BROMINE

By Phyllis A. Lyday

International distribution of bromine production in 1994 was as follows: The United States, 47%; Israel, 33%; the United Kingdom, 7%; and other countries, 13%. The U.S. portion of world production has decreased steadily since 1973, when the United States produced 71% of the world supply. The decrease in world share has been a result of environmental constraints and the emergence of Israel as the world's second largest producer. Domestic capacity decreased 14% during the same period. The quantity of bromine sold or used in the United States was 195 million kilograms (kg) valued at $155 million. The value of bromine sold or used was $0.80 cents per kg. Primary uses of bromine compounds were in flame retardants (47%), agriculture (18%), water treatment and sanitizing (6%), petroleum additives (6%), well drilling fluids (5%), and other (18%).[1]

Legislation and Government Programs

The Environment Protection Agency (EPA) began its first study of organobromine (OB) chemicals in 1984, when ethylene dibromide (EDB) was the most important product of the OB industry. EDB was used with tetraethyl lead in additives designed to increase the octane rating of gasoline. Other industry products included methyl bromide, used as a soil fumigant, and brominated fluorocarbons, which were sold mainly as fire-extinguishing agents. During the decade that has elapsed, the product mix has changed, due primarily to several environmental regulatory programs. The phaseout of leaded gasoline is almost complete. The use of methyl bromides has been restricted, and two of the important fire extinguishing compounds are being phased out under the terms of the Montreal Protocol on Substances that Deplete the ozone layer, to which the United States is a signatory. Most OB chemicals are sold as flame retardants that are incorporated into polymer mixes. Smaller bromine-producing firms manage all their solid waste as hazardous and ship it off site to incinerators or landfills operating under authority of RCRA Subtitle C. Because bromine is an element and cannot be destroyed by chemical transformations, the production processes at the major facilities are designed to make the most effective use of all bromine extracted from the brine. As a result, there are many bromine recovery processes built into each operation. EPA proposed in the May 11, 1994, Federal Register to list one stream as hazardous wastes under Subtitle C of RCRA.

EPA added 286 chemicals to the Toxic Release Inventory (TRI) to bring the total added to 654 chemicals. Most of the 286 chemicals added to the TRI list are pesticides, such as alachlor, aldicarb, benomyl, bromine, carboduran, diazinon, malathion and simazine. EPA said that it may expand the scope of facilities that must report to include dealers and mining.[2] EPA did not list nine other waste streams and deferred action on one waste stream.

EPA proposed the Federal Register on January 12, 1994, to add 313 chemicals and chemical categories to the list of toxic chemicals required to be reported under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 and section 6607 of the Pollution Prevention Act of 1990. EPA believes that these chemicals and chemical categories meet the criteria of acute human health effects, carcinogenicity or other chronic human health effects, and/or their environmental effects for addition to the list of toxic chemicals. Included on the list was bromine and seven other brominated compounds. Under Section 304(b) of the Emergency Planning and Community Right-to-Know Act (EPCRA) immediate notification must be given the EPA within 15 minutes after having knowledge of the spill or leak.[3]

The Toxic Substance Control Act (TSCA) requires manufacturers and importers to report specified data on certain substances on a 4-year cycle. The Federal Register on June 14, 1994, p. 30652 reported that the period was August 25 through December 23, 1994. Reported information includes: Chemical Name and Chemical Abstracts Service (CAS) Registry number; name and address of each site at which 4,536 kg (10,000 pounds) or more is manufactured or imported; a statement of whether the substance is manufactured and processed only within the site, and the total volume (in pounds).

The EPA finalized a baseline production and consumption allowance for methyl bromide and hydrobromofluorocarbon (HBFC) (22B1-1). Methyl bromide production is frozen at 1991 levels until the fumigant is banned in 2001. HBFC production is frozen at 1991 levels until phaseout at the beginning of 1996. Great Lakes Chemical Corp. is limited to 19,945,788 kg of production and 15,414,746 kg for consumption of methyl bromide. Albemarle Corp.'s yearly baseline for production is 8,233,894 kg and consumption was 6,379,906 kg for methyl bromide. AmeriBrom Inc. baseline production is 3,524,393 kg and consumption is 4,535 kg for methyl bromide. Great Lakes is limited to 45,211 kg for production and 40,110 kg for consumption.[4] Under the Clean Air Act, methyl bromide production must be phased out by January 2001. Methyl bromide is a coproduct of tetrabromobisphenol A production. U.S. farmers used about 19,700 tons (43.5 million pounds) of methyl bromide.[5]

The Interagency Testing Committee (ITC) established under section 4(e) of TSCA revised the Priority Testing List by removing two chemicals and four chemical groups from the list for priority consideration by the EPA Administrator. The chemicals being removed included brominated flame retardants (23 chemicals). The report says that removal of these chemicals and chemical groups from the list should be interpreted only as a reordering of priorities, and not a statement that the testing recommended earlier has been completed or is not needed.[6]

