene Markets with our disposable cylinder product line."

The specialty gases of 2013 can be broken down into a number of categories and sub-categories by end-user applications, each of which has its own nuances and demands. But there are also a variety of gases and hydrocarbons used in some sectors, which we might not necessarily term 'specialty gases'. In the aerosol industry, for example, the main propellants (liquefied gases) are hydrocarbons (pure or blends of butane/propane) and Dimethylether (DME). To a lower extent, hydrofluorocarbons (HFCs), specifically HFC-134a, are also used, primarily for technical aerosols which need to be non-flammable.

We understand from Alain D'Haese, Secretary General of the European Aerosol Federation (FEA), that HFO-1234ze, which has a lower Global Warming Potential (GWP), is starting to be used too. "Could we quote them as specialty gases?" D'Haese questions. "The industry also uses compressed gases: air, carbon dioxide, nitrogen. I do not think that we can quote them as specialty gases."

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Today's electronics gases

Electronics gases are a very diverse family depending on manufacturing process. In the electronics sector, nitrogen, argon, oxygen and hydrogen are used as utility gases, as well as in the processing.

Electronics specialty gases and electronic precursors (which could be also liquids) are more broadly known as electronic materials (EM). These molecules are used as critical reactants in the chip manufacturing process and the use of EMs can be broadly classified into four categories: deposition, etch/clean, lithography and implant.

In terms of deposition, thin films form the basis of semiconductor devices. Most of the deposition steps involve some silicon-based film, whether it is silicon (Si), silicon dioxide ($Si\ O_2$), or silicon nitride (SiN). Metal and metal oxide films are also commonly deposited, while silane and its derivatives are used to form oxide and nitride films. Etching is required to remove layers and to form the device structure. Clean gases are used to clean deposits off the process chamber walls, with chamber cleaning mostly achieved via nitrogen trifluoride (NF_3); however, we understand that more and more companies are thought to be considering using fluorine (F_2) because it delivers better cleaning performance while having zero global warming potential.

"There is always a need for high purity gases of all types, but hydride mixtures and metal hydrides are driving some of those to the forefront," Gasco Affiliates says. "Hydride gases such as phosphine, silane and arsine continue to be used in these areas, along with HCL."

Linde alludes to 'some exciting developments in the semiconductor world' and describes how higher purity deuterium gas, BF_3 and boron trichloride are coming into use.

"Advanced devices use new elements that require gases such as germane (GeH_4) and precursors for materials such as hydrogen fluoride (Hf), zirconium (Zr), tanatalum (Ta), titanium (Ti) and copper (Cu)," the company says. "Also, lower temperature deposition requires new Si deposition materials such as hexachlorodisilane (HCDS). Some of these materials are not gases at room temperature and pressure, but are vaporized and delivered as a gas in the process."

Advanced lithography applications such as immersion lithography use carbon dioxide and the next generation extreme ultraviolet lithography (EUV) technology will consume large amounts of hydrogen. A further point of note in the electronics business is the much talked about 450mm wafer transition. As manufacturers strive to 'supersize' their wafers and embark upon the next wave of growth in electronics, there is of course a consequence for the gases industry. With the rise of larger diameter silicon wafers, and the 450mm wafer in particular, it is anticipated that larger quantities of helium will be required to meet the related cooling requirements.

Also falling under the banner of electronics gases are laser gases, usually comprised of rare gas – halide laser mixtures using krypton or argon and fluorine. These are used in the photo-lithography process. Such lasers are commonly referred to as eximer lasers.

SO_2, SF_6 and NF_3

Several gases used in the semiconductor industry have been linked to global warming, with the key culprits being sulfur hexafluoride (SF_6), sulfur dioxide (SO_2) and NF_3. Of these, NF_3 is by far the largest volume consumed. The most obvious and increasingly popular alternative to NF_3 is the aforementioned F_2 gas, which delivers better clean performance at a lower cost, but with no global warming contribution.

As described, SF_6 has a very high global warming potential (GWP). Therefore its use is increasingly being controlled by legislation or voluntary restrictions. Examples include US-EPA voluntary partnerships, specific restrictions in the state of California and EU 'f-gas' regulations. Substantial focus is put on reducing emissions during and after use, as well as restrictions on its use in applications where more environmental friendly alternatives exist that are technically and economically viable.

SGR understands that this environmental consideration is seeing the market for some

applications, such as electrical switch gear inerting, shift to hydrogen usage. In response to this trend Linde, for example, offers the HOGEN® hydrogen generator as a solution for the switchgear industry.

Boise, Idaho-based Norco has also noticed the effects of environmental concerns on the market for SF_6. Partch adds, "This gas is becoming much more regulated as it is a greenhouse gas. And most of our customers own and control their own cylinder inventories to monitor their specific usage. I think this market will continue to fall under greater regulation by government regulatory agencies."

