

BROMINE

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Bromine is a natural element widely found in nature, principally in seawater, salt lakes, and underground brines associated with oil. The quantity of bromine sold or used in the United States in 2001 was 212 million kilograms (Mkg) valued at \$159 million (table 1). The average value of bromine sold or used was \$0.75 per kilogram (table 1). Primary uses of bromine compounds were in flame retardants (40%), drilling fluids (24%), brominated pesticides (mostly methyl bromide) (12%), water-treatment chemicals (7%), and others (17%) (Chemical Market Reporter, 1999). International distribution of bromine production for 2001 was estimated to be as follows: the United States, 39%; Israel, 38%; the United Kingdom, 9%; China, 7%; and other countries, 7% (table 5). Because of depleting reserves, distribution and economics, environmental constraints, and the emergence of Israel as the world's second largest producer, the U.S. portion of world production has decreased steadily since 1973 when the United States produced 71% of the world supply.

Legislation and Government Programs

The U.S. Department of Defense was directed by the chairman of the Senate Appropriations Committee in October 2001 to ensure that military housing units undergoing renovation in the next few years are safe and free from preventable hazards, specifically with fire protection in mind. The Department of Defense was to give priority to fire safety in purchasing construction materials that meet the highest specifications of fire safety. The major use for bromine is in fire retardants (Dead Sea Bromine Group, 2001c§¹).

Methyl bromide was listed as a class I ozone-depleting substance in the 1990 Clean Air Act (CAA) and was scheduled to be phased out in the United States by January 1, 2001. The U.S. Congress extended the phase out of methyl bromide until January 1, 2005, to coincide with the deadline for developed countries under the Montreal Protocol on Substances that Deplete the Ozone Layer. Under the Clean Air Act Amendments of 1990 (CAAA) (Public Law 101-549), U.S. production and imports of bromine must be reduced from 1991 levels as follows: 25% by 1999; 50% by 2001; 70% by 2003; and a full ban by 2005. Domestically, methyl bromide had proven to be a difficult pesticide to replace because of its low cost and usefulness against a large variety of agricultural pests. The CAAA allowed for the exemption of critical uses of methyl bromide that have not yet been defined. The Environmental Protection Agency (EPA) held its third in a series of stakeholder meetings on the process on October 26, 2001, and will continue

sector based meetings. The EPA will evaluate these applications based on technical and economic criteria and will develop with other agencies a nomination package for submission to the Secretariat of the Montreal Protocol in January 2003 (U.S. Environmental Protection Agency, [undated]§). The dominant use was for preplanning soil treatments. It was also used for structural applications, such as termite treatments. Three producers—Albemarle Corp., Great Lakes Chemical Corp., and Israel's Dead Sea Bromine Co. Ltd.—were the major manufacturers. Under the Montreal Protocol, developing countries had until 2015 to phase out methyl bromide production.

Bromine was taxed under the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund), that had gone through two reauthorizations since its enactment in 1980. The 1986 Superfund Amendments and Reauthorization Act made considerable changes to the remedy selection component of the law. A second reauthorization in 1990 extended only the program and its taxing authority. Superfund taxes on industry, which generated \$1.6 billion per year, had not been collected since December 1995. The Superfund Trust Fund was projected to run out of money in 2000. The 107th Congress passed H.R. 2869 (Public Law 107-118), which formally established the EPA's brownfields program and provided relief from superfund liability for small businesses.

The EPA, the Environmental Defense Fund, and the American Chemistry Council announced that 192 of the Nation's largest chemical and oil companies, including 2 that produce bromine, had volunteered to ensure that approximately 1,100 commonly used chemicals were screened for basic toxicity; the companies were members of the Chemical Manufacturers Association (CMA) (Johnson, 1999). The agreement was a significant step toward gathering complete screening data for 2,800 high production volume chemicals that were used or imported in quantities exceeding 454 metric tons per year (t/yr) (1 million pounds per year). The CMA's Internet tracking system publicly displayed the chemicals and timetables set for the companies (Chemical Manufacturers Association, [undated]§). The Council of Chemical Associations, an international industry trade association, set a goal of testing 1,000 chemicals by 2004. The toxicity testing would be carried out under a cost-sharing program operated by the Organization for Economic Cooperation and Development, which comprised 29 countries, including the United States. The Synthetic Organic Chemical Manufacturers Association announced its support of the program as a result of commitments made by the EPA.

The U.S. Consumer Product Safety Commission (CPSC) held public hearings that were followed by the National Academy of Sciences (NAS) conducting a congressionally mandated study

¹References that include a section twist (§) are found in the Internet References Cited section.

of potential health risks for selected fire retardant chemicals that may be suitable for use in residential upholstered furniture. Of the 16 compounds and classes of compounds reviewed, the NAS identified 8 including decabromodiphenyl oxide (DBDPO) and hexabrocyclododecane (HBCD), that would pose minimal risk and recommended further study of the remaining 8. The CPSC staff subsequently completed its own risk assessment and identified DBDPO and HBCD among those compounds that would not be considered hazardous if used in furniture fabrics (U.S. Consumer Product Safety Commission, 2001§). The CPSC had not voted to propose any regulations at yearend 2001, but additional public meetings were planned for June 2002 (D.R. Ray, U.S. Consumer Product Safety Commission, written commun., May 10, 2002).