The U.S. Department of Agriculture (USDA) published Agricultural Economic Report Number 877 on the "Economic Effects of Banning Methyl Bromide for Soil Fumigation." Methyl bromide has been used since the 1930's as a soil fumigant to control pests and protect stored commodities. The methyl bromide ban is limited to 21 crops produced in 5 States. The crops studied include 10 fruit and nut crops, 8 vegetable and specialty crops, and 3 miscellaneous crops. The economic effects derived were based on 1991-92 crop year estimates of available alternatives, treated acres, and production losses that could change with atypical changes in weather, pest population outbreaks, loss of available alternatives, or new nonchemical and chemical pest control strategies. An estimated 29,000 tons (64 million pounds) of methyl bromide were used in 1990 in the United States. The estimated production costs and prices effects

assume that growers will use alternative chemical fumigants that cost more for some crops, and that these alternatives are generally less effective. Based on discussions with commodity experts in USDA's Economic Research Service, it was assumed that 70% of tomato, 90% of tobacco, and 15% of strawberry production losses would be replaced by imports.

A reauthorization of the Hazardous Material Transportation Act of 1990, which regulates bromine transportation, was approved by Congress and signed into law August 26. The bill contains a compromise measure that gives the Department of Transportation the discretion to decide whether to provide $1 million in grants for a study demonstrating the feasibility of establishing and operating a computerized telecommunications emergency response information system.[7]

Production

Domestic production data for bromine were developed by the U.S. Bureau of Mines from a voluntary survey of U.S. operations. Of the all operations to which a survey request was sent, six responded, representing 100% of total elemental bromine sold or used. *(See table 1 and 2.)*

Ethyl Corp. and Great Lakes produced and marketed bromine chemicals from plants in Arkansas. Small amounts of unpurified bromine were produced in Michigan as a byproduct in the extraction of magnesium from brine and reprocessed for consumption in Arkansas. The Arkansas plants accounted for 94% of U.S. elemental bromine capacity at yearend 1994 and 100% of bromine sold or used.

In February, Ethyl spun-off bromine chemicals into one of three global chemical businesses and named the new company Albemarle Corp. The name dates back to the roots of the company as Albemarle Paper founded in 1887. Albemarle's 1993 sales were $903 million including bromine chemicals, olefins, and derivatives. At the time of the spinoff, the company employed 3,800 workers in the United States, Belgium and France. In 1993, the company acquired Potasse et Produits Chimique (PPC) a maker of inorganic bromine compounds from Rhône-Poulenc S.A.[8] At PPC the main products are synthesized organobromine intermediates and organic bromine compounds. PPC's purchase boosted bromine division sales by 50%.[9] In March, Albemarle began startup of the new flame retardant facilities. The new facility at Magnolia, AR, was part of a $20 million project to add capacity in fire retardants.[10] The flame retardant is used in expandable polystyrene, foamed polystyrene, high-impact polystyrene, adhesives, and coatings.[11]

Albemarle formed a new water treatment chemical business for marketing sodium bromine. Sodium bromide 40 and 45 are registered by EPA for use as a disinfectant, fungicide, algicide, and molluscicide in water treatment. Sodium bromide 40 and 45 inhibit corrosion and are compatible with most construction materials. The products are clear, nonflammable liquids that are used in power generation facilities, refineries, industrial chemical plants, and pulp and paper mills. Bromine is three times more effective than chlorine in controlling algae in cooling towers.[12]

Great Lakes restructured into six autonomous business units during 1994. Bromine is a major raw material in five of the six.[13] Great Lakes was spending an estimated $40 million to upgrade its elemental bromine capacity domestically and in Europe. The move was tied to a related $60 million outlay in flame retardant products. The company had about 106,600 tons (235 million pounds) per year of capacity in 1992, representing 20% of the world's supply.[14]

Great Lakes and Albermerle use Bromine Recovery Unites (BRUs) to recover bromine values from organic liquid and vapor waste streams. In these units, organics are burned and the combustion products are removed by a wet scrubber. The BRUs are halogen acid furnaces (HAFs), which meet the regulatory definition of industrial furnace in 40 CFR 260.10.

