BROMINE

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The quantity of bromine sold or used in the United States was 239 million kilograms (Mkg) valued at \$213 million (table 1). The value of bromine sold or used was \$0.89 per kg (table 3). 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, including photographic chemicals and rubber additives (17%) (Chemical Market Reporter, 1999b). International distribution of bromine production in 1999 was as follows: the United States, 45%; Israel, 35%; China, 9%; the United Kingdom, 5%; and other countries, 6% (table 6). Because of depleting reserves, environmental constraints, and the emergence of Israel as the world's second largest producer with 35% of the world market, the U.S. portion of world production has decreased steadily since 1973, when the United States produced 71% of the world supply, to 45% in 1999.

Legislation and Government Programs

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 phaseout 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 change to the CAA Amendments of 1990 (Public Law 101-549), U.S. production and importation 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 has proven to be a difficult pesticide to replace because of its low cost and usefulness against a large variety of agricultural pests. The amendment allows for the exemption of "critical uses" of methyl bromide that have not yet been defined. The dominant use was for preplanning soil treatments. It is also used for structural applications, such as termite treatments. About 4% of its use is as a chemical intermediate. Quarantine uses accounted for 5% to 8% of the total worldwide consumption of methyl bromide. Three producers, Albemarle Corp., Great Lakes Chemical Corp., and Israel's Dead Sea Bromine Co. Ltd. (DSB) are the major manufacturers. Under the Montreal Protocol, developing countries have until 2015 to phase out methyl bromide production (Morse, 1998).

The U.S. Environmental Protection Agency (EPA) reported that 640 chemicals, including bromine, were included on the Toxics Release Inventory (TRI) list of hazardous chemicals. The current TRI chemical list contains 579 individually listed chemicals and 28 chemical categories (including 2 delimited categories containing 39 chemicals). Three chemicals on the current list are under administrative stays and are not currently reportable (U.S. Environmental Protection Agency, [no date], Toxics release inventory: Community right to know, accessed April 25, 2000, at URL http://www.epa.gov/tri/chemical.htm). The TRI was passed by Congress in 1986 after a chemical catastrophe in India as Section 313 of the Emergency Planning and Community Right-to-Know Act (Public Law 99-549). It was intended to give communities the information they need to plan for chemical emergencies. The TRI, considered to be one of the Nation's most significant environmental laws, requires more than 26,000 industrial facilities to report to the U.S. Government. Starting in 1999, the EPA planned to present data for individual industry sectors and will make comparisons between similar facilities. In 1997, the reporting was extended to July 1999 to include the following sectors: metal mining, coal mining, electric utilities, commercial hazardous-wastetreatment facilities, chemical and allied product wholesalers, bulk petroleum terminals, and solvent recovery services. The chemical industry and other businesses objected to releasing chemical data use, arguing that doing so would give competitors access to proprietary production information.

EPA released a CD-ROM model that links air emissions from individual plant to the toxicity of each chemical emitted as well as exposure to residents living near the plant. The Risk-Screening Environmental Indicators model is based on EPA's TRI. Chemical Manufacturers Association (CMA) members are concerned about EPA exposure assumptions when data are missing. The model is designed to be a risk screening tool and not to perform risk assessments. Information on the CD model is available at URL http://www.epa.gov/opptintr/ env_ind/index.html (Johnson, 1999).

EPA required that 50,000 domestic companies that make or use large quantities of toxic or flammable chemicals prepare risk management plans. The plans will be posted at EPA's Envirofacts web site (http://www.epa.gov/enviro).

EPA announced a new office for information management, information policy, an'd technology stewardship, that will be headed by a national program manager. The new office included the highly visible TRI program, which will be moved from its current location in the Office of Pollution Prevention and Toxics. The data collection and analysis functions that are now scattered throughout the agency will be consolidated to include one-stop reporting, single-facility identification, environmental statistics, and watershed information (U.S. Environmental Protection Program, Pesticides, [no date], Toxics and Chemical Projects and Programs, accessed April 25, 2000, at URL http://www.epa.gov/epahome/pestoxpgram.htm). Bromine is taxed under the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund), that has 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, have not been collected since December 1995. Superfund's trust fund is projected to run out of money in 2000.

The EPA, the Environmental Defense Fund, and the CMA announced that 62 of the Nation's largest chemical companies, including 2 that produce bromine, have volunteered to ensure that some 600 commonly used chemicals are screened for basic toxicity; the companies are CMA members (U.S. Environmental Protection Agency, [no date], High production volume (HPV) chemical, accessed April 25, 2000, at URL http://www.epa. gov/opptintr/chemrtk/volchall.htm). The agreement was a significant step to gather complete screening data for 2,800 HPV chemicals that are used or imported in quantities exceeding 454 metric tons per year (t/yr) (1 million pounds per year). CMA's Internet tracking publicly displays the chemicals and timetables set for the companies (Chemical Manufacturers Association, [no date], accessed April 25, 2000, at URL http://www.cmahq.com/). The Council of Chemical Associations, an international industry trade association, set a goal of testing 1,000 chemicals by 2004. The Synthetic Organic Chemical Manufacturers Association announced its support of the program as a result of commitments made by EPA. The testing will be carried out under a cost-sharing program operated by the Organization of Economic Cooperation and Development, which comprises 29 countries, including the United States.