Gasco Affiliates affirms, "SO_2 remains a constant market due to the wastewater treatment demands, while SF_6 and NF_3 have been a slower growing demand area. SF_6 has seen a reduction of use in the electrical power distribution arena. New circuit breakers use less SF_6 and companies are working harder at reclaiming the gas, as well as preventing leaks. This has caused the reduction in demand."

"However," Linde counters, "SF_6 remains an extremely important gas for a number of high voltage applications where no viable substitute remains and/or its properties provides environmental benefits."

Turning to SO_2, let's rewind a second to those comments of Gasco. The company cites a 'constant market' that is perhaps due to the gas' vital application in many industries around the world. SO_2 has multiple applications – as a chemical for synthesis, optimizing the production efficiency of manufacturing plants, as a food preservative to the packaging industry, and as a disinfectant in wine making. It is also common to the glass industry, water treatment services, and the mining and metallurgy sectors.

An interesting new application, we understand, is in the gold purification process, with SO_2 used as a solvent to allow higher purities of gold to be refined than were previously possible.

Regulation and compliance

As discussed earlier, there is little escaping the influence of new regulation and compliance on the market for today's specialty gases. But what effect *is* being felt in the industry?

"With the publication of the new Green Book and the lengthening of expiration dates, it appears that government entities can have a profound impact," answers Gasco Affiliates. "Challenges in climate change will drive regulators to seek more precise causes and controls. Other concerns for worker safety have increased the number of detectors out there and increased awareness of calibration and bump-testing before the instruments are put to use."

While ever-tightening environmental regulations put pressure on industrial operations to reduce their environmental emissions, producers and distributors of specialty gases are expanding their portfolios of certified or EPA protocol type mixes to support the monitoring required. Linde tells us that it is involved in producing specialty gases to measure gases such ammonia, nitrous oxide, formaldehyde, volatile organic compounds (VOC), ethanol and methanol.

The EPA has discussed regulation around gases that contribute to global warming. If new regulations are introduced, then it is likely that manufacturers will have to track and measure emissions of gases such as NF_3 and SF_6. But it will not be just NF_3 and SF_6 that are affected, with the production of a range of gases having to conform to tighter tolerances in the future, says Norco. Partch projects, "I think that as our economy grows and as technology moves forward with newer cleaner technologies, which will provide us with lower emissions and pollutants, the EPA will regulate and set lower standards which will in turn drive our industry to manufacture and produce standards at lower contaminant and concentration levels – with tighter tolerances to meet the lower regulations set by the regulatory agencies."

In Europe, regulation is also changing the face of the aerosol industry and the refrigerants used in this business. The FEA explains that the European Commission has proposed a phase-down of fluorinated greenhouse gases

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in the coming years, which will trigger a shift away from HFC-134a and 'most probably to HFO-1234ze'.

The role of regulation and compliance, in the present, is clear. Looking ahead, however, we understand there is a feeling that additional regulation will be minimal; there is a limit to how low emissions can be measured, and we are close to both that limit and what makes sense for regulation and compliance.

Market trends

When companies were asked what trends were being witnessed as producers and distributors of specialty gases, the same key factors appeared to resonate regarding the supply chain: accuracy, reliability and delivery.

Customer growth seems to trend toward accuracy, reliability, delivery and customer service, with customers seeking to do business on a more regional basis with their gas suppliers due to the level customer service and technical knowledge provided. "Customers want a quality product and the peace of mind that if they have a question or concern, we are there locally with the knowledge base to help them solve and improve their processes to put profits to the bottom line," says Partch.

One of the biggest trends to be seen in the area of specialty gas calibration mixtures is the increasing demand from customers for accredited calibration gas mixtures in line with international standards, both in North America and globally. As the developing economies also become more concerned about environmental issues, this leads to a demand for calibration gas mixes for environmental monitoring.

Linde reflects on the very nature of the specialty gases business and the lab environments it serves as driving an ongoing trend for innovation within the industry. "There are always new and exciting R&D products coming into the world of special gases. While a certain product may just be a 'pipe dream' in someone's laboratory today, it could become a mainstream specialty gas in the future and, after several years in the market, there's a good chance it will become a standard technical or industrial gas."

Technology and today's specialty gases

Although the fundamental analytical techniques of measurement harnessed by processes such as gas chromatography and flame spectrometry have not changed that much, we understand, the electronics in these analytical devices have advanced immensely – enabling much more sophisticated measurement to take place.

All of this has a trickle down effect on specialty gases. For the first time, for example, high purity gases – zero gases – will soon also need to be accredited in addition to the longstanding requirement for accreditation of calibration gas mixtures. Sophisticated and costly detectors are all drivers that will affect the market, we're told. Analytical technologies are improving and therefore the ability to find smaller amounts of impurities is causing this drive.