The process for converting bromide brines to bromine requires that the brine be acidified and chlorinated. This reaction generates sodium chloride, which remains in the brine. Most organobromine chemicals are produced by simple one- or two-step reactions of bromine with an organic feedstock. Many of these reactions liberate hydrogen bromide gas, which is normally scrubbed by a sodium hydroxide solution, forming a sodium bromide stream that is recycled to the bromine plant. The gas is scrubbed with a lime suspension to produce calcium bromide, a salable byproduct.[15]

Consumption

SRI International estimated 1994 U.S. end uses markets for bromine as follows: Flame retardants, 47.6%; agriculture chemicals, 17.8%; other uses, 17.8%; gasoline additive, 6.0%; biocides, 6.0%; and drilling fluids 5.3%. The growth of two major brominated flame retardants was expected to grow at 5%-6% per year. U.S. bromine compound imports reached 14,000 metric tons (30.8 million pounds); exports were 25,000 tons (55 million pounds).[16]

Great Lakes completed the purchase of E.I. du Pont de Nemours & Co.'s petroleum additives business for $41 million plus purchase of inventory. Under the purchase, Octel America Inc., a wholly owned subsidiary of Great Lakes, acquired the non-TEL side of the business, which consists of numerous additives that improve the performance of fuels, lube oils, and greases. Associated Octel is a majority-owned subsidiary of Great Lakes.

Great Lakes purchased a fine chemicals subsidiary named EniChem Synthesis (Milan, Italy). The polymer additives and related specialty chemicals business was priced at about $90 million. Production is carried out in Pedrengo and Ravenna, Italy.[17]

Tetrabromobisphenol oxide (TBBA), a specialty flame retardant, was estimated to have a world capacity of 80,000 metric tons per year.[18] Albemarle increased capacity by 50% to make TBBA at Magnolia, AR. The company has increased capacity twice in the last 2 years.[19]

Water Management Inc., Electrocatalytic Inc.'s newly formed water treatment firm, will supply electrochemical bromination systems. The organization will supply on-site manufacture of bromine-based biocides for use in cooling water towers and other applications regarding biological control and disinfection.[20]

The major halons used for fire suppression are halon 1301 and 1211. In the stratosphere, these compounds change to form bromine radicals. Although the concentration of bromine in the stratosphere is low, bromine has a more significant impact on the stratospheric balance. The Armed Forces uses halon for fire extinguishment and explosion suppression in helicopters, fixed-wing aircraft, ships, maritime craft, ground armored vehicles, and other applications. Halons are used in commercial applications to protect valuable electronics, in oil and gas production, and on civilian aircraft. There is an urgency to find suitable halon replacements. Halon alternatives are nonhalocarbon substitutes that include water sprinklers, dry chemical extinguishants, carbon dioxide, misting systems, particulate aerosols, and inert gas blends. Halon replacement should have low toxicity, cleanliness, low global environmental impact, and effectiveness as a fire extinguisher. The Department of Defense plans to have the alternatives identified by October and in place by September 30, 1995.[21]

Foreign Trade

The chemical industry was in favor of the General Agreement on Tariffs & Trade (GATT) that was signed by more than 117 nations on December 15, 1993. Congress passed the GATT in December 1994, which will take

effect January 1, 1995. The Uruguay Round GATT agreement concluded after 7 years of negotiations will lower chemical tariffs by an average of 30%. The agreement's intellectual property provisions include greater patent protection for products developed by American firms. GATT changes patent enforcement from 17 years from the date of issue to 20 years from the date of application. Patents issued on applications filed before June 8, 1995, will be enforceable for either 17 years form the issue date or 20 years from the filing date, whichever is longer. Companies believe that trade disputes will be more effectively settled through the World Trade Organization. Chemicals, including bromine, are the nation's largest export commodity, as more than 10 cents out of every export dollar is a product of the chemical industry.[22] [23]

Bulk purified (99.95%) bromine was reported CIF main European port at $0.53-0.55.[24] *(See tables 3 and 4.)*

World Review

China.—Joint ventures were sought in several bromine compounds plants in the Shouguang Province by Weifang Salt & Chemical Industry Group General Corp. The State-owned enterprise is the largest base for the production of salt and salt chemicals in China. Projects are to include technology and equipment. Project No. 7 is a 1,000-ton-per-year decabromodiphenol oxide project of the Shouguang Salt Industrial Co. that would consist of 6,000 tons per year of bromine from 2.26 million tons per year of salt. The products were intended for sale in China. Project No. 26 would produce lithium bromide at the Shouguang Salt Chemical Industrial Factory that presently produces sodium and ammonia bromide. Project No. 29 is with the Shouguang Chahe Saltworks and would produce 300 tons of lithium bromide as a byproduct; present production is 460,000 tons of salt, 1,500 tons of bromine, and 100 tons per year of bromate per year. The bromate has been sold on the international market. Project No. 32 is with Shouguang Chahe Saltworks and would produce hydrobromic acid as a byproduct of the present production of 460,000 tons of salt, 1,500 tons of bromine, and 100 tons of bromate per year. *(See table 6.)*

Weifang City is situated in the middle of Shandong Province and Peninsula and has been qualified by the Government of China as a "key" city with the capacity of conducting its own business with the world. The Jiaoji railway traverses the east and west and radiates in all directions. The leading industries are light-industry, textiles, electronics, machinery, chemical, and building materials. More than 400 projects introduced or run by foreign investment have been approved by the local government, with nearly 120 joint-venture, cooperative, and solely foreign-investment enterprises.[25]

The proposed potash joint venture between China and Israel was delayed when the Chinese encountered problems in obtaining credit terms.