The EPA was peer reviewing reports on Class V Underground Injection Control (UIC) wells that included manufacturing facilities producing specialty chemicals, such as boron, bromine, magnesia, or their derivatives. A study of UIC Class V wells is being conducted to satisfy a consent decree with the Sierra Club Legal Defense Fund, Inc., and must be completed by September 1999. The results of the reports will determine whether to regulate each subclass of Class V wells and whether to propose any necessary regulations by April 2001 (U.S. Environmental Protection Agency, 1999).

Ethylene dibromide was included in the list of 33 hazardous air pollutants that the EPA believes pose the greatest potential threat to public health in the largest number of urban areas. As part of the national air toxics program, EPA on July 7 announced a strategy to further reduce toxic air emissions in hundreds of areas across the country to protect public health and the environment, particularly in urban areas. Toxic air pollutants include those known or suspected to cause cancer or other serious health effects in people (U.S. Environmental Protection Agency, [no date], Unified air toxics web site, accessed April 25, 2000, at URL http://www.epa.gov/ttn/ uatw/urban/urbanpg. html). Under the national air toxics program, EPA has and will continue to develop a number of national standards for stationary and mobile sources to improve air quality in urban and rural areas. The strategy complements the existing national efforts by focusing on achieving further reductions in air toxics emissions in urban areas. The strategy outlines actions to reduce emissions of air toxics, as well as assessment activities to improve EPA's understanding of the health and environmental risks posed by air toxics in urban areas.

The U.S. Department of Transportation (DOT) published a notice of proposed rulemaking amending the Hazardous Material Regulations (HMR) that included bromopropane to maintain alignment with international standards by proposing numerous changes. The DOT also published a notice of proposed rulemaking for the Research and Special Programs Administration amending certain requirements in the HMR that included bromotrifluoromethane to establish four new DOT cylinder specifications and to revise the requirements for maintenance, requalification, and repair of all DOT specification cylinders (U.S. Department of Transportation, 1998a, b).

The Consumer Product Safety Commission held public hearings in 1998 to receive scientific and technical information relating to the toxicity, exposure, bioavailability, and environmental effects of flame retardant chemicals, including bromine compounds that may be suitable for use in residential upholstered furniture. The Commission will evaluate the information obtained from the hearings as part of its deliberations on whether to propose a standard to address the hazard associated with small open flame ignitions of upholstered furniture. At yearend 1999, the study was still in the information gathering stage.

The U.S. Department of Justice and the European Commission are investigating the bromine industry for possible violations of antitrust laws since spring 1998. Great Lakes has been granted U.S. amnesty from criminal prosecution in the investigation. DSB disclosed in first quarter financial statements that it was aware of an investigation into possible antitrust infringements (McCoy, 1999).

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 98% of total elemental bromine sold or used (table 2).

Albemarle has 27 bromine production wells, 6 of which also produce oil. Brine wells are twice as big and twice as deep as typical Arkansas oil wells, and the brine that comes out exceeds 110^{N} C (230^{N} F). Albemarle reported that the 50,000 t/yr tetrabromobisphenol-A (TBBA) plant, a flame retardant marketed as SAYTEX RB-100, was operational by third quarter 1999 in Magnolia, AR. TBBA is used in epoxies, phenolic, acrylonitrile-butadiene-styrene, polystyrene, polycarbonate, and unsaturated polyesters. Bromine flame retardants are used in electronic equipment to increase the fire resistance of the plastic housings and the computer printed circuit boards. TBBA is also used in computer housings and electrical connectors and in carpet and office furniture (Warren, 2000). Albemarle entered the nonhalogenated flame-retardant business with a new phosphorus-based flame retardant to be produced in a 5,400-t/yr (12 million-pound-per-year) plant in Orangeburg, SC (Chemical & Engineering News, 1999a). According to Albemarle, end uses are as follows: gasoline additives and oilfield completion fluids, 20%; agricultural chemicals and fumigants, 22%; communications, construction, electronics, textiles application, and transportation, 28%; and halons, pharmaceuticals, photography, rubber, and water treatment, 30% (Chemical Market Reporter, 1999a). Albemarle also operates a bromine derivatives plant in France.

Great Lakes continued production of bromine from brines at four plants in Arkansas. To expand the product base, Great Lakes completed the acquisition of FMC Corp.'s process additives division (PAD) for \$162 million. PAD has 500 employees and includes manufacturing operations in Nitro, WV, and Manchester, United Kingdom (Chemical Market Reporter, 1999e). The company also owns Associated Octel Co. Ltd., a United Kingdom-based company.

TETRA Technologies, Inc. was one of the largest users of brominated products in the world. Calcium, sodium, and zinc bromide were produced for oil and gas applications. The West Memphis, AR, facility produces calcium bromide and zinc bromide using zinc-containing sludge from electroplating operations and low-cost hydrobromic acid. The company was awarded a U.S. patent on this new production process. The expanded plant became operational during the first quarter, increasing capacity and producing a high-quality product. TETRA began operation of merchant bromine, calcium bromide, and sodium bromide at the Ludington, MI, facility in mid-1998. TETRA had brine leases in Arkansas, but had not made a decision to retrofit the plant purchased from Dow Chemical Co. in 1988 or to begin virgin bromine production (TETRA Technologies, Inc., 1999).

