Linde and Air Products Hydrochlor 50-50 JV Scribed in Stone

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After more than four years of incessant worries over the eclipse of a domestic source of anhydrous hydrogen chloride (AHCl), a critical specialty gas, suppliers and users in the US can finally breathe a sigh of relief. Following much conjecture amid rumors of failed negotiations, Linde Gas North America and Air Products announced at the beginning of 2011 the formation of Hydrochlor, a 50-50 joint venture to supply high-purity AHCl to the electronics and other industries.

As *G&I* reported in the May/June 2010 issue of the magazine[1] and the June 2010 issue of the newsletter[2], the AHCl market has been besieged by fears of uncertain supply, rising prices, and speculation ever since Dow Chemical announced in 2006 its intention to exit the AHCl merchant market in the US.

Dow produces hydrogen chloride at the following sites: Freeport and Oyster Creek, Texas; Plaquemine, Louisiana; Midland, Michigan; Aratu, Brazil; Stade and Schkopau Germany; and Estarreja, Portugal. Global HCl production capacity was estimated to be 79 billion pounds (36 million metric tons or 36 MMT) in 2005.[3] Much of this HCl is captured downstream and consumed onsite, with only a small fraction available for sale. Dow's anhydrous HCl (AHCl) is sold as a liquefied gas and its aqueous hydrochloric acid is produced by mixing AHCl with water.

Unlike aqueous hydrochloric acid which is readily available on an industrial scale from multiple sources, AHCl has historically only been available in the open US market from a limited number of suppliers. The majority of by-product AHCl is recycled for internal production or integrated operations within a facility. Until December 2009, when Texas-based HCl Innovations entered the wholesale market with industrial grade AHCl extracted from a Formosa Plastics Corporation USA's facility in Baton Rouge, Louisiana, Dow Chemical had been the only merchant producer for suppliers and distributors that sell the purified, packaged AHCl gas to end users.

Since the initial 2006 announcement, the major gas suppliers have been working closely with Dow to establish a permanent solution and to extend the AHCl supply in the interim. Various attempts to replace Dow with a third-party producer failed due to funding or technical difficulties. As a leader in the chlorine and chlorinated chemical market, Dow serves as the standard bearer. It is a trusted and qualified source with the proven capability to provide a consistent, reliable supply of high-purity products. For the highly-standardized semiconductor and pharmaceutical industries, which purchase over a third each of commercially-available electronic-grade AHCl, their users are resistant to change and the Dow product remains the preferred choice.

Dow's desire to leave its role as merchant in the AHCl market coincides with its decision to phase out transportation of AHCl to customers by railcar in favor of tube trailers. The latter was based upon Dow's effort to reduce the risks involved in transport of highly hazardous materials, which include those that have toxic inhalation hazards (TIH), such as hydrogen chloride (anhydrous) and chlorine. Suppliers have also been focusing their search for alternative sources of AHCl that can deliver the gas directly via tube trailers. The new company HCl Innovations, for example, has a tube-trailer filling station at Formosa Plastics in Baton Rouge, Louisiana. When the filled tube trailer arrives at its facility in La Porte, Texas, HCl Innovations repackages the gas for distribution in either tube trailers or ton-containers.

Among the majors, Linde and Air Products have been exploring options to construct a tube-trailer filling facility to process and package AHCl supplied via pipeline at Dow's plant in Freeport, Texas. As direct global competitors, both companies must adhere to complex regulations and legal guidelines, secure long-term commitment from all parties involved and the customers they serve, as well as seek individual board approvals. These hurdles and resulting delays provided much fodder for rumors in the market.

As part of the JV agreement between Linde and Air Products, announced in January 2011, Hydrochlor will build a facility to process and package AHCl supplied via pipeline from Dow. Preparations for this new facility on Dow's Freeport site have already begun. Oversight for Hydrochlor will be governed by a team of managers from each partner company. The facility, scheduled to be commissioned in the second quarter of 2012, will meet current merchant requirements and can be expanded to serve growth in market demand. When completed, the facility will be the largest AHCl transfill plant in the US.