The Eisenberg group was responsible for raising the necessary finance. The 800,000 to 1 million-tons-per-year potash mine in Qinghai is expected to cost $480 million. The Qinghai potash lakes are reported to contain high concentration of bromine. The joint venture is between The Eisenberg Group (16.4%) and Dead Sea Works (DSW) (16.5%) Sinochem, and the Chinese Government and the province of Qinghai.[26]

Europe.—Members of the European Parliament have approved a proposal to ban the production and use of the fumigant methyl bromide by the year 2000. International agreements on methyl bromide call for a production freeze only.[27]

France.—France's sole producer of Potash at Mines de Potasse d'Alsac, part of State-owned chemicals group Entreprise Miniere et Chimique (EMC) operated two underground mines near Mulhouse in eastern France. During 1993, output at the Amelie Mine in Wittelshein for potash amounted to 890,000 tons of potassium oxide and 2,287 tons of bromine.[28] Mines de Potasse d'Alsace will phase out all the government operation by 2004. Marketing is through the trading subsidiary Socíeté Commerciale de Potasse et d'Azote.[29]

Germany.—Bromine is produced from the waste bittern of potash production in Germany. German potash and salt producers Kali und Salz AG (K:S), based in Kassel, and Mitteldeutsche Kali AG (MdK), based in Sondershausen, formed Kali und Salz GmbH in 1993. The merger was seen as a means of achieving lower unit costs and increasing their competitiveness by merging the entire German potash industry under one company. The Bischofferode Mine, located in Thuringia, received a stay from closing. The 600,000-ton-per-year mine planned to operate at a much reduced level of production and guaranteed employment for the workers until the end of 1995.[30]

Bischofferode was transferred to MdK for a promised (DM1.3 billion). The joint- venture company was formed as Mitteldeutsche Kali by Kali und Salz and Treuhandanstalt. Kali und Salz will own 51% and manage the company.[31]

A temporary suspension of the merger between German potash producers MdK and K&S was obtained by French potash producer Socíeté Commerciale de Potasse et de l'Azote (SCPA). K&S and the joint venture formed between it and MDK must withdrawn from Vienna-based marketing organization Kali-Export GmbH, before the M&S-MdK merger can proceed.

Israel.—Bromine has been produced as a byproduct from waste bitterns associated with potash production from the Dead Sea since 1957. After potash is removed in solar ponds, the waste bitterns are processed with chlorine to recover bromine. The bromine-free bitterns are then processed to recover magnesium.

The Government began efforts in 1985 to sell a share of Israeli Chemical Co. Ltd. (ICL) to offset an investment program. ICL planned to split Dead Sea Bromine (DSB) from DSW. Much of the organic and inorganic chemical activity takes place within the framework of the massive ICL, which in 1986 was composed of 28 companies with a work force of 7,000. Formal bids were accepted in 1990, but a number of Government representatives favored a public sale rather than sale to a foreign investor. In 1991, privatization terms for ICL were approved, and ultimately 25% of ICL was sold by 1993. On October 11, the Israeli government published a tender for the sale of 25% of ICL to a single investor or group of investors. Israel Corp., (IC) Tel Aviv, is buying a 24.9% share of the ICL. IC will pay $230 million for the ICL stake. The sale will be concluded in February 195. The family of Israeli businessman Shoul Eisenberg controls 50% of the IC and 50% by an offshore corporation he also controls. Another 22% will be sold in an international offering in March or April 1995.[32] The Government will continue to hold a 27.1% share after completion of the international offering.[33]

The Knesset approved the Dead Sea Mineral Rights Law Interim Amendment November 10, 1993, clearing the way for DSW to proceed with expansion projects already under way. Unlike companies in the United States, all production is exported.[34] DSB has two production plants at Sdom and Ramat Hovav.[35] DSB announced plans to implement a $500 million expansion over the next 5 years that will increase bromine production to 200,000 tons per year. Part of the expansion effort involves construction of a salt refinery at Sdom that will use solar salt to produce electrolysis-grade salt.[36] Present salt production is used to produce chlorine, which is vital to the bromine process. Another $525 million project allocates $350 million for magnesium plant and expansion of bromine compounds production. A 50-50 joint venture between Great Lakes and DSB to build a $22 million flame retardant plant at Ramat Hovav was approved by Israel's Ministerial Economic Committee. The 25,000-

ton-per-year unit will come on-stream in 1996 and reach capacity by 1998. Each partner will market product separately.[37] DSB announced plans in 1994 to construct a $11.4 million bromine plant at Sdom. The plant is due on-stream by the last quarter of 1995 and is projected to increase capacity from 140,000 tons per year to 180,000 tons per year.[38 39] DSB a subsidiary of ICL, planned to build a fine chemicals plant. A broader partnership is being considered by the parent company for the project.[40]

Japan.—At yearend 1994, Japan agreed to drop import tariffs on five brominated compounds. The tariffs on the compounds would decrease from 4.6% to zero by April 1995.