Ambar Inc. opened a 14-Mkg (30-million-pound) elemental bromine facility in Manistee, MI, to produce elemental bromine and brominated salts on-stream early in 1999. This will be the first new elemental bromine plant constructed since the mid-1970's, when two separate plants began producing elemental bromine. The next decade brought the closure of four plants in California and Michigan as bromine use in gasoline was phased out. Ambar would be supplied by pipeline with bromine-containing brines after production of magnesium hydroxide from Martin Marietta Magnesia Specialties Inc. Ambar planned to manufacture and consume brominated well drilling fluids, but was considering selling excess elemental bromine. The plant opened, operated, and closed in 1999.

The Paris, France building where the chemist Antoine-Lauent Lavoisier discovered the element bromine was designated an International Historic Chemical Landmark. The designation was conferred jointly by the American Chemical Society and the Société Française de Chimie (Raber, 1999).

Consumption

Albemarle's fine chemicals division also includes surface actives, bromine, and oil-field chemicals. The company has manufacturing units in Thann, France, and Teesport, United Kingdom. Brominated flame retardants have caused concern in Europe because of the formation of dioxin during pyrolysis. Dioxin will not form during pyrolysis with Albemarle Corp.'s Saytex 8010 brominated flame retardant, TBBA.

The EPA's Methyl Bromide Phaseout Program stated that by 2005, those applications still using methyl bromide will do so because they have no choice. Methyl bromide is 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 has been found in material at 26 scattered warehouse and residential sites in 14 States. China may have to use over 12,500 tons of methyl bromide to treat wood destined for the United States. This represents a 75% increase in use compared with 1996 levels for all applications, including soil treatment, in Asia. The EPA figures showed that only 4,069 metric tons (t), about 6% of all methyl bromide used globally, was used to fumigate timber worldwide in 1996 (Reisch, 1998).

Pesticides, such as bromine compounds, were used to protect food from pests, such as insects, rodents, weeds, mold, and bacteria. 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. The jurisdiction of foodcontact antimicrobial shifted from the Food and Drug Administration to the EPA. The Society of Toxicology wrote that the EPA asserts that conclusions concerning the dangers of pesticides in food are not credible and are unnecessarily alarmist (Chemical Market Reporter, 1999f). The EPA sets standards on the amount of pesticides that may remain on food, if pesticides were applied. The FQPA set a tougher standard for pesticides use on food. By 2006, the EPA must review all old pesticides to make sure that their use on food meets the new safety standard. If a pesticide was authorized that does not meet the safety standard, then the EPA will work with grocery stores to inform consumers of such pesticides, foods that might contain them, and equally nutritious alternatives.

Bromine is used in the free radical polymerization of isoprene rubber. Light causes the bromine molecule to dissociate into two active bromine atoms called free radicals, because of an unpaired electron, and is therefore not used for rubber exposed to sunlight. Isoprene was used in an inner liner for tubeless tires and in tubes for tires because of its low air permeability compared with natural rubber and other synthetic rubbers. Goodyear Chemical, a division of Goodyear Tire & Rubber Co., began construction of a sixth plant in Texas to produce polyisoprene for production of tires. The annual capacity of the Beaumont facilities is planned to be more than 450,000 t (1 billion pounds) of synthetic rubber annually by August 2000. A cogeneration facility is planned with the new plant (Chemical Market Reporter, 1999c).

World Review

Publication of the International Organization for Standardization (ISO) 9000 was planned for November 2000. Bromine operations were three of more than 200,000 ISO-9000-based quality-management systems being operated worldwide to ensure their efficiency and customer requirements (International Organization for Standardization, [no date], ISO revisions, accessed July 2, 1999, at URL http://www.bsi.org.uk/ bsi/services/isorevs.htm). Information may also be obtained from ISO's national members. (International Organization for Standardization, [no date], Welcome, accessed July 2, 1999, at URL at <http://www.iso.ch/).

Canada.—Ocean Chemicals Group (OCG) entered the North American bromine market with a Burlington, Ontario-based Storchem Inc. as its exclusive distributor. Storchem will initially target the organic and inorganic bromine markets and sidestep the flame retardant market, except for specific sales requests. Storchem expected photographic chemicals and water treatment industries to make up 40% of its business. Adhesives and metal finishing should account for another 40%, with npropyl bromide growing to more than 4,500 t (10 million pounds) in the next 2 years. Flame retardants and pharmaceuticals will split the remaining 20% of demand. The company's production facilities are in China (Chemical Market Reporter, 1999d).

China.—OCG produced 50,000 t/yr of elemental bromine at facilities north of Laizhou Bay off the Bohai Sea (Chemical Market Reporter, 1999d).