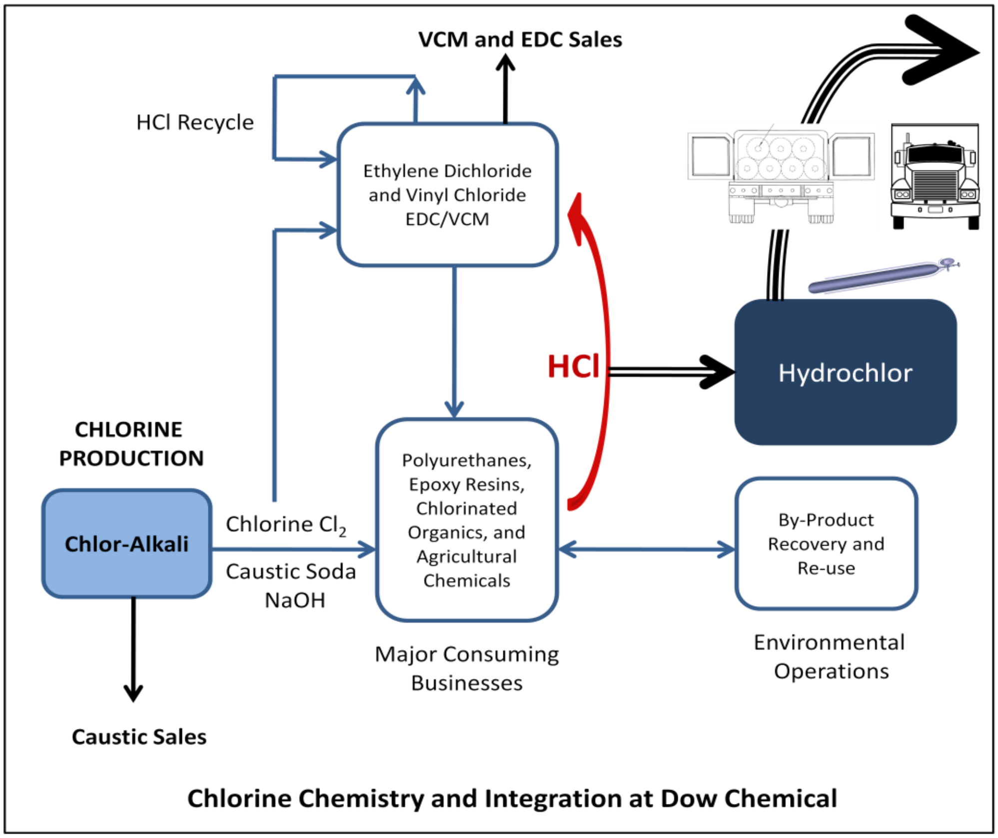
Hydrochlor will sell AHCl exclusively to the joint venture partners, Linde and Air Products, which will continue to market AHCl independently. Until the new facility's startup, Dow will continue to supply industrial-grade (high-purity, 99.9%) and electronic-grade (99.99%) AHCl by rail independently to Linde at its Lovington, New Mexico, facility, to Air Products at its Hometown, Pennsylvania, location, and to other current railcar customers.

In 2008, Linde began a series of expansions and improvements at its facility in Lovington and another transfill and purification plant in Phoenix, Arizona to enable the company to fill, store, and ship more AHCl to customers. Linde can currently handle inventory in excess of 15,000 standard 60-pound cylinders (total 900,000 pounds or 408 MT) annually, in addition to a fleet of ton containers and tube trailers. For the time being, AHCl from Dow is still sent by rail to Lovington for purification into electronic (99.997%), VLSI (very large scale integration) (99.999%), and ULSI (ultra large scale integration) grades (99.999%), and then by truck to Phoenix for repackaging into cylinders, tube trailers, and ton containers.