Jordan.—Jordan is the only developing country producing potash. Arab Potash Co. Ltd. (APC) and Albemarle were negotiating to form a joint-venture company to produce bromine; ownership of the company was expected to be distributed 51% and 49%, respectively. Albemarle has operations in Houston, TX, Magnolia, AR, and Orangeburg, SC, in the United States and overseas operations at Feluy, Belgium and Thann, France.[41]

APC is planning several diversification projects for the brines of the Dead Sea. The proposed projects are for the production of bromine and bromine derivatives, industrial and table salt, and magnesium oxide. Waste brines from the potash production would be used to process bromine and magnesium chloride. The diversification hopes to attract foreign participation from companies with technical and marketing knowledge. The project will be implemented by a holding company formed by a consortium of local businesses including: APC, The Jordan Investment Corp., the Social Security Corp., Jordan Phosphate Mines Co., and the Jordanian private sector.[42] The new company is called the Jordan Industrial Chemicals of the Dead Sea Minerals Co. The decision to form the company follows a memorandum of understanding with Albemarle for construction of a 50,000-ton-per-year plant. The investment in the plant would be $145 million, and the plants are to be operational by 1997.[43]

Russia.—A large deposit of bischofite was discovered in the 1960's while exploring for oil in the territory of Lower Povolzhie, Volgograd, region in middle permian strata. The bromine existed with magnesium chloride in large concentrations. A cubic meter of the bishofite brine has a concentration of 1.4 grams per cubic centimeter of bishofite contains approximately 107 kg of metallic magnesium and 6 to 9 kilograms of bromine. Geophysical drilling of 300 wells identified reserves between 150 and 500 billion cubic meters of bischofite. The deposit is estimated to contain total resources of 345 million tons of bromide salts and 160 million tons of magnesium chloride. The salt occurs between 1,200 and 1,800 meters in strata between 20 and 70 meters thick. The uniqueness of the deposit in thickness and concentration would allow for solution mining with minimum environmental detriment to the ecology. The State-owned company, Kaustic A/O, presently operating the mine and facilities produces 3,000 tons per year of bromine (99%) and 100,000 tons per year of magnesium oxide (98%). The company is seeking joint-venture investors to expand the production.[44]

The business climate for development in oil and gas has improved as a result of privatization. Before oil and gas or mineral development, the country will need to obtain new technology and improvements to the existing infrastructure. In the near term, foreign investors will face expensive and time-consuming procedures for mining and exporting mineral resources. Mining will be subject to royalties and taxes and sometimes export duties and currency conversion requirements (up to 50%). The basic framework for acquiring the legal right to use and development mineral resources are the Law on Mineral Resources (1992) and the Regulation on Procedures for licensing the Use of Mineral Resources (1992). Actual ownership of mineral resources remains with the State. Under the new Constitution ratified in 1993, Russian citizens and private domestic enterprises should eventually be able to own land and mineral resources. The distinction between common and scarce minerals is significant in terms of jurisdiction, export restriction, and the amount and apportionment of fees and royalties, there is no formal designation of which resources or common or scarce.

Under the Law of Foreign Investment, enterprises with more than 30% foreign investment, which export its own products, are fully exempt from quota limits, export duties, and licensing requirements. Since August 1993, enterprises with more than 30% foreign investment can apply to the foreign trade association for certificates for exemption from quotas and licensing.[45]

United Kingdom.—Great Lakes' affiliate, Associated Octel, was renovating and repacking a blowing out tower used for extracting bromine from seawater at the Anglesey site.[46] Octel signed a long-term agreement to supply Ethyl's requirement for lead antiknock compounds, effectively making Octel the world's only producer of tetraethyl lead (TEL). Octel also signed an agreement to supply antiknock compound to E. I. du Pont de Nemours & Co. (Dupont) for the Mexico market. Octel's three facilities in Paimboeuf, France; Bussi, Italy; and Ellsmere Port, United Kingdom, will become the only significant sources of TEL in the world. In the United States, Dupont ended TEL production at its Deepwater, NJ, plant in 1991. Dupont closed its operation in Mexico in November 1992. PPG Industries Inc., Pittsburgh, PA, closed its U.S. Beaumont, TX, facility in 1983, and Nalco Chemical Co. closed its Freeport, TX, facility in 1985. Ethyl closed a plant in Baton Rouge, LA, in 1985 and another in Pasadena, TX, in 1980.[47]

Great Lakes (U.S.) purchased Dupont's North and South American TEL petroleum additives business through Associated Octel Co. Ltd., a wholly owned subsidiary. This purchase will almost double Octel's current production of petroleum additives.