"Twenty years ago we wouldn't have thought of looking for nitrous oxide at the 500 parts per billion level, which is common today," acknowledges Stephen Harrison, global head of speciality gases and speciality equipment at Linde Gases. "The kind of analyzers necessary for this were prohibitively expensive, but today they've become affordable and this advancement gives legislators the ability to set greatly reduced emissions levels for industry."

"Measurement enables enforcement – and in the next decade we're likely to be able to look at traceability levels as low as parts per trillion."

Aside from advances in measurement, the evolution in electronics is beginning to blow the wind of change through the specialty gases business. Moore's Law is becoming about 'More than Moore' which means that instead of just shrinking devices, new materials are being used. This has resulted in the use of many more elements than the usual silicon, hydrogen, carbon and nitrogen. For example, Si-Ge, hafnium dioxide (HfO_2) metal gates, and zirconium dioxide ($Zr\ O_2$) capacitors have all become routinely used.

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will not be gases – many will be liquids and some solids. This means that new challenges in vaporization and delivery systems will need to be solved," explains Linde.

Specialty gases and the US economy

The intrinsic link between economic performance, GDP growth and the demand for gases is well documented, it is widely accepted that as an economy grows, so too does the region's demand for industrial and specialty gases.

With this indicator in mind, how has the much talked about status of the US economy affected the specialty gases industry – and what lies ahead? While it is true that Asia may be a key dynamic in the electronics business, it is also important to point out that the end demand for semiconductor chips is still strongly dependent on the US economy and consumer behavior. It follows, therefore, that the market for electronics specialty gases will still be 'somewhat sensitive' to the US economy.

Linde adds, "The specialty gas business is certainly linked to the economy. For example, a lot of electronics producers typically carry about three months' worth of stock on hand, but in recessionary times, they tend to reduce their stockholding to a couple of weeks, running as leanly as possible. This dip in manufacturing volumes impacts the volume of specialty gases required."

Gasco Affiliates agrees, "A large portion of the specialty gas business is dependent on manufacturing, so it follows the economy into slow and fast times. There will always be a base load of gases needed to maintain emissions monitoring and medical support, but the real cycle of specialty gas is tied to manufacturing."

"There is a major drive from business, government and academia to develop manufacturing operations and jobs in the US."

Other economic and demographic factors to consider include an aging population and the stimulus this creates in both homecare and the wider medical market. This has been exemplified in the last two years with the considerable mergers and acquisitions activity that has taken place in the gases industry with a view to healthcare. Norco's Partch affirms, "I can see the medical field continue to be a source of growth for R&D as our baby boom generation ages."

Tomorrow's specialty gases world

So there you have it, a picture of the specialty gases business of today and tomorrow emerges, full of bright new opportunities, intriguing challenges and multiple talking points.

Helium will undoubtedly still be one of those key talking points, despite the expected new capacity in the market. The long-term scarcity of helium is driving R&D to identify safe and fit-for-purpose substitutes, for example hydrogen, which can substitute helium in some gas chromatography applications.

Continued M&A activity and consolidation within the industry will also likely be a factor in the future development of the specialty gases business, while equipment developments will naturally be significant, trends which we touch on in features over the next few pages.

Environmental considerations, the rise of clean fuels and, it seems, the ongoing evolution in the electronics sector will have a bearing on future trends in specialty gases.

From an emissions perspective, for example, we understand from Linde Gases that there will be demands in emissions monitoring. "While many coal-fired power plants are shutting down and therefore no longer requiring calibration mixes for emissions monitoring, there is a robust uptake in the establishment of the small peak power plants that generate about 100 to 500 MWs combined and are designed to come on-board at short notice during spikes in energy demand," says Harrison. "These plants also generate emissions that need to be monitored. Emission reductions have changed by an order of magnitude compared to previous decades and it is anticipated that this significant trend will continue at least for the next 10 years."

Environmental factors are driving aerosol fillers to look at ways of decoupling growth from their impact on the environment too, we understand.

From an electronics point of view, the semiconductor EM market will continue to exhibit strong growth in the mid-term, with companies still investing strongly in new manufacturing capacity. In addition, each new technology generation is more gas intensive than the previous one, and Moore's Law challenges are spurring the addition of new materials and opening up new opportunities for precursors.

Asked what future lies ahead for the specialty gases and equipment markets, the responses *SGR* received were generally optimistic in their nature. "These markets are going to continue to grow," Partch answered on behalf of Norco. "As sampling and analysis equipment are able to sample and analyze more data at lower levels, there will be a need for equipment cylinders, regulators and other apparatus that will be needed to take us to the next level. I also see the LNG market as an area of growth for the specialty gas market."

Gasco Affiliates appears to see a 'steady' future for the industry and concludes, "There will always be a demand for higher purity and exact mixtures in manufacturing, emissions, workplace safety monitoring or elsewhere. The US will continue to set the standard for pushing manufacturing limits and workplace safety. The degree of accuracy and ability to deliver on time will be direct indicators for the winning players." SGR

Our thanks...

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