The EPA asked the chemical manufacturers to voluntarily test 23 substances, including ethylene dibromide, to which children were exposed in everyday life. The EPA would use data generated in the first round of its Voluntary Children's Chemical Evaluation Program to examine the risk from chemicals found in the human body that come from air, food, or water. The agency planned to evaluate and revise the program after the first tests and expand it to include more chemicals (Hogue, 2001).

Production

Domestic production data for bromine were developed by the U.S. Geological Survey from a voluntary survey of U.S. operations. Of the operations to which a survey request was sent, six responded, representing 100% of total elemental bromine produced (table 1).

Albemarle Corp.'s bromine production included three plant sites in south Arkansas with the addition of their new satellite facility in Union County, which was started up in July 2000. Albemarle had 31 bromine production wells, 6 of which also produced oil. Brine wells were twice as wide and twice as deep as typical Arkansas oil wells, and the brine that was produced exceeded 110° C (230° F). Albemarle owned 17.4% of the production from the west unit operated by Great Lakes Chemical Corp. in Union County and, as a result, produced bromine at their satellite plant from five additional wells in the unit.

On June 14, ChemFirst Inc. signed an agreement to sell its custom and fine chemicals business to Albemarle for \$74 million plus an adjustment for working capital at the time of closing, currently estimated to be \$9 million, in an all-cash transaction. The company's pharmaceutical contract research and development business and fine chemicals product lines, including FirstCure performance polymer products, were also included in the sale. The agreement includes plants in Dayton, OH, and Tyrone, PA. The sale closed on July 9 (McArthur, 2001).

Great Lakes continued production of bromine from brines at three plants in Arkansas. The company also owned Associated Ocel Co. Ltd. of the United Kingdom. Great Lakes is organized into four global business units—polymer additives, performance chemicals, water treatment, and energy services and products. The company's water treatment business unit, through BioLab Water Additives (a division of the Great Lakes

subsidiary BioLab Inc.), is the world's leading provider of recreational water care products to the consumer. In addition, through its proprietary position in polymaleate chemistry and as the world's foremost provider of bromine-based biocides, BioLab Water Additives is a leading supplier of corrosion inhibitors, scale control, and desalination solutions. A major portion of the company's sales is sold to industrial or commercial users for use in the production of other products. Some products, such as recreational water treatment chemicals and supplies, are sold to a large number of retail pool stores, mass merchandizers and distributors.

During 2001, Great Lakes announced a restructuring program to reduce operating costs by \$30 million by consolidating of facilities and jobs primarily in the areas of polymer additives and fine chemicals. The consolidation was planned over a 12-month period to eliminate about 390 jobs or 8% of the work force (Chemical Market Reporter, 2001).

TETRA Technologies, Inc., was one of the largest users of brominated products in the world. Calcium, sodium, and zinc bromide, collectively referred to as clear brine fluids (CBFs), were used in oil and gas applications. CBFs have high specific gravities and were used in completion and workover activities to reduce the likelihood of damage to the well bore and productive pay zone. Calcium bromide and zinc bromide were purchased from two domestic and one foreign manufacturer, and TETRA recycled calcium and zinc bromide CBFs repurchased from its oil and gas customers. The West Memphis, AR, facility produced calcium bromide and zinc bromide using zinc-containing sludge from electroplating operations and low-cost hydrobromic acid. TETRA began operation of merchant bromine, calcium bromide, and sodium bromide plant at Dow Chemical Co.'s Ludington, MI, facility in mid-1998 using purchased crude bromine from Dow's calcium-magnesium chemicals operation. The liquid sodium bromide was sold to the industrial water treatment markets. TETRA also owned a plant in Magnolia, AR, that was designed to produce calcium bromide but was not operational in 2000. Approximately 13,400 hectares (33,000 acres) of bromine-containing brine reserves in the vicinity of the plant were under lease (TETRA Technologies, Inc., 2000, p. 5).

Consumption

There were many different flame retardants that included bromine, chlorine, phosphorus, nitrogen, and other elements. Flame retardants are chemicals that suppress the combustion process. They prevent the spread of fires or delay the time of flashover so that people have additional time to escape. During 2001, halogenated hydrocarbons accounted for the highest dollar volume among fire retardants used globally, and the percentage of bromine by weight varied between 45% and 80% (Lerner, 2001). It is estimated that brominated flame retardants (BFRs) accounted for 39% of the worldwide bromine market in 1998. Consumption by final applications was reported as follows: electronics and electrical, 56%; building and construction, 31%; textile, 7%; and transformers, 6%. The distribution of BFR use in electrical and electronic components use was reported as follows: household appliances, 59%; printed wiring boards, 30%; connectors and relays, 9%; and

wire and cabling, 2%. In 1999, consumption by region was as follows: Asia, 56.2%; the Americas, 28.7%; and Europe 15.1% (Bromine Science and Environmental Forum, 2000§).