Under the Montreal Protocol, production of halons ceases at the end of this year, except those uses deemed essential by all parties to the protocol. The United Kingdom listed six uses on the list covering halons 1211 and 1301 in aircraft, airport vehicles, offshore oil and gas installations, and certain train engine rooms. The essential uses must be agreed upon by the end of 1994.[48]

Current Research and Technology

Researchers at the National Institute of Technology have recommended several chemicals as replacements for Halon 1301, a fire-fighting agent used aboard aircraft. The agent is being phased out because of its ozone-destroying properties. The U.S. Air Force is testing possible replacements and plans to install new fire-fighting agents in its fleet in 1996.[49]

Regulations and economics have increased the use of techniques to control volatile organic compounds (VOC), such as waste steams with methyl bromide. Recuperative thermal processes transfer the heat of combustion to another air stream via heat exchange. The hot air produced from the process can be used for other processes therefore lowering energy costs.[50]

Oxidation Reduction Potential (ORP) is a useful process that is often misunderstood. Typical oxides include bromine. Oxidizer chemicals have the ability to donate electrons and the greater the rate of donation, the faster is the rate of reaction.[51] Bromine can be substituted for other oxidizer to increase the rate of reaction.

An acetylene based resin shows promise for replacing thermosets such as epoxies and polyimides, especially in electronics uses.

Using propargyl bromide, bisphenol A, and potassium carbonate in acetone under reflux for 3 days, a resin with good resistance to moisture at high temperature was produced. The monomer is a crystalline solid that can be purified by recrystallization and freed of metal ions.[52]

One year after the manufacture of halons was banned, teams of scientists at six European laboratories ended a 2-year project to examine a range of possible substitutes. Halon 1301 is one of two halons widely used in commercial and military applications for fire suppression. Halon 1211 is used to protect valuable electronics in oil and gas production and on civilian aircraft, and by the military in fixed-wing aircraft, helicopters, ships, and ground armored vehicles such as tanks. Fire extinguishing agents are of two types. Additive agents, operate primarily by heat absorption. Reactive agents operate by removing free radicals from flames and combustion systems. Reactive chemical inhibition is much quicker because the rates of gaseous free-radical reactions in flames are extremely fast. The fire is put out in less time with less damage to humans and property. Substitutes for halons (SUBSTHAL) inhibit by their heat capacities, not by free-radical reactions. During explosions, halon 1301 can completely extinguish the detonation dependent upon pressure and concentration of hydrogen in the mixture. The research has shown that none of the fluorinated hydrocarbons tested are as efficient at extinguishing fires as are the halogens. Compounds that were screened or assessed with in the SUBSTHAL project were less effective than halon 1301 as a fire retardant. Bromine is the optimum halogen to have in this class of compounds. The ozone depletion potential of the proposed replacement compounds are known to be either zero or significantly smaller than those of the fully halogenated chlorofluorocarbons. However, the environmental impact of the products formed when these compounds are degraded in the atmosphere has not been fully assessed.[53]

Factors such of soil pH and moisture affect how much methyl bromide escapes to the atmosphere after agricultural fields are treated with the fumigant. In field experiments, researchers measured the flux of methyl bromide into the atmosphere, the amount of the gas in the soil at varying depths, and the bromide content of the soil before and after fumigation. Less of the fumigant escapes to the atmosphere with higher soil pH, greater moisture content and organic matter in the soil, and greater injection depth.[54]

The August issue of Die Makromolekulare Chemie: Macromolecular Symposium, v. 85, pp. 1-392) published many of the key papers presented at the 11th International Symposium on Cationic Polymerization and Related Ionic Process. Bromine is used as an initiator and as an additive salt in the living polymerization reactions.[55]

Outlook

Sales of bromine, primarily in compounds, have decreased 195,000 from 226,000 kg. This represents an annual rate of decrease of about 1% per year. These decreases have been offset by increased use of bromine in fire retardants, sanitizer, and well-drilling fluids. Bromine is expected to increase in demand at (the same) rate through the next 5 years. Demand as a fire retardant will offset any decreases in other uses.

Petroleum.—Demand for bromine as a gasoline additive has declined each year since the EPA issued regulations in the 1970's to reduce the lead in gasoline. Bromine in the form of EDB is used as a "scavenger" for the lead to keep the lead from depositing in the engine. In 1979, the amount of bromine sold reached a peak of 225 million kg. The rapid decline to 141 million kg in 1986 was a direct result of the limits on lead in leaded gasoline. The EC continued discussions to reduce lead levels in gasoline.

Federal laws enacted to encourage alternative forms of power in automotive engines are likely to have a depressive effect on increases in petroleum demand. The Clean Air Act Amendments of 1990 has an amendment that will require 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 are already on the market in California.