Once the Hydrochlor facility is qualified, Linde's Lovington facility will be taken down, said Cliff Caldwell, Vice President of Electronics and Specialty Gases for Linde North America. Linde will move its AHCl transfill operation to Hydrochlor in Freeport and AHCl will be transported directly to Phoenix in tube trailers for distillation and packaging. At the Air Products electronic-specialty-gas manufacturing plant in Hometown, where AHCl is processed into electronic grade (99.997%) and VLSI (99.999%) packages, there will be no changes to the AHCl transfill business until the Hydrochlor facility is qualified, onstream, and operational. The AHCl railcar-filling operation will cease but some components, primarily the fleet maintenance portion, may remain.

While neither Linde nor Air Products would comment on Hydrochlor's production capacity or term limits for its operation, Caldwell said the agreement with Dow will establish a long-term, stable supply of AHCl. "This significant investment in Hydrochlor secures a vital domestic supply of high-purity HCl for a variety of end markets," said Corning Painter, Vice President and General Manager of Electronics for Air Products.

The current annual volume of AHCl from Dow in the merchant market is approximately 20 million pounds (9,027 MT), according to Rich Brown, Global Business Development Manager of Chlorinated Organics at Dow Chemical. This figure reflects a drop in Dow's external sales to less than half of the volume of earlier years, noted Brown. Dow's Freeport facility will continue to produce AHCl as a by-product in volumes far in excess of what the entire AHCl merchant market demands. Figure 1 shows the integrated chlorine chemistry at Dow.



Source: Adapted from The Dow Chemical Company 2010 Databook, p. 80 (2010)

Figure 1. Integrated chlorine chemistry at Dow Chemical: hydrogen chloride is created as a by-product from the manufacturing of polyurethane, epoxy resins, chlorinated organics, and agricultural chemicals. The EDC/VCM production provides the integration that allows reuse of the chlorine molecule through HCl consumption, reducing raw material costs, providing cost advantages to Dow, and enabling a more sustainable approach to EDC/VCM (ethylene dichloride/vinyl chloride monomer) manufacturing. A small volume of the by-product HCl is sold as anhydrous HCl in the merchant market and transported via railcars to current customers. The HCl produced as a by-product in EDC/VCM manufacturing is recycled back to the EDC reactor and is not part of the AHCl merchant stream. When the Hydrochlor plant on Dow's facility in Freeport is completed, AHCl will be sent via pipeline at Dow's facility in Freeport directly to Hydrochlor. Hydrochlor will sell AHCl exclusively to Linde and Air Products, which will continue to market AHCl independently. The gas will be transported as a compressed liquid in high-pressure cylinders or tube trailers to Linde's process facility in Lovington, New Mexico and Air Product's electronic specialty gas plant in Hometown, Pennsylvania.

Industry veterans are hopeful that the recent announcement will revive the market and lure back users who have abandoned the use of AHCl in favor of alternative chemistries or more expensive source models (e.g., importing AHCl, direct synthesis on site, on-site stripping of hydrochloric acid). As Dow continues to take its railcar customers off line, Hydrochlor will be able to expand to meet the demands of customers that have made the transition to the new transport mode.

Some Clarifications

The manufacture of vinyl chloride monomers (VCM) accounts for much of the total (captive and merchant) AHCl by-product volume. The majority of this AHCl is recycled for use in ethylene dichloride (EDC) production. While VCM production is a possible source of AHCl for commercial use, only by-product HCl from Dow's Plaquemine site contributes to the volume of AHCl it sells in the open market. The merchant AHCl from Dow Freeport can come from a range of other chlorine derivative processes within Dow's integrated production facility (see Fig. 1)

