Bromine

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Elemental bromine sold or used by U.S. producers returned to the rising trend in annual growth experienced prior to 1977. Expanding foreign markets and the changing composition of the domestic market were the important factors affecting U.S. production, which was centered in the State of Arkansas, with additional production in Michigan.

The primary manufacturers of brominated compounds operated plants in Arkansas, Michigan, and Texas. One of them, however, discontinued its Michigan operation in 1978. Primary producers' sales of all types of bromine compounds increased, although demand for the industry's major product, ethylene dibromide, as a leaded-gasoline additive continued to fall with the Government-regulated decline in use of leaded gasoline. As laboratory tests were completed on several potentially harmful bromine compounds, Federal regulatory agencies acted in accordance with significant test results.

Legislation and Government Programs.—The Interagency Regulatory Liaison Group (IRLG), which is composed of Federal regulatory agencies, took an important step to coordinate the attack on potentially hazardous chemicals and other substances. The original member agencies (Consumer Product Safety Commission, Environmental Protection Agency, Federal Drug Administration, and Occupational Safety and Health Administration) formed IRLG in 1977 to share individual research, data, and analyses; avoid duplicative regulations; and attempt to set consistent standards to control hazards. In 1978, the group released a list of 24 compounds, or categories of substances, targeted for special attention.[2] Three brominated organic compounds were included on the list: Dibromochloropropane, an insecticide; ethylene dibromide, a gasoline additive and pesticide; and polybrominated biphenyls, the industrial fire retardant that in 1973 was accidentally mixed with cattle feed in Michigan. In 1979, IRLG drafted guidelines for uniform testing among Federal agencies for five ill effects to humans that could be caused by potentially harmful chemicals.[3] The IRLG goal is to develop a single set of tests to replace the different tests the agencies now use to determine the same ill effects. These effects cover acute inhalation, birth defects, acute oral toxicity, acute eye irritation, and acute skin effects.

The Occupational Safety and Health Administration (OSHA) issued final rules in 1978 for workplace exposure to dibromochloropropane (DBCP).[4] The compound has been linked to worker sterility in several chemical plants and also was labeled a possible carcinogen by the National Cancer Institute (NCI).[5] The final exposure limit of 1 part per billion (ppb) averaged over an 8-hour workday is 10 times stricter than the 10-ppb emergency temporary standard ordered by OSHA in 1977. The final standard also prohibits eye and skin contact with the agricultural insecticide. Following the recommendation in 1979 of an administrative law judge, the Environmental Protection Agency (EPA) banned all applications of DBCP except in Hawaiian pineapple groves.[6] Other agricultural uses of DBCP will be suspended indefinitely while further research is conducted.

EPA issued its final rule extending the compliance deadline for reducing the amount of lead antiknock compounds in gasoline.[7] The rule delays the agency's deadline for a 0.5-gram-per-gallon limit on lead in gasoline from October 1979 to October 1980; however, refiners must comply with certain requirements on gasoline production to qualify for the extension. Increased use of low-lead and unleaded gasoline will reduce domestic consumption of ethylene dibromide (EDB), which is used primarily as a scavenger for lead added to gasoline in antiknock compounds.

OSHA reportedly was considering making the workplace standard for EDB more stringent, and EPA was considering restricting its use as a pesticide.[8] These proposals followed the announcement by NCI that EDB proved to be a potent carcinogen in ingestion tests conducted on rats and mice.[9] The Dow Chemical Co. and Ethyl Corp., producers of EDB, disputed the validity of the test procedures and the extrapolation of results to humans. They contend that actual industrial experience does not agree with the laboratory findings.

NCI reported another bromine chemical to be an animal carcinogen following 130-week tests on rats and mice.[10] The compound was tris (2,3-dibromopropyl) phosphate, the flame retardant that the Consumer Product Safety Commission (CPSC) banned in 1977 for use in children's sleepwear. The CPSC was involved in several actions in 1978 concerning tris: It abandoned its attempt to force eight manufacturers of tris-treated products to repurchase the millions of dollars of these goods they had sold.[11] CPSC also ruled that it has the authority to ban exports of tris-treated apparel.[12] This authority, however, was expected to be challenged in the courts. Following Congressional passage of a bill to provide government payments to clothing manufacturers, retailers, and others in the apparel industry that had incurred losses as a result of the tris ban, President Carter pocket vetoed the legislation.[13] Among several reasons given for the veto, the President stated that the law would have set an "unwise precedent" to pay industry's losses when a product is used to meet a regulatory standard and that product is later judged to be hazardous.

OSHA reportedly was contemplating regulation of workplace exposure to the chemical vinyl bromide, based on reports that rats had developed cancer following low-level exposure.[14]

The State of Michigan issued a report on a special study of the health effects of small amounts of polybrominated biphenyls (PBB) in the bodies of Michigan residents.[15] Although the State will continue monitoring the health of the general population for a 10-year period, the initial study concluded that low-level PBB contamination of an estimated 90% of residents, which resulted from accidental introduction of the chemical into the food chain in 1973, has caused no adverse health effects.

DOMESTIC PRODUCTION

Six companies operated nine plants to extract bromine from brines in Arkansas and Michigan. The producers of elemental bromine were also the major manufacturers of bromine compounds, with two additional plants, one in Texas and one in Michigan; however, the St. Louis, Mich., plant of Velsicol Chemical Corp. was closed on September 1, 1978.[16] The September deadline was a result of a 1976 settlement made with the State of Michigan following pollution problems involving the plant and its products. Negotiations to sell the plant before the deadline failed when certain conditions specified by the State Department of Natural Resources could not be resolved between Velsicol, the buyers, and the State. In December, Velsicol announced a $3 million program for its El Dorado, Ark., bromine production plant to enable the plant to meet current and future environmental regulations.[17] The program was scheduled to be completed in 1979.

Table 1.—Elemental bromine sold as such or used in the preparation of bromine compounds by primary U.S. producers

(Million pounds and million dollars)

	1977		1978		1979[p]	
	Quantity	Value	Quantity	Value	Quantity	Value
Sold	59.0	12.8	53.2	11.3	59	13
Used	374.8	86.9	393.4	88.7	443	102
Total	433.8	99.7	[1]446.5	100.0	502	115

[p]Preliminary.
[1]Data do not add to total shown because of independent rounding.

Table 2.—Bromine compounds sold by primary U.S. producers

(Million pounds and million dollars)

	1977			1978			1979[p]		
	Quantity		Value	Quantity		Value	Quantity		Value
	Gross weight	Bromine content		Gross weight	Bromine content		Gross weight	Bromine content	
Ethylene dibromide	279.6	237.8	75.1	259.2	220.5	63.9	288	245	67
Methyl bromide	32.9	27.7	15.7	42.6	35.8	20.9	55	46	28
Other compounds[1]	125.1	86.7	99.2	170.3	119.5	129.5	228	163	171
Total[2]	437.6	352.2	190.0	472.1	375.8	214.4	571	454	266

[p]Preliminary.
[1]Includes hydrobromic acid, tetrabromobisphenol-A, ethyl, calcium, ammonium, sodium, potassium, and other bromides, plus some methyl bromide exports.
[2]Data may not add to totals shown because of independent rounding.

Table 3.—Bromine-producing plants in the United States

State and company	County	Plant	Production source
Arkansas:			
Arkansas Chemicals, Inc	Union	El