Sanitary Preparations.—Bromine has found usage in swimming pools, hot tubs, and whirlpools. The sanitary preparation field is an area where bromine has been found to be safer than its substitutes because bromine has a higher biocidal activity level for the same amount of product. Applications in the pulp and paper industry and in cooling towers and Government-regulated food-washing applications are growth areas. The use of bromine will continue to grow in this area, closely following the gross national product in real growth.

Fire Retardants.—Federal regulations covering flammability of private and public building materials and furnishings have required greater amounts of fire retardant chemicals to be used in these materials and furnishings. Fire retardants are expected to grow as organic materials replace metals in transportation, infrastructure, and packaging. Several State governments continue to support strong consumer laws that protect State residents from products with potential fire hazards produced in other States. Fredonia Group reported in a Flame Retardants study that demand was expected to increase by an average 5% per year to a level of $1.8 billion in 1998. Due to cost and applicability advantages, additive flame retardants demand was expected to increase faster than reactive types.[56]

Other Uses.—Usage of calcium bromide and zinc bromide in well-drilling fluids decreased during the 1980's as the domestic petroleum industry suffered a severe recession. During 1994, the number of workover rigs in the field in the United States was down 12%.[57] Oilfield chemicals used in drilling, completion and workover, and production operations have remained significantly more profitable internationally than in U.S. operations. The competition market included corrosion inhibitors, bactericides, viscosities and defoamers, as well as commodities such as calcium chloride and calcium bromide brines used to maintain well productivity.

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TABLE 1
SALIENT BROMINE AND BROMINE COMPOUND STATISTICS 1/
(Thousand kilograms unless otherwise specified)

		1990	1991	1992	1993	1994
United States:						
Bromine sold or used: 2/						
Quantity		177,000	170,000	171,000	177,000	195,000
Value	thousands	$131,000	$124,000	$125,000	$123,000	$155,000
Exports:						
Elemental bromine:						
Quantity		2,930	2,560	5,320	6,010	6,470
Value	thousands	$4,000	$7,670	$5,540	$7,440	$7,270
Bromine compounds: 3/						
Gross weight		17,100	17,100	20,000	15,800	13,700
Contained bromine		14,400	14,600	16,900	13,400	11,500
Value	thousands	$18,200	$21,300	$26,400	$21,800	$21,100
Imports: 4/						
Elemental bromine:						
Quantity		756	142	851	850	319
Value	thousands	$508	$91	$522	$513	$194
Compounds:						
Ammonium bromide:						
Gross weight		1,530	2,060	1,790	1,240	1,120
Contained bromine		1,250	1,680	1,460	1,010	917
Value	thousands	$2,400	$3,130	$2,870	$2,020	$1,850
Calcium bromide:						
Gross weight		11,600	14,600	5,370	9,650	4,510
Contained bromine		9,300	11,700	4,290	7,720	3,610
Value	thousands	$5,240	$7,130	$3,210	$3,740	$5,380
Potassium bromate:						
Gross weight		199	386	407	280	166
Contained bromine		42	185	195	134	79
Value	thousands	$615	$1,240	$1,250	$892	$538
Potassium bromide:						
Gross weight		593	888	883	1,180	1,280
Contained bromine		461	595	592	790	858
Value	thousands	$1,030	$1,590	$1,660	$2,170	$2,270
Sodium bromate:						
Gross weight		NA	229	176	290	276
Contained bromine		NA	121	93	153	146
Value	thousands	NA	$391	$469	$725	$714
Sodium bromide:						
Gross weight		1,630	3,040	1,100	1,270	1,400
Contained bromine		1,270	2,360	852	983	1,090
Value	thousands	$2,130	$3,880	$1,620	$1,730	$1,770
Other:						
Gross weight		11,600	11,600	11,700	12,500	14,300
Contained bromine		7,080	7,100	7,160	7,600	8,680
Value	thousands	$50,400	$24,600	$21,500	$36,500	$42,600
World: Production		390,000	392,000	393,000	393,000 r/	412,000 e/

e/ Estimated. r/ Revised.

1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits, may not add to totals shown.

2/ Elemental bromine sold to nonproducers, including exports, or used in the preparation of bromine compounds by primary U.S. producers.

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

4/ Bureau of the Census.

TABLE 2
BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 1994

State and company	County	Plant	Production source	Elemental bromine plant capacity 1/ (million kilograms)
Arkansas:				
Arkansas Chemicals Inc.	Union	El Dorado	Well brines	23
Ethyl Corp.	Columbia	Magnolia	do.	45
Do.	do.	do.	do.	73
Great Lakes Chemical Corp.	Union	El Dorado	do.	48
Do.	do.	Marysville	do.	36
Do.	do.	El Dorado	do.	23
Michigan:				
The Dow Chemical Co.	Mason	Ludington	do.	11 2/
Total				259

1/ Actual production capacity is limited by brine availability.
2/ Bromine produced at this plant is reprocessed in Arkansas.