DSB Group, the world's largest bromine producer, has established a new joint venture with China's largest bromine compound manufacturer, Shangdong Haihua Shareholding Co. Ltd., to manufacture and market bromine compounds in Weisang, China, near Shandong. Investment in the venture, a 50-50 split between DSB and Shandong will be around \$30 million. The new company plans to have a capacity of 16,200 t/yr to manufacture bromine flame retardants, including decabromodiphenyl oxide and five inorganic bromides, including, ammonium- and potassium bromide, and hydrobromic acid. The \$200 million Chinese bromine market is growing at 5% to 8% per year (Industrial Minerals, 1999).

European Union.—The countries of the European Union are starting to phase in the Biocidal Products Directive (BPD), a rule intended to harmonize biocide laws in the countries that have laws and implement them in those countries that do not. Registration is required of all commercial biocides including bromine compounds during the next 10 years. Of the 900 active ingredients used as biocides in Europe, only about 200 are expected to remain after BPD.

France.—Elf Atochem SA continued the switch from bromide derivatives to fine chemicals at its Port-de-Bouc plant in southeast France. The plant had been threatened with closure because 70% of plant capacity was in bromidesdibromethane and methyl bromide that will be banned after 2005 (tables 5 and 6).

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

In 1985, the Israeli Government began efforts to sell a share of Israeli Chemical Co. Ltd. (ICL) to offset an investment program. ICL was a group of chemical and mineral industrial companies, with research institutes, technical facilities, and commercial and marketing services. Israel Corp. bought an additional 17% stake in March 1997, which brought its share of ICL to 41.9%. In 1997, the Israeli Government announced a 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 (Phosphorus & Potassium, 1998).

Israel's finance ministry proposed to accelerate infrastructure projects, which included bromine expansions, throughout the country to help with high unemployment. The national unemployment rate was 8.3% in May 1998, more that 1% higher than that of 1997 (Engineering News Record, 1998). DSB announced an expansion of production capacity for bromine and bromine compounds from 200,000 to 250,000 t/yr at its Sdom plant. Bromine Compounds Ltd., a wholly owned subsidiary of DSB, increased its production capacity to 80,000 t/yr of calcium bromide at its plant at Ramat Hovay. Calcium bromide was used as a clear fluid in oil and gas wells in the completion and workover stage. DSB was a major producer of bromine and bromine compounds. The company was 90% owned by ICL. DSB, in turn, owned a number of subsidiaries, including AmeriBrom, Inc. and Eurobrom, B.V., through which it markets its bromine products (Industrial Minerals, 1998).

Japan.—Tosoh Corp. was Japan's only producer of bromine and hydrobromic acid used in the manufacturer of dyes, flame retardants, pharmaceuticals, and photosensitive materials (Tosoh, [no date], Bromines & flame retardants, accessed January 7, 2000, at URL http://www.tosoh.com/EnglishHome Page /tcdiv/tcdinbro.htm).

Jordan.—The Jordan Bromine Co. was reported to have secured a \$22 million loan from the European Investment Bank for the development of a plant to produce bromine-based products and potassium hydroxide from brines extracted from the Dead Sea. Jordan Bromine was established in May 1999 as a joint venture between Arab Potash Co. (APC) and its subsidiary, the Jordan Dead Sea Industries Co. (JODICO) and the U.S. company, Albemarle Holdings Co. Ltd. (Fertilizer International, 2000).

Albemarle finalized a joint venture with JODICO and the Kingdom of Jordan for the construction of a \$150 million bromine complex in Safi, Jordan, that includes a 50,000-t/yr bromine plant, a 30,000-t/yr calcium bromide plant, and a 50,000-t/yr TBBA plant. Construction was set to begin in the third quarter of 2000 and run through third quarter 2002, at which time the complex will begin pilot operations. Full scaleup should be achieved by the end of 2002. JODICO was established by APC as a holding company to undertake the extraction of chemicals, other than potash, from the Dead Sea. The plant will produce bromine for the merchant market, calcium bromide for oilfield completion fluid, and TBBA as a flame retardant, primarily for marketing in Europe and Asia (Chemical Market Reporter, 1999a; Reisch, 2000).

United Kingdom.—Albemarle UK Ltd., a subsidiary of Albemarle, announced the acquisition of the Teesport operation

of Hodgson Specialty Chemical Division of BTP plc for approximately \$14 million. Teesport was completed in 1991 and served as a custom manufacturing and oilfield chemicals plant. The addition of products that Teesport produced will complement Albemarle's clear completion fluids, amines, and chemicals to the oilfield services industry (McChesney and Whitlow, 1998).

After bidding against a Rhodia affiliate ISPG for Albright & Wilson (A&W), a maker of nonhalogenated flame retardants, Albemarle U.K. Holdings Ltd. will sell its remaining shares (11%) of A&W stock to ISPG PLC, a wholly owned subsidiary of Donau Chemie AG. (Chemical & Engineering News, 1999b).

Ukraine.—JSC Brom, of Krasnoperekopsk, located at the Sivash Gulf, Sea of Azov, Crimea, was reported to have 52,000 t/yr of bromine capacity (Industrial Minerals, 1998).

Current Research and Technology

The drug, pyridostigmine bromide (PB), was given to 250,000 U.S. troops during the Gulf War. According to a 2year study by the Rand Corp. and underwritten by the Pentagon, 100,000 Gulf veterans have complained of a wide range of unexplained ailments. PB is the only known antidote to Soman, a deadly gas developed by the Soviet Union. The Pentagon has called for more research on the drug (Dyhouse, 1999).