At Dow, VCM is manufactured by cracking ethylene dichloride (EDC), which is produced either through direct chlorination where ethylene reacts with chlorine, or through oxychlorination where ethylene reacts with dry hydrogen chloride and oxygen. A significant amount of AHCl is produced as a by-product during EDC cracking, which is recycled back to the oxychlorination EDC reactor. With a global capacity of about 76 billion pounds (35 million metric tons or 35 MMT) in 2005, Dow Chemical and its consolidated subsidiaries are one of the largest producers of VCM in the world. Dow has VCM manufacturing facilities in Freeport, Texas; Plaquemine, Louisiana; and Schkopau, Germany. A VCM manufacturing facility located in Fort Saskatchewan, Alberta, Canada closed permanently in 2006, as will the Plaquemine VCM manufacturing facility by the third quarter of 2011. After the Plaquemine VCM facility closes, Dow will have 2.5 billion pounds (1.1 MMT) of global VCM capacity operating.[4,5]

Dow sells vinyl chloride monomers (VCM) as a raw material to make polyvinyl chloride (PVC). Dow has a strong business relationship with Japan's Shin-Etsu Chemical Co. Ltd., which started in Freeport in 1974 with the supply of VCM for Shin-Etsu's operations in the US (Shintech). This partnership with Shintech is changing during 2011 as Dow shuts down VCM production plants and Shintech expands its own VCM production capacity in Louisiana. Dow will continue to supply a significant quantity of VCM to Shintech's Freeport site for many years to come.

Contrary to rumors, Dow's decision to shut down its VCM facility in Plaquemine later this year does not translate to an end to its historic partnership with Shin-Etsu. It will, however, result in a transfer of all AHCl supply for sales to the merchant market from Plaquemine to Freeport.

Primer on Anhydrous Hydrogen Chloride

Most of the hydrogen chloride available in the US, Europe, and Japan is a derivative from the manufacture of a wide range of chemicals, including organic synthesis of: isocyanates, fluorocarbons, chlorinated methanes and ethanes, and vinyl chloride monomer. It is also formed from inorganic manufacturing of magnesium, fumed silica, titanium dioxide, and sodium bisulfate and potassium bisulfate.[3,6]

Anhydrous (dry) hydrogen chloride (AHCl), also referred to as hydrogen chloride gas, is a clear, colorless, nonflammable gas with its water content removed. It is heavier than air and has a strong, irritating odor. Aqueous solutions of hydrogen chloride are known as hydrochloric acid or, if the hydrogen chloride in solution is of commercial grade, as muriatic acid. Hydrochloric acid typically contains 24–36% by weight hydrogen chloride, with water as the remaining component.

Over 90% of the HCl is produced in the US:

(1) as a by-product in the chlorination of hydrocarbon;
(2) as a by-product from the thermal cracking of chlorinated hydrocarbons; and
(3) as a by-product from phosgenation of amines for isocyanates and halogenations in the manufacture of chlorofluorocarbons.

It can also be produced

(4) from direct synthesis: the combustion of hydrogen and chlorine; reaction of sodium chloride with sulfuric acid (Mannheim Process); or reaction of sodium chloride, sulfur dioxide, oxygen, and water (Hargreaves Process).

Various techniques are available to treat the crude by-product HCl streams to obtain either AHCl or hydrochloric acid and pyrolyzing waste organics to recover chlorine in the form of HCl.[7] Anhydrous HCl can also be produced by evaporation of 36 wt% hydrochloric acid and AHCl can be absorbed in water to produce HCl acid.