Albemarle's fine chemicals division also included surface actives, bromine, and oilfield chemicals. The company had manufacturing units in Feluy, Belgium; Port-de-Bouc and Thann, France; and Teesport, United Kingdom. The Teesport facility functioned as a custom manufacturing and oilfield chemicals plant.

Flame retardants was Albemarle's most visible market segment. Albemarle serves four primary market segments with its fire retardants—printed circuit boards, electronic enclosures, electrical connectors, and construction products. Albemarle reported the following end uses during 2000: Fire retardants, 31%; pharmaceuticals and agriculture, 18%; catalysts and additives, 21%; and performance chemicals, 30%. The overall end markets served by the company in 2000 included: electronics, 23%; household and industrial, 22%; construction and other, 29%; packaging material, 8%; and automotive, 8% (Lerner, 2001).

Flame retardants become more important to the home as the volume of polymer or plastic material increases. The continued presence of polymers, which are produced from organic fuels, contribute to the increased fire death statistics. Fire retardants could significantly decrease the risk of fire, and BFRs, which react in the gas phase, provide unique advantages. Criticism of brominated fire retardants has failed to acknowledge that the most deadly gases in any fire are carbon monoxide and carbon dioxide, which are natural products of combustion. Bromine is used to meet the fire safety of electrical and electronic appliances by preventing fires or by providing building occupants up to 15 times more escape time (Bromine Science and Education Forum, 2001).

Most deaths occur from fires that start at night while families are asleep. Four times as many victims die from inhaling smoke and toxic gases than from burns. Products most often ignited in fatal fires are upholstered furniture, mattresses, and bedding. These items are associated with over one-third of the residential fire deaths. In 1998, there were an estimated 420 deaths, 1,080 injuries, and \$120 million in property damage that could be addressed by a standard or other action. As part of its annual performance plan, the CPSC reported that over 3,000 people die and over 16,000 are injured each year because of fires in their homes. These fires result in property losses of about \$3.7 billion. The total annual cost to the Nation of residential fires is about \$20 billion (U.S. Consumer Product Safety Commission, 2002§).

It was estimated in 2001 that about 100 kilograms of plastic is used in a car, or about 10% by weight. For various technical and economic reasons, plastics were the best material for the task because of emission requirements, which require lower weight, and impact requirements that mandate stronger and more ductile materials. The decision as to which flame retardant is used ultimately depends on processing temperature and price. Examples of some types of car parts made out of plastics that contain BFRs included air and oil filters, battery cases, bumper fascias, carpeting, connectors, corrugated wire conduits, dash board covers, blastomeric gaskets, electrical insulations, engine acoustic insulation, fan blades and housings,

films, fuel hoses, head-liners, glove box, internal trim, instrument cluster, padding and fabric backing, sound deadening, and wheel well liners (Edenburn, 2001, p. 1, 9, 11, 13).

The plastics used in cars must meet U.S. Department of Transportation motor vehicle regulations under 49 CFR 571.302. In Europe, passenger cars do not require flammability testing. During 1996, plastics accounted for about 23% of fires in automobiles in the United States. Currently there are three types of flame retardant categories in commercial use, one of which is a group of halogens that include bromine. Halogens are known as gas phase flame retardants; they act as gasses and reduce the creation of fuel as follows: acting as a free radical trap, which prevents the polymer from breaking down into smaller segments, which are more flammable; excluding oxygen by forming a blanket of noncombustible gasses around the flame front; and removing heat because the reaction whereby the flame retardant decomposes is endothermic. For these reasons, halogens are the most effective type of flame retardant for most polymer systems (Edenburn, 2001).

The EPA's methyl bromide phase-out program stated that those applications still using methyl bromide by 2005 would do so because they had no choice. Methyl bromide was still the common chemical used to limit the spread of damaging insect populations around the world. The U.S. Department of Agriculture recommended the use of methyl bromide to treat wood packaging materials from China because of the lack of good alternatives. A voracious, nonnative insect pest had been found in material at 26 scattered warehouse and residential sites in 14 States. China could end up having to use more than 12,500 metric tons (t) of methyl bromide to treat wood destined for the United States. This would represent a 75% increase in use in Asia compared with 1996 levels for all applications, including soil treatment.

Pesticides, such as bromine compounds, were used to protect food from pests, such as bacteria, insects, mold, rodents, and weeds. In 1996, Congress passed the Food Quality Protection Act (FQPA) to improve the safety of food and to protect the public from exposure to pesticides. With the passage of this act, the jurisdiction of food-contact antimicrobials shifted from the Food and Drug Administration to the EPA. The EPA asserted that conclusions concerning the dangers of pesticides in food were not credible and were unnecessarily alarmist (Chemical Market Reporter, 1999). The EPA set standards on the amount of pesticides that may remain on food if pesticides were applied. The FQPA set a tougher standard for pesticide use on food. By 2006, the EPA was required to review the safety standards applicable to all old pesticides to make sure that their use on food met the new safety standard. If a pesticide was authorized that did not meet the safety standard, then the EPA would work with grocery stores to inform consumers of such pesticides and foods that might contain them.