Scientists at Dartmouth College have identified two organohalogen compounds that occur naturally in seabird eggs, one of which appears to be the major compound in a group of $C_{10}H_6N_2Br_4C_{12}$ compounds. The results provide evidence that organohalogens naturally produced by many types of algae, marine bacteria, and other marine organisms bioaccumulate in higher animals. The charting of a synthetic route to produce the halogenated dimethyldipyroles will allow sufficient quantities to be produced for toxicity testing and for identification of natural product (Chemical & Engineering News, 1999f).

Harvard University reported that global climate change can exacerbate ozone depletion in the Arctic. An increase in water vapor means that polar stratospheric clouds, which provide surfaces that convert relatively inert halogen compounds, such as bromine, to active forms that catalyze ozone destruction, can form at higher temperatures. Collection of field measurements will run through March 2000 under the sponsorship of the National Aeronautics and Space Administration (NASA) and the European Commission (Chemical & Engineering News, 1999d).

NASA, Boulder, CO, and colleagues reconstructed the atmospheric histories of chloro-carbon solvents, chlorofluorocarbons, halons (including bromides), methyl bromide, CH₃Br, and sulfur hexafluoride, based on analysis of firn, consolidated snow, collected at Antarctica, Greenland, and the South Pole. The presence of methyl bromide in even the deepest samples implies that this gas has both natural and anthropogenic sources. The Antarctic samples show more of the methyl bromide at the top than at the bottom, implying that manmade sources have been augmenting major natural sources

during the recent past, while the samples from Greenland show a completely different profile–a discrepancy the researchers have not been able to explain. Concentrations of the other gases show histories back to the 19th century, indicating that there were no significant sources before those gases began to be manufactured in the middle to late 20th century (Chemical & Engineering News, 1999g).

A research team at the National Center for Scientific Research, University of Paris-South, and the Afga-Gervaert Group in Mortsel, Belgium, have used a silver bromide dopant to improve the performance of photosensitive silver halide emulsions used to make photographic films. During the conventional photographic process, photos falling on silver halide microcrystals cause the halide ions to generate pairs of electrons and positive holes. The silver ions capture the electrons and the resulting neutral silver atoms group into clusters of metallic silver that form the "latent image." This image is then developed into a visible image. The theoretical limit is one silver atom per absorbed photon. The dopant formate ions produce carbon dioxide radicals that transfer energy to silver cations. The overall process is known as photo induced bielectronic transfer because two electrons are generated. The theoretical yield for this process is two silver atoms per photon absorbed. The bielectronic nano-silver halide system leads to the highest light efficiencies ever measured. All the light energy is used to produce the latent image without fogging (Chemical & Engineering News, 2000a).

Molecular geneticists at the University of Illinois, Chicago, and their colleagues, have enabled mice to survive what would be lethal doses of gamma radiation used against cancer by using a brominated protein. By temporarily blocking a protein involved in cell response to a variety of stresses, marginally damaged cells are given a chance to recover (Chemical & Engineering News, 1999e).

Chemists at the University of Auckland, New Zealand, reported the first electrophillic aromatic substitution reaction in a metallabenzene using to form the nitro or bromo derivative to form a compound that acts like an aromatic (Chemical & Engineering News, 2000b).

Chemists at the University of Utah, Salt Lake City, UT, have made a tetrabromo material that exhibits coercivity as high as 27,000 oersteds, thus exceeding the coercivity seen in commercial samarium and neodymium-boron magnets. The coercive field needs to be large for many applications, such as magnetic memory devices. The magnets retain large amounts of magnetism in the absence of a magnetic field. The main drawback is the magnet works only below 11° K. (Chemical & Engineering News, 2000c).

Outlook

Petroleum.—Demand for bromine as a gasoline additive has declined each year since the EPA issued regulations in the 1970's to reduce and eliminate the lead in automotive gasoline. In 1979, the amount of bromine sold 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 European Community continued discussions to reduce lead

levels in gasoline. Bromine in petroleum additives was expected to continue to decline over the long term. Federal laws enacted to encourage alternative forms of power in automotive engines are likely to have a depressive effect on bromine demand. The CAA requires mobile sources, such as cars and trucks, to use the most effective technology possible to control emission. Electric cars that do not require bromine gasoline additives were on the market in California. Newer prototypes of the fuel cell that burn gasoline can double the mileage and thereby decrease emissions by using unleaded gasoline.

Sanitary Preparations.—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 amount of product. Growth areas are in the pulp and paper industry, cooling towers, and Government-regulated food-washing applications. Albemarle reported double-digit sales growth of brominated biocides as it replaced chlorine and other products in a variety of applications (McCoy, 1998). The use of bromine will continue to grow in sanitary preparation, closely following the gross national product in real growth.

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, that is, it increases the effectiveness of the fire retardant. A new nonbrominated material, a precursor to polybenzoxazole (PBO), a polyhydroxyamide, upon heating is converted to PBO, which could limit flammability. This could have a major effect negative upon the use of brominated fire retardants, especially in airplanes, prisons, submarines, and ships (Chemical & Engineering News, 1999c).