In general, aqueous HCl is used as a non-oxidizing acid while anhydrous HCl is usually consumed for its chlorine value.[7] Anhydrous HCl is a critical specialty gas used in many industries:

- In semiconductor manufacturing, it is used for plasma and thermal etching of silicon (Si) and gallium arsenide (GaAs) wafer surfaces to remove defects prior to epitaxial Si and GaAs growth.
- In photovoltaics, an industry that is becoming a major consumer of electronic specialty gases, AHCl is used to react with metallurgical silicon to form trichlorosilane ($SiHCl_3$ or TCS) in polysilicon production for thin film solar cells (also called thin film photovoltaics, TFPV). In the manufacturing of crystalline silicon (c-Si) solar cells, hydrochloric acid (aqueous HCl) is used with hydrofluoric acid (HF), hydrogen peroxide (H_2O_2) and/or ammonium hydroxide (NH_4OH) to clean the silicon wafer and remove organic or metal residues from deposition of the glass layer on the Si wafer, prior to deposition of the antireflection coating.
- AHCl is used in reactor cleaning in compound semiconductor manufacturing.
- Outside of electronic applications, AHCl is an intermediate for rubber and pharmaceutical production.
- AHCl can be used to produce chlorinated compounds such as organic chlorides (e.g., methyl and ethyl chlorides) and chlorinated metals such as alkyl chlorides (e.g., AlCl), to enhance the separation coefficient of ores in hydrometallurgy.
- AHCl can be used in hot galvanizing.
- AHCl can be used to calibrate gas mixtures for environmental emission monitoring.
- AHCl can be used with xenon to produce wavelengths that vary with operating conditions in excimer lasers.
- In the textile industry, AHCl serves as a stripping agent for textile fibers.

Industrial uses for aqueous hydrochloric acid include:[3]

- Steel pickling

- Chemical manufacturing
- Oil-field acidizing
- Industrial cleaning
- Mining and metal production
- Food processing applications

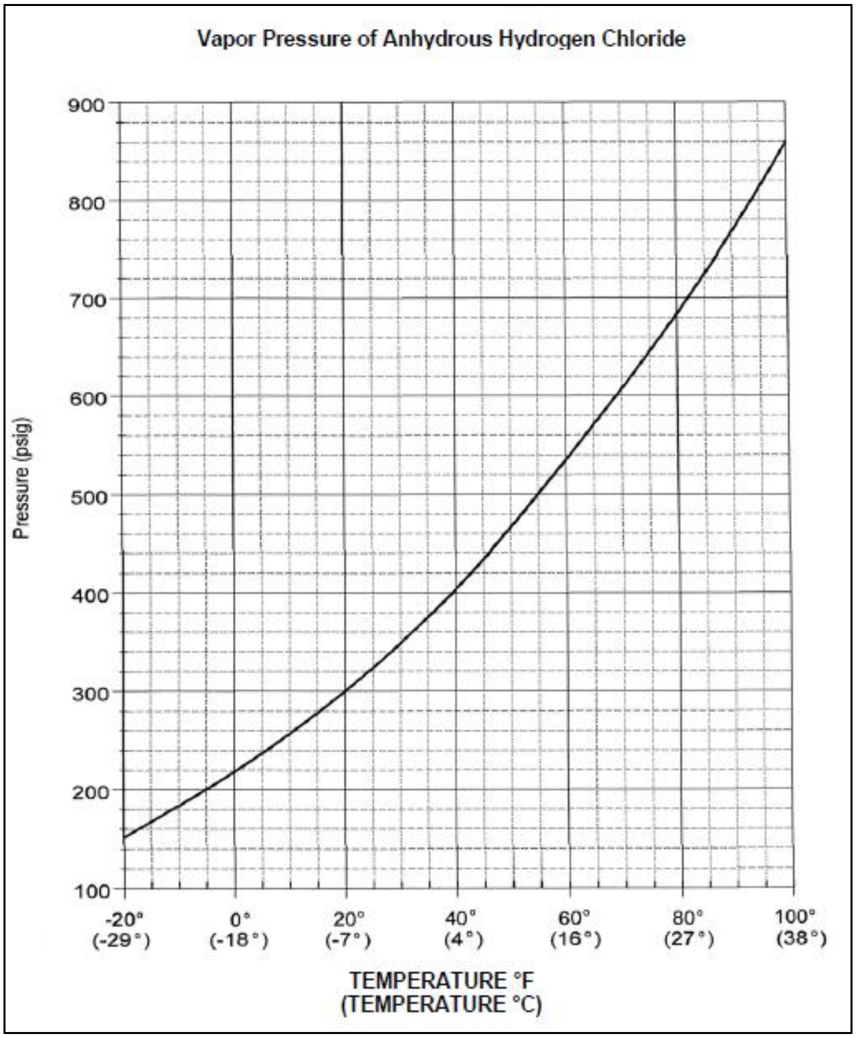
A recent study reports that about 40 manufacturing processes generate HCl as a by-product and about 110 chemical manufacturing processes use HCl as a raw material.[8]