Bakers mix oxidizing agents, such as potassium bromate, into dough to improve breadmaking quality. The oxidant results in formation of disulfide bonds in the gluten in proteins that lead to the formation of larger gluten in polymers. Tyrosine cross-links that exist in gluten are affected by such ingredients as potassium bromate (Wilkinson, 2001).

In June, GreenPeace International released a study that

reported on dust samples from bags of vacuum cleaners analyzed for BFRs. The exposure level of 2.2 milligrams is a factor of 1.4 million times below acceptable levels and was reported as a nonexistent risk. Therefore toxicological studies are not indicated at the reported level of consumer exposure (Alsopp, Santillo, and Johnston, 2001).

World Review

European Union.—The European Council of Ministers for the internal market rejected the decision by the European Parliament to phase out octabromodipheyl ether and decabromodipheyl ether, until they have been proven harmful. The European Parliament initially voted to ban the two chemicals by 2006. The chemicals will undergo risk assessment (Industrial Minerals, 2001).

The European Commission made three separate pieces of legislation out of the original draft directive on waste electrical and electronic equipment, which served to intensify the focus on BFRs. European manufacturers of BFRs have studies that claim BFR-treated plastics can be recycled. The Brussels-based Bromine Science and Environmental Forum (BSEF) (2001§) planned to build a recycling pilot plant to test the recyclability of the plastics containing the two flame retardants.

Azerbaijan.—The Neftchala iodine-bromine plant produces 4,000 t/yr of bromine from waters from oil wells in the Neftchala and Khillinsky oilfields in the Prikurinsky Basin. The bromine reserves were estimated to be 100,000 t. To modernize and commission the plant, an investment of \$1.4 million was required (Industrial Minerals, 2000).

China.—Construction began on the first phase of a bromide manufacturing joint venture in Weifang, Shandong Province. The venture was split between Dead Sea Bromine Group (DSBG) of Israel and Haiha Group of Weifang. The new plant would produce a range of high-technology products of which the company planned to export 60%. Storchem Inc. of Burlington, Canada, planned to represent Ocean Chemical Group in the North American bromine market. The initial market target will be the organic and inorganic bromine markets that include the photographic chemicals and water-treatment industries (Harben, 2001).

Denmark.—The Danish Environmental Protection Agency had drawn up a plan to progressively limit and stop the use of BFRs. A major part of BFR consumption was in imported goods, such as cars, computers, and television sets. In March, the Danish Environmental Protection Agency published its action plan for BFRs. The report revived the action plan and brought it up to date regarding national and international initiatives. The plan was to serve as the foundation for future regulation of BFRs in Denmark. Too little was known about two BFRs, and further investigations and assessments therefore are needed before it can be determined if they pose a risk. The BSEF (2001§) believed that the brominated chemical found in milk accumulated from its historic use in offshore oil drilling in the North Sea in the early 1990s and as a hydraulic fluid by the German coal mining industry. Two BFRs will be phased out in the next few years. Alternatives to BFRs will be assessed in an effort to promote cleaner products that meet current fire safety requirements. Dispersal of BFRs into the environment is

mainly by evaporation into the air where electrical and electronic equipment is scrapped or repaired.

France.—Elf Atochem SA continued to switch from producing bromide derivatives to fine chemicals at its Port-de-Bouc plant in southeast France. The complex included a 12,000-t/yr bromine plant that supplied the downstream units. The company invested \$12.8 million in the plant to produce alkyl bromides and dibromide as well as ultrapure hydrobromic acid. Autofina completed a new 1,200-t/yr bromo-acids and bromo-esters plant. Albemarle operated a bromine derivatives facility in Thann and a flame retardants plant in Port-de-Bouc. Most of the production of brominated intermediates was sold to the pharmaceutical industry. The inorganic bromide capabilities were expanded during 2001 (Lerner, 2001).

Polypropylene carpets that contained 70% of a bromine flame retardant and 3% phosphorus passed the M1 classification according to National Forest Plan standard 92-503, better known as *epiradiateur*. The final material has ultraviolet and light stability with flame retarding capabilities. The carpets also are recyclable (Dead Sea Bromine Group, 2001b§).

French TV announced on October 17, 2001, that a fire breaks out in France once every 2 minutes (260,000 fires per year) resulting in 800 deaths per year and 10,000 injuries. The major cause of death is said to be gas toxicity. The increased use of flame retardants in plastics used in housing for appliances, television sets, and audio and other electronic equipment found is associated with domestic fires. Brominated flame retardants are cost-effective additives that reduce the production of toxic smoke and are recycled to contribute to the quality of the environment (Dead Sea Bromine Group, 2001a§).

Israel.—The production of bromine and potash began in 1931 at Kalia. The soluble minerals existed mainly as bromine and chloride anions and magnesium, potassium, and sodium cations. Bromine had been produced as a byproduct from waste bitterns associated with potash production from the Dead Sea since 1957 by DSBG. After potash was removed in solar ponds, the waste bitterns were processed with chlorine to recover bromine. The brine contained 14,000 parts per million of bromine. The bromine-free bitterns were then processed to recover magnesium.