Other Uses .--- Use of calcium, sodium, and zinc bromides in well-completion fluids decreased during the 1980's as the domestic petroleum industry suffered a severe recession. In 1997, however, the oil-services sector posted another strong performance, with drilling rig counts up by 18% compared with those of 1996. Domestic demand for calcium bromide clear fluids peaked in 1997 at an estimated 104,000 t (230 million pounds), 31% of which was imported. About 95% of calcium bromide produced was used as an oil and gas completion fluid. In 1998, demand began decreasing because of a reduction in well completion activity as a result of a reduction in demand for petroleum and petrochemicals caused an economic crisis in Asia (Mannsville Chemical Products Corp., 1998). Oilfield chemicals used in drilling, completion and work over, and production operations remained significantly more profitable internationally than in the United States.

References Cited

- Chemical & Engineering News, 1999a, Business concentrates–Albemarle to enter nonhalogenated flame retardants: Chemical & Engineering News, v. 77, no. 23, June, 17, p. 12.
- ——1999b, Business concentrates–Business roundup: Chemical & Engineering News, v. 77, no. 23, June 6, p. 12.

77, no. 20, May 17, p. 6.

——1999d, Science/technology concentrates–A closer look at Arctic ozone depletion: Chemical & Engineering News, v. 77, no. 48, November 29, p. 29.

_____1999f, Science/technology concentrates–Organohalogens occur naturally in bird eggs: Chemical & Engineering News, v. 77, no. 47, November 22, p. 55.

- ——2000a, Dopant boosts AgBr emulsion photosensitivity: Chemical & Engineering News, v. 78, no. 1, January 3, p. 8.
- 2000b, Science/technology–A metallobenzene that acts like it's aromatic: Chemical & Engineering News, v. 78, no. 8, February 21, p. 29.

2000c, Science/technology–Porphyrin-based magnet has intriguing properties: Chemical & Engineering News, v. 78, no. 4, January 24, p. 32.

- Chemical Market Reporter, 1999a, Albemarle pushes ahead with multiple bromine projects: Chemical Market Reporter, v. 256, no. 6, August 9, p. 24.
- ——1999c, Goodyear breaks ground: Chemical Market Reporter, v. 255, no. 24, June 14, p. 3.
- 1999d, OCG enters the bromine market in NA and picks Storchem as its
- distributor: Chemical Market Reporter, v. 256, no. 18, November 11, p. 7. ——1999e, News capsule–Great Lakes inks purchase: Chemical Market

Reporter, v. 256, no. 6, August 9, p. 9.

_____1999f, Society of Toxicology denounces report on pesticide resides: Chemical Market Reporter, v. 255, no. 13, March 29, p. 20.

Chemistry International, 1999, Other societies and unions: Chemistry International, v. 21, no. 1, January, p. 12-13.

- Dyhouse, Tim, 1999, Service-drug could be cause of gulf illness: Washingtonwire Veterans of Foreign War, v. 87, no. 4, December, p. 10.
- Engineering News Record, 1998, Infrastructure–Israel eyes boost to cut jobless: Engineering News Record, May 11, p. 21.
- Fertilizer International, 2000, Bromine progress: Fertilizer International, no. 374, January-February, p. 19.
- Industrial Minerals, 1998, Ukraine Minerals: Industrial Minerals, no. 373, October, p. 41.
- Johnson, Jeff, 1999, TRI emissions linked to population, toxicity: Chemical & Engineering News, v. 77, no. 30, December 7, p. 11.

McCoy, Michael, 1998, Biocides succeed despite regulations: Chemical & Engineering News, v. 76, no. 46, November 9, p. 21-39.

- McChesney, John, and Whitlow, Michael, 1998, Albemarle UK Ltd. acquires Teesport, United Kingdom manufacturing: Richmond, VA, PRNewswire, November 2, 1998, 1 p.
- Mannsville Chemical Products Corp., 1998, Calcium bromide: Chemical Products Synopsis, November, 2 p.
- Morse, Paige, 1998, Methyl bromide gets new lease on life–And new pest to fight: Chemical & Engineering News, v. 76, no. 43, October 26, p. 9-10.
- Phosphorus & Potassium, 1998, Israeli government to divest remaining stake in ICL: Phosphorus & Potassium, no. 314, March-April, p. 10.
- Raber, Linda, 1999, Revolution in chemistry: Chemical & Engineering News, v. 77, no. 26, June 28, p. 74 and 75.

Reisch, Marc, 1998, Methyl bromide alternatives pose challenges to producers: Chemical & Engineering News, v. 76, no. 45 November 9, 46 p. 2000, Albemarla sizes up opportunities: Chemical & Engineering News

——2000, Albemarle sizes up opportunities: Chemical & Engineering News, v. 78, no. 4, January 24, p. 21-22.