TABLE 3
YEAREND 1994 PRICES FOR ELEMENTAL BROMINE AND SELECTED COMPOUNDS

Product	Value per pound (cents)	Value per kilogram (cents)
Ammonium bromide, National Formulary (N.F.), granular, drums, carlots, truckloads, f.o.b. works	131	289
Bromine:		
Drums, truckloads, works 1/	123	271
Bulk, tank cars, works 1/	56 - 68	123
Bromochloromethane, drums, carloads, f.o.b. Midland, MI	127	280
Calcium bromide, bulk 2/	14	36
Ethyl bromide, technical, 98%, drums, truckloads	127	280
Ethylene dibromide, drums, carloads	95	209
Hydrobromic acid, 48%, drums, carloads, truckloads, f.o.b.	42	93
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	245
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 per pound higher for 30,000-pound minimum.
2/ Bureau of the Census. Average c.i.f. import value.

Source: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials. V. 247, No. 1, Jan. 2, 1995, pp. 26-33.

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

Compounds	Harmonized Schedule Code	1993		1994		Principal sources, 1994
		Gross weight (kilograms)	Value 2/ (thousands)	Gross weight (kilograms)	Value 2/ (thousands)	
Methyl bromide	2903301520	3,570	$4,400	3,300	$4,090	Israel 100%.
Chlorobromodifluormethane	2903400020	4,680	26,700	4,700	33,900	United Kingdom 45%, France 37%, Netherlands 11%, Belgium 3%, Japan 3%, Germany 1%.
Hydrobromic acid	2811195050	294	250	255	174	Israel 100%.
Dibromoethyldibromocycloxehane	2903591500	73	1,080	59	392	Germany 48%, Netherlands 38%, Belgium 8%, Slovakia 6%.
Dibromoneopentyl glycol	2905505000	88	215	188	478	Israel 100%.
Tetrabromobisphenol A	2908102500	34	41	168	207	Do.
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909300700	1,910	3,800	1,760	3,340	Israel 99%, Japan 1%.
Bromoxynil 3/	NA	1,400	NA	2,820	NA	United Kingdom 100%.
Brominanine 3/	NA	412	NA	1,040	NA	Japan 100%.

NA Not available.
1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits, may not add to totals shown.
2/ Declared c.i.f. value.
3/ The Journal of Commerce Port Import/Export Reporting Service.

Source: Bureau of the Census.

TABLE 5
WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES 1/, DECEMBER 31, 1994

Country and company	Location	Capacity (thousand kilograms)	Source
China:			
Laizhou Bromine Works	Shandong	11,500	Underground brines.
France:			
Atochem	Port-de-Bouc	13,600	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse	2,300	Bitterns of mined potash.
Germany:			
Kali und Salz AG: Salzdetfurth Mine	Bleichrode	2,500	Do.
India:			
Hindustan Salts Ltd.	Jaipur		
Mettur Chemicals	Mettur Dam	1,500	Seawater bitterns from salt production.
Tata Chemicals	Mithapur		
Israel:			
Dead Sea Bromine Co. Ltd.	Sodom	140,000	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	Seawater.
Russia:			
Kaustic A/O	Volgograd	3,000	Solution mining of Bischofite.
United Kingdom:			
Associated Octel Co. Ltd.	Amlwch	30,000	Do.

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

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

(Thousand kilograms)

Country 3/	1990	1991	1992	1993	1994 e/
Azerbaijan e/	XX	XX	5,000	4,000	3,000
China e/	8,080	12,100	16,700 r/	18,000 r/	19,000
France e/	3,100	3,000	3,200 4/	2,290 r/	2,500
Germany e/	1,500 4/ 5/	1,500	750	750	750
India e/	1,300	1,300	1,300	1,400	1,400
Israel e/	130,000	135,000	135,000	135,000	135,000
Italy e/	400	400	300	300	300
Japan e/	15,000	15,000	15,000	15,000	15,000
Spain e/	300	300	250	200	200
Turkmenistan e/	XX	XX	12,000	10,000	8,000
U.S.S.R. e/ 5/	25,000	24,000	XX	XX	XX
Ukraine e/	XX	XX	7,000	5,000	4,000
United Kingdom	28,000 e/	29,300	29,900	27,400 r/	28,000
United States 6/	177,000	170,000	171,000	177,000	195,000
Total	390,000	392,000	397,000 r/	396,000 r/	412,000

e/ Estimated. r/ Revised. XX Not applicable.

1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits; data may not add to totals shown.

2/ Table includes data available through May 25, 1995.

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

4/ Reported figure.

5/ Excludes Eastern States.

6/ Dissolved in Dec. 1991.

7/ Sold or used by producers.