In addition of the valuable mineral resources, the Dead Sea area is a unique natural site owing to such factors as its location 400 meters (m) below sea level and the resulting special biodiversity system. The environmental nongovernmental group Friends of the Earth Middle East (2001§) reported that between 1947 and 1994 the surface of the Dead Sea decreased by 1,031 square kilometers, which was attributed to the installation of the potash projects and the decrease of the inflow of surface water owing to agricultural irrigation.

In 1985, the Israeli Government began efforts to sell its share of Israeli Chemical Co. Ltd. (ICL) to offset an investment program. ICL was a group of chemical and mineral industrial companies with commercial and marketing services, research institutes, and technical facilities. Israel Corp. bought an additional 17% stake in March 1997, which brought its total share of ICL to 41.9%. In 1997, the Israeli Government had announced its decision to sell off its 31.5% stake of ICL valued at \$441 million; the sale required the approval of the finance committee of the Israeli Parliament. In 1999, Potash Corp. of

Saskatchewan, Canada, planned to purchase as much as 30% of ICL.

DSBG was a major producer of bromine and bromine compounds. The company was 89% owned by ICL. DSBG, in turn, owned a number of subsidiaries. ICL made an offer to purchase the remaining 11% of DSBG for \$60 million (Chemical Market Reporter, 2000). DSBG had bromine manufacturing facilities at the Sdom plant and organic and inorganic bromine compounds at Ramat Hovav. Broomchemie BV (a subsidiary) operated in the Netherlands.

Japan.—Tosoh Corp. was Japan's only producer of bromine and hydrobromic acid used in the manufacture of dyes, flame retardants, pharmaceuticals, and photosensitive materials (Tosoh Corp., [undated]§).

Jordan.—In April 2000, Jordan acceded to the World Trade Organization, a process which entailed extensive legislative and regulatory reform. The United States and Jordan negotiated a free trade agreement that was signed on October 24, 2000. The agreement would eliminate all tariff and nontariff barriers to bilateral trade in virtually all industrial goods and agricultural products within 10 years of signing. Joint ventures in mining and contracting require 50% local partnership (U.S. Embassy, Amman, Jordan, 2000).

Jordan Bromine Co. Ltd. (JBC) [a joint venture between Arab Potash Co. (APC), its subsidiary Jordan Dead Sea Industries Co. (JODICO), and Albemarle Holdings Co. Ltd. of the United States (a subsidiary of Albemarle)] was incorporated in Jordan on January 11, 1999. Since then, APC had purchased JODICO's shares in the joint venture resulting in a 50-50 joint venture between APC and Albemarle Holdings. A \$150 million bromine complex in Safi included a 50,000 t/yr bromine plant, a 40,000-t/yr calcium bromide plant, and a 12,500-t/yr initial capacity tetrabromobisphenol-A (TBBA) plant expandable to 37,500 t/yr. The plant was expected to create 280 new jobs and be operational in 2002 (Euromed Synopsis, 2000). The plant would produce bromine for the merchant market and derivatives facilities including inorganic bromides for oilfield completion fluids and TBBA as a flame retardant, primarily for marketing in Europe and Asia. AGRA Monenco Inc. of Canada was awarded a contract to perform engineering, procurement, and construction management. JBC obtained a loan from the European Investment Bank for the project. During 2001, JBC awarded 10 major construction contracts, completed site development, and was underway laying the foundations and constructing buildings.

King Abdullah called for conservation of the Dead Sea and emphasized the importance of maintaining its water level. Environmentalists attribute the decrease to industrial and tourism projects implemented by Israel, Jordan, and the Palestinian National Authority. The water level was expected to drop by 1.2 m during 2001 compared with around 80 centimeters in past years. The level has already dropped by 25 m over the past three decades (Farawati, 2001§).

Russia.—On October 30, the new Land Code of Russia came into force; it represented a significant reform owing to sanction and encouragement given to the creation of private ownership rights to land. The full provisions of the Land Code apply only to certain nonagricultural land that constitutes approximately 2% of Russia's land surface. Foreigners are expressly permitted

to lease land subject to the general restrictions placed upon Russian citizens and legal entities. Any of the restrictions imposed on foreigners can be avoided by the use of a Russian subsidiary entity (Moore, 2001).

Astrakhan Oblast contains a gas condensate field discovered in 1976 for use by the Ltd. Astrakhangazprom enterprise. The operating field is the largest in the Russian south and is unique for its reserves of gas and condensates. The depth of the field is 3,827 to 3,990 m. Iodine and bromine occur at depths of 100 to 200 m and 3,000 to 3,500 m. Output of raw material is as follows: iodine, up to 30 t/yr, and bromine, up to 150 t/yr. An investment of \$6 million is needed for the project, and costs are expected to be recovered in 0.6 to 1.6 years (Russian Foreign Investment Promotion Center, [undated]§).