- TETRA Technologies, Inc., 2000, TETRA Technologies, Inc–1999 annual report: TETRA Technologies, Inc., 50 p.
- U.S. Environmental Protection Agency, 1998, National Advisory Committee for acute exposure guideline levels for hazardous substances: Federal Register, v. 65, no. 339, February 19, p. 8450-8451.
- U.S. Department of Transportation, 1998a, Research and special program administration: Federal Register, v. 63, no. 159, August 18, p. 44322-44344.
 ——1998b, Research and special program administration: Federal Register, v. 63, no. 210, October 30, p. 58459-58521.
- Warren, Susan, 2000, A new bromide–Brine is much better than oil in Arkansas: Wall Street Journal, v. 235, February 14, p. A1 and A14.

GENERAL SOURCES OF INFORMATION

^{——1999}c, Letters-fire-resistant polymers: Chemical & Engineering News, v.

U.S. Geological Survey Publications

Bromine. Ch. in Mineral Commodity Summaries, annual.¹

Bromine. Ch. in Minerals Yearbook, annual.¹

Evaporites and brines. Ch. in United States Mineral Resources, Professional Paper 820, 1973.

Other

¹Prior to January 1996, published by the U.S. Bureau of Mines.

Bromine. Ch. in Mineral Facts and Problems, U.S. Bureau of Mines Bulletin 675, 1985.

TABLE 1 SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS 1/

(Thousand kilograms and thousand dollars)

	HTSUS 2/ number	1995	1996	1997	1998	1999
United States:	number	1995	1990	1997	1998	1999
Bromine sold or used: 3/	-					
Quantity	-	218,000	227,000	247,000	230,000	239,000
Value		\$186,000	\$150,000	\$111,000	\$162,000	\$201,000
Exports: 4/ 5/		\$100,000	\$150,000	<i></i>	\$102,000	\$201,000
Elemental bromine:	2801.30.2000					
Quantity	2001.0012000	3,220	2,920	2,330	1,490	2,110
Value		\$3,790	\$3,970	\$3,590	\$3,440	\$2,429
Bromine compounds: 6/	(7/)	45,170	\$3,770	\$3,370	45,110	φ2,12>
Gross weight	(///	13,300	13,100	10,700	10,200	9,515
Contained bromine		11,200	11,100	9,050	8,550	8,019
Value		\$19,900	\$22,100	\$21,200	\$18,000	\$15,962
Imports: 4/ 8/		<i>Q</i> 17,700	<i><i><i>q</i>==,100</i></i>	<i>Q21,200</i>	\$10,000	\$10,902
Elemental bromine:	2801.30.2000					
Quantity		2,220	415	1,650	1,200	1,972
Value		\$1,460	\$305	\$1,200	\$1,060	\$2,113
Bromine compounds:		+-,	+++++	+-,	+-,	+_,
Ammonium bromide:	2827.59.2500					
Gross weight		288 9/	11,700 10/	33,000 10/	471 9/	1,514 9
Contained bromine		235 9/	9,370 10/	2.690 10/	384	1,235
Value		\$832 e/ 9/	\$9,580 10/	\$22,000 10/	\$1,280 e/	\$1,938
Calcium bromide:	2827.59.2500		1	1 ,	. ,	
Gross weight		730 9/		803 9/	350 9/	
Contained bromine		584 9/		642	280	
Value		\$262 e/ 9/		\$289	\$213 e/	
Potassium bromate:	2829.90.0500					
Gross weight		275	301 9/	378 9/	141	373
Contained bromine		132	144 9/	181	67	178
Value		\$933	\$1,140 9/	\$1,650 r/	\$571	\$1,473
Potassium bromide:	2827.51.0000 11/		· · ·			
Gross weight		171 9/	733 9/	705 9/	910 9/	1,171
Contained bromine		115 9/	493	474	611	786
Value		\$420 e/ 9/	\$1,780	\$1,710	\$2,220 e/	\$2,834 e
Sodium bromate:	2829.90.2500					
Gross weight		944	1,200	1,220	1,100	1,047
Contained bromine		500	634	646	584	554
Value		\$2,360	\$3,030	\$3,170	\$2,900	\$2,427 e
Sodium bromide:	2827.51.0000 11/					
Gross weight		1,400 9/	1,240 9/	2,730 9/	3,960 9/	4,635 9
Contained bromine		1,070 9/	965	2,120	3,070	3,600
Value		\$2,550 9/	\$1,910	\$4,210	\$6,090 e/	\$5,544 e
Other compounds:	2903.30.1550					
Gross weight		5,850 12/	6,520	8,910	8,990	7,400
Contained bromine		4,880 12/	5,090	6,900	6,770	785
Value		NA	\$14,900	\$16,700	\$18,900	\$17,000
World, production e/		432,000 r/	483,000	542,000 r/	514,000	526,000

e/ Estimated. r/ Revised. NA Not available. -- 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/ Bureau of the Census.

5/ Export values are "free-alongside-ship" (f.a.s.).

6/ Bureau of the Census. Includes methyl bromine and ethylene dibromide.

7/ Data for these compounds are derived from HTSUS numbers 2903.30.0500 and 2903.30.1500 information.

8/ Import values are "Cost, insurance, and freight" (c.i.f.).

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

10/ The respective data for "bromides/bromines and oxides" of ammonium, calcium and zinc are combined and reported here; imports for 1996 included 568 thousand kilograms and imports for 1997 included 83 thousand kilograms of zinc bromide.