Due to HCl's reactive and corrosive nature, it must be handled with extreme care, especially when it is also a toxic inhalation hazard (TIH). Aqueous hydrochloric acid is thermally stable at typical usage temperatures and can decompose when exposed to elevated temperatures. Heat is generated when the acid is mixed with water, and pattering and boiling can result. It is corrosive to most metals and contact with common metals can generate hydrogen gas, which is flammable. In the anhydrous state, HCl is thermally stable, relatively inactive, and corrosive to a few metals. AHCl is extremely attracted to water, however, and when exposed to air, it will react exothermically with atmospheric moisture to form the highly corrosive hydrochloric acid. Since AHCl is heavier than air, it may accumulate in confined spaces, particularly at a below-ground level. OSHA lists AHCl as a highly hazardous chemical in quantities above 5,000 pounds (2.27 metric tons or 2.27 MT).

As shown in Fig. 2, AHCl has an equilibrium vapor pressure of 603 psia (588.3 psig) at 68°F (20°C) and 940 psia (925.3 psig) at 104°F (40°C). Its high vapor pressure means that it is volatile and evaporates very quickly at room temperature. With a critical temperature of 51.4°C, it can be stored as a liquefied, compressed gas at temperatures not exceeding 125°F (52ºC).

The gas industry has historically preferred rail systems for long-distance transportation because of the tank cars' capacity for large volumes of gas. By design, storage tanks are not built to withstand the high pressure of liquefied AHCl at normal temperatures. Since HCl's liquid and gas phases are in equilibrium at a vapor pressure of 150 psig at -20 F, AHCl can be transported by rail as a refrigerated liquid at -20°F (-29 ºC) and 275 psig. Railcars with refrigerated loads must remain cooled and have finite periods of transit and unloading, especially during warm weather, when the internal temperature could rise and the cargo pressure could exceed the safety-relief valve setting. Given that AHCl is toxic when inhaled, rail transport is especially risky. Recent studies by the US Department of Transportation and the National Transportation Safety Board on transportation risks by rail through populated areas of TIH, such as anhydrous ammonia, AHCl, and chlorine, are increasingly discouraging this mode of supply without tank car improvements, changes in traffic control, modifications to delivery routes and schedules, and other risk-reduction strategies.

Without refrigeration, AHCl can be carried by truck as a compressed liquid under its own vapor pressure in small high-pressure cylinders (minimum 1800 psig at 65% fill density) containing up to 65 lb, in 600-lb containers, and in tube trailers containing up to 21,000 lb.[9] The Chlorine Institute and the Compressed Gas Association have more information and extensive guidelines on safe use and handling of AHCl.



Source: Chlorine Institute Pamphlet 99, "Hydrogen Chloride, Anhydrous (Non-Refrigerated) Use, Handling and Transportation of Cylinders and Tube Trailers," Edition 3 (October 2008)

Figure 2. Equilibrium vapor pressure of hydrogen chloride. Compressing the vapor beyond the equilibrium pressure at a specific temperature leads to a phase change from gas to liquid. The unit "psia" denotes absolute pressure in pounds per square inch; "psig" denotes gauge pressure in pounds per square inch; x psia = (x + 14.696) psig; 1 atm = 14.696 psia.

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