Current Research and Technology

Bromine is a gas at normal temperature and pressure, and concentrations as low as 0.5 part-per-million bring tears to the eyes. A study on the production and handling of about 200 Mkg of bromine plus substantial derivatives in southern Arkansas had Occupational Safety and Health Administration occupational injury/illness rates (OIIR) in the range of 0.74 to 1.60 reportable OIIR per 200,000 man hours. OIIRs for similar industries and a wide section of other U.S. industries range from 1.6 to 23.9. These results show that bromine and its compounds can be considered as safe chemicals as a result of the bromine safety standards and practices (Myers, 2001, p. 3, 7).

Studies with Michigan State University scientists demonstrated tandem reactivity by carrying out one-pot reactions with multiple metal-catalyzed couplings using a dibromobenzene with a palladium catalyst to form a hyperbranched brominated polyphenylene. The principal factor that enables the one-pot transformation is the extremely high selectivity of the iridium boryl catalysts for carbon-hydrogen activation. The reaction has a potential to increase the scope of industrial applications of the Suzuki coupling. The addition of halogens significantly increased the reaction rate. The study demonstrated that carbon-hydrogen activations and functionalization could be developed into a practical synthetic tool. Chemical feedstocks could be converted to common reagents used in the synthesis of pharmaceuticals and sophisticated organic materials (Ritter, 2002).

It has been 50 years since the discovery of ferrocene and the birth of modern organometallic chemistry. The coupling to two molecules of cyclopentadienyl magnesium bromide gave dihydrofulvalene, which would then be dehydrogenated to yield dicyclopentadienyliron. Today, ferrocene is being incorporated into polymers to introduce new material properties. Molecules derivatized with ferrocene groups are providing new, more potent agents for biomedical applications (Dagani, 2001).

Chemists at Inha University in Incheon, Republic of Korea, used bromine to produce difficult to make compounds by electrophilic aromatic substitution. P-bromoaniline was converted to 4-bromo-2,6-dichloroaniline and boiled with hydrobromic and acetic acid to yield 86% 2,6-dichloroaniline. The added aniline acted as a bromine acceptor to form more p-bromoaniline. The research could lead to greater use of bromine as a protecting group in aromatic systems (Chemical &

Engineering News, 2001).

Changes in energy cost may make more prevalent the use of hydrobromic acid to produce energy in a fuel cell reaction that is reversible. A previous study by Oronzio de Nora Group to produce hydrobromic acid as an electrical energy storage medium in reversible proton exchange membrane (PEM) showed cost of 2.0 to 2.5 times the prevailing base rate at the time of the study in 1979. A separate study by General Electric Co. also showed marginal performance advantages for hydrobromic acid. The stimulus for the early work on halogen electrochemistry was the threat by the Organization of Petroleum Exporting Countries of reducing crude oil production. During that time, increased attention was given to raising the efficiency of energy production. In PEM devices, the protons and oxygen ions are created by platinum catalyzed ionization from water in electrolyzer mode or from platinum catalyzed hydrogen and oxygen in fuel cell mode. PEM electrochemical devices are particularly receptive to the use of halogens in the oxygen role, have long life expectancy, and are free from the secondary chemical reactions present in liquid electrolyte devices. A halogen-halogen PEM fuel cell delivers 84% of the hydrogen energy. These high efficiencies for reversible operation create a clear advantage for electrochemistry to serve as the means for storing solar, off-peak central station energy for more appropriate delivery times (Myers, 2001 p. 3, 13, 17).

Outlook

Apparent U.S. demand for bromine exceeded 227 Mkg (500 million pounds) each year since 1997, which was the peak year. The volume of U.S. bromine sold or used declined by 4.8% in 2000. However, the general upward trend in bromine demand has been in BFRs. Demand for flame retardants can fluctuate along with overall economic swings. The economic slowdown, which began in 2000, had a significant adverse effect on demand in 2001. Polymer chemical markets are weak across the board. Compounding the difficulties is a large inventory correction in the electronics industry, which is the largest consumer of BFRs (Mannsville Chemical Products Corp., 2001).

Fire Retardants.—Bromine is a reactive flame retardant in that it enters into chemical reactions with the components of the systems in which it is used. In addition, bromine acts as a synergist with many other fire-retardant materials and so increases the effectiveness of the fire retardant. Environmental and health concerns may reduce long-term growth potential for halogenated flame retardants in general; however, growth in TBBA and certain other products is expected to replace some of the reduction. TBBA's accounted for one-half the bromine-based flame retardant volume (Mannsville Chemical Products Corp., 2001).

Petroleum.—Demand for bromine as a gasoline additive has declined each year since the EPA issued regulations in the 1970s to reduce and eliminate lead in automotive gasoline. In 1979, the amount of bromine sold for this application reached a peak of 225 Mkg. The rapid decline to 141 Mkg in 1986 was a direct result of the limits on lead in leaded automotive gasoline. The CAA requires mobile sources, such as cars and trucks, to

use the most effective technology possible to control emissions. In 2001, electric cars were on the market in California. Newer prototypes of the fuel cell that burns gasoline can double the mileage and thereby decrease emissions by using unleaded gasoline.