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

12/ Certain compounds reported for 1995 are not included in the total.

TABLE 2

ELEMENTAL BROMINE-PRODUCING PLANTS IN THE UNITED STATES, 1999

			Production	Capacity 1/ (million	
State and company	County	Plant	source	kilograms)	
Arkansas:					
Albemarle Corp.	Columbia	Magnolia (a)	Well brines		
Do.	do.	Magnolia (b)	do.	140 2/	
Great Lakes Chemical Corp.	Union	Newell	do.	25	
Do.	do.	Catesville	do.		
Do.	do.	El Dorado	do.	93 2/	
Do.	do.	Marysville	do.	59	
Michigan:					
The Dow Chemical Co.	Mason	Ludington 3/	do.	20	
Total 4/				337	

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.

4/ Chemical Marketing Reporter, v. 251, no. 13, p. 37.

TABLE 3 YEAREND 1999 PRICES FOR ELEMENTAL BROMINE AND SELECTED COMPOUNDS

	Val	Value		
	(cen	(cents)		
Product	Per pound	Per kilogram		
Bromine:				
Drums, truckloads, works 1/	123	271		
Bulk, tank cars, works 1/	56-68	123-150		
Bromochloromethane, drums, bulk, f.o.b. Magnolia, AR	127	280		
Ethyl bromide, technical, 98%, drums, truckloads	127	280		
Ethylene dibromide, drums, carloads	95	209		
Hydrobromic acid, 48%, drums, carloads, truckloads, f.o.b.	56	123		
Hydrogen bromide, anhydrous, cylinders, 2,500 pounds, truckloads	475	1,047		
Methyl bromide, tank cars	77	170		
Potassium bromate, granular, powdered, 200-pound drums, carloads, f.o.b. works	179	395		
Potassium bromide, N.F., granular, drums, carloads, f.o.b. works	110-112	242-247		
Sodium bromide, technical, truckloads	70	154		

1/ Delivered prices for drums and bulk shipped west of the Rocky Mountains, 1 cent per pound higher. Bulk truck prices 1 to 2 cents higher per pound for 30,000-pound minimum.

Source: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials, v. 256, no. 26, December 27, 1999 p. 19-24.

U.S. IMPORTS OF OTHER BROMINE COMPOUNDS 1/ 2/									
		1998		1999					
	HTSUS 3/	Gross weight	Value 4/	Gross weight	Value 4/				
Compounds	Number	(kilograms)	(thousands)	(kilograms)	(thousands)	Principal sources, 1999			
Hydrobromic acid	2811.19.3000	257	\$263	250	\$285	Israel 100%.			
Ethylene dibromide	2903.30.0500	170	418	506	553	United Kingdom 100%.			
Methyl bromide	2903.30.1520	3,740	6,820	2,300	5,000	Israel 100%.			
Dibromoneopentyl glycol	2905.50.3000	1,110	3,620	1,470	4,890	Do.			
Tetrabromobisphenol A	2908.10.2500	1,490	2,690	752	1,380	Do.			
Decabromodiphenyl oxide and									
octabromodiphenyl oxide	2909.30.0700	2,220	5,100	2,120	4,920	Do.			
Total		8,990	18,900	7,400	17,000				

TABLE 4 U.S. IMPORTS OF OTHER BROMINE COMPOUNDS 1/2/

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: Bureau of the Census.

TABLE 5

WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES, DECEMBER 31, 1999 1/

		<i>a</i> .	
		Capacity	
	т.,:	(thousand	c
Country and company	Location	kilograms)	Source
Azerbaijan:			
Neftechala Bromine Plant	Baku	5,000	Underground brines.
China:			
Laizhou Bromine Works	Shandong	30,000	Do.
France:			
Atochem	Port-de-Bouc	13,600	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse	2,300	Bitterns of mined potash.
India:			
Hindustan Salts Ltd.	Jaipur		Seawater bitterns from salt
Mettur Chemicals	Mettur Dam	1,500	production.
Tata Chemicals	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:			1
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 canacity. See table 2)		

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

TABLE 6 BROMINE: ESTIMATED WORLD REFINERY PRODUCTION, BY COUNTRY 1/ 2/

(Thousand kilograms)

Country 3/	1995	1996	1997	1998	1999
Azerbaijan	2,000	2,000	2,000	2,000	2,000
China	32,700	41,400	50,100 r/	40,000	45,000
France	2,260	2,024 4/	1,974 r/4/	1,950 r/4/	2,000
India	1,500	1,500	1,500	1,500	1,500
Israel	130,000 r/	160,000	180,000	185,000	185,000
Italy	300	300	300	300	300
Japan	15,000	15,000	20,000	20,000	20,000
Spain	200	100	100	100	100
Turkmenistan	100	102 4/	130 4/	150	150
Ukraine	3,500	3,000	3,000	3,000	3,000
United Kingdom	26,200 4/	30,600 4/	35,600 r/4/	30,000	28,000
United States 5/	218,000 4/	227,000 4/	247,000 4/	230,000 4/	239,000 4/
Total	432,000 r/	483,000	542,000 r/	514,000	526,000

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 20, 2000.

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.