Sanitary Preparations.—Growth potential remains high for bromine-based biocides for use in industrial cooling systems because of environmental restrictions on chlorine and new alkaline-based chemical treatment programs. The most common bromine compounds used in cooling water are 1-bromo-3-chloro-5,5-dimethylhydantoin and mixtures of sodium bromide with sodium hypochlorous acid. The use of bromine compounds is also growing in sanitizing applications in the pulp and paper industry and food-washing applications. Use of calcium, sodium, and zinc bromides in oil well completion fluids has benefited in recent years from the rebound in world oil prices (Mannsville Chemical Products Corp., 2001). Bromine was used in indoor swimming pools, hot tubs, and whirlpools. The sanitary preparation field is an area where bromine was found to be safer than its substitutes because bromine has a higher biocidal activity level for the same volume of product.

Other Uses.—Use of calcium, sodium, and zinc bromides in well-completion fluids decreased during the 1980s because the domestic petroleum industry suffered a severe recession. In 1997, however, the oil-services sector posted another strong performance. About 95% of calcium bromide produced was used as an oil and gas completion fluid. Oilfield chemicals used in drilling, completion and workover, and production operations remained significantly more profitable internationally than in the United States. Use of calcium, sodium, and zinc bromides in oil well completion fluids has benefited in recent years from the rebound in world oil prices (Mannsville Chemical Products Corp., 2001).

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TABLE 1
SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS 1/

(Thousand kilograms and thousand dollars)

	HTSUS number 2/	1997	1998	1999	2000	2001
United States:						
Bromine sold or used: 3/						
Quantity		247,000	230,000	239,000	228,000	212,000
Value		\$111,000	\$162,000	\$213,000 r/	\$206,000	\$159,000
Exports: 4/ 5/						
Elemental bromine: 2801.30.2000						
Quantity		2,330	1,490	2,110	1,870	3,710
Value		\$3,590	\$3,440	\$2,430	\$2,560	\$3,600
Bromine compounds: 6/ (7/)						
Gross weight		10,700	10,200	9,520	9,210	7,990
Contained bromine		9,050	8,550	8,020	7,740	6,740
Value		\$21,200	\$18,000	\$16,000	\$26,200	\$14,900
Imports: 4/ 8/						
Elemental bromine: 2801.30.2000						
Quantity		1,650	1,200	1,970	5,470	5,610
Value		\$1,200	\$1,060	\$2,110	\$3,730	\$4,240
Bromine compounds:						
Ammonium bromide: 2827.59.2500						
Gross weight		33,000 9/	471 10/	1,510 10/	48,100	59,700
Contained bromine		2,690 9/	384	1,240	3,930	4,870
Value		\$22,000 9/	\$1,280 e/	\$1,940	\$22,000	\$29,200
Calcium bromide: 2827.59.2500						
Gross weight 10/		803	350	--	7,860	5,880
Contained bromine		642	280	--	6,280	4,700
Value		\$289	\$213 e/	--	\$4,780 e/	\$3,580 e/
Potassium bromate: 2829.90.0500						
Gross weight		378 10/	141	373	245	124
Contained bromine		181	67	178	117	59
Value		\$1,650	\$571	\$1,470	\$1,100	\$450
Potassium bromide: 2827.51.0000 11/						
Gross weight		705 10/	910 10/	1,170	871 10/	433 10/
Contained bromine		474	611	786	585	291
Value		\$1,710	\$2,220 e/	\$2,830 e/	\$2,130	\$1,060 e/
Sodium bromate: 2829.90.2500						
Gross weight		1,220	1,100	1,050	1,160	1,020
Contained bromine		646	584	554	615	538
Value		\$3,170	\$2,900	\$2,430 e/	\$2,750	\$2,190
Sodium bromide: 2827.51.0000 11/						
Gross weight 10/		2,730	3,960	4,640	3,130	NA
Contained bromine		2,120	3,070	3,600	2,430	NA
Value		\$4,210	\$6,090 e/	\$5,540 e/	\$4,820 e/	NA
Other compounds: 2903.30.1550						
Gross weight		8,910	8,990	7,400	7,760	1,890
Contained bromine		6,900	6,770	785	582	141
Value		\$16,700	\$18,900	\$17,000	\$15,500	\$5,360
World, production e/		542,000	521,000 r/	547,000 r/	560,000 r/	538,000

e/ Estimated. r/ Revised. -- Zero.

1/ Data are rounded to no more than three significant digits.

2/ Harmonized Tariff Schedule of the United States.

3/ Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.

4/ Source: U.S. Census Bureau.

5/ Export values are free alongside ship.

6/ Source: U.S. Census Bureau. Includes methyl bromine and ethylene dibromide.

7/ Data for these compounds are derived from HTSUS numbers 2903.30.0500, 2903.30.1500 (1997, 1998, and 1999), and 2903.30.1520 (2000) information.

8/ Import values are on a cost, insurance, and freight valuation.

9/ The respective data for "bromides/bromines and oxides" of ammonium, calcium, and zinc are combined and reported here; imports for 1997 included 83,000 kilograms of zinc bromide.

10/ The Journal of Commerce Port Import/Export Reporting Service.

11/ "Bromides of sodium" or of "potassium" import data are usually reported by a mutual HTSUS number, 2827.51.0000.

TABLE 2
ELEMENTAL BROMINE-PRODUCING PLANTS IN THE UNITED STATES, 2001

State and company	County	Plant	Production source	Capacity 1/ (million kilograms)
Arkansas:				
Albemarle Corp.	Columbia	Magnolia (a)	Well brines	
Do.	do.	Magnolia (b)	do.	310 2/
Do.	Union	Maryville	do.	25
Great Lakes Chemical Corp.	do.	El Dorado	do.	205
Do.	do.	Maryville	do.	130
Michigan, The Dow Chemical Co.	Mason	Ludington 3/	do.	45
Total				715

1/ Actual production capacity is limited by brine availability.

2/ This represents the cumulative capacity of the two identified plant sites.

3/ Bromine produced at this plant is reprocessed in Arkansas.

TABLE 3
U.S. IMPORTS OF OTHER BROMINE COMPOUNDS 1/ 2/

Compounds	HTSUS number 3/	2000		2001		Principal sources, 2001
		Gross weight (kilograms)	Value 4/ (thousands)	Gross weight (kilograms)	Value 4/ (thousands)	
Hydrobromic acid	2811.19.3000	370	\$366	410	\$362	Israel, 98%; Canada, 2%.
Ethylene dibromide	2903.30.0500	2,000	2,020	448	446	United Kingdom, 100%.
Methyl bromide	2903.30.1520	671	1,690	610	1,620	Israel, 100%.
Dibromoneopentyl glycol	2905.50.3000	1,390	4,640	1,320	4,330	Israel, 96%; China, 4%.
Tetrabromobisphenol A	2908.10.2500	700	1,030	1,130	1,700	Israel, 100%.
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909.30.0700	2,630	5,800	2,040	4,600	Israel, 99%, Mexico, 1%.
Total		7,760	15,500	5,950	13,100	

1/ These data detail the information included in table 1, imports of "Other bromine compounds."

2/ Data are rounded to no more than three significant digits; may not add to totals shown.

3/ Harmonized Tariff Schedule of the United States.

4/ Declared cost, insurance, and freight valuation (c.i.f.).

Source: U.S. Census Bureau.

TABLE 4
WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES, DECEMBER 31, 2001 1/

Country and company	Location	Capacity (thousand kilograms)	Source
Azerbaijan, Neftechala Bromine Plant	Baku	4,000	Underground brines.
China, Laizhou Bromine Works	Shandong	30,000	Do.
France:			
Atochem	Port-de-Bouc	12,000	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse	2,300	Bitterns of mined potash.
India:			
Hindustan Salts Ltd.	Jaipur		
Mettur Chemicals Ltd.	Mettur Dam		
Tata Chemicals Ltd.	Mithapur		
Israel, Dead Sea Bromine Co. Ltd.	Sdom	190,000	Bitterns of potash production from surface brines
Italy, Societa Azionaria Industrial Bromo Italiana	Margherita di Savoia	900	Seawater bitterns from salt production.
Japan, Toyo Soda Manufacturing Co. Ltd.	Tokuyama	20,000	Seawater.
Spain, Derivados del Etilo S.A.	Villaricos	900	Do.
Turkmenistan:			
Nebitag Iodine Plant	Vyshka	3,200	Underground mines.
Cheicken Chemical Plant	Balkan	6,400	Do.
Ukraine, Perekopskry Bromine Plant	Krasnoperckopsk	3,000	Do.
United Kingdom, Associated Octel Co. Ltd.	Amlwch	30,000	Seawater.

1/ Excludes U.S. production capacity. See table 2.

TABLE 5
BROMINE: ESTIMATED WORLD REFINERY PRODUCTION, BY COUNTRY 1/ 2/

(Thousand kilograms)

Country 3/	1997	1998	1999	2000	2001
Azerbaijan	2,000	2,000	2,000	2,000	2,000
China	50,100	40,000	42,000	42,000 r/	40,000
France	1,974 4/	1,950 4/	1,950 r/	2,000	2,000
Germany	700	600	500	500	500
India	1,500	1,500	1,500	1,500	1,500
Israel	180,000 4/	185,200 r/ 4/	181,000 r/ 4/	210,000 r/ 4/	206,000
Italy	300	300	300	300	300
Japan	20,000	20,000	20,000	20,000	20,000
Spain	100	100	100	100	100
Turkmenistan	130 4/	150	150	150	150
Ukraine	3,000	3,000	3,000	3,000	3,000
United Kingdom	35,600 4/	35,900 4/	55,000 4/	50,000 r/	50,000
United States 5/	247,000 4/	230,000 4/	239,000 4/	228,000 4/	212,000 4/
Total	542,000	521,000 r/	547,000 r/	560,000 r/	538,000

r/ Revised.

1/ World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

2/ Table includes data available through April 17, 2002.

3/ In addition to the countries listed, several other nations produce bromine, but output data are not reported; available general information is inadequate to formulate reliable estimates of output levels.

4/ Reported figure.

5/ Sold or used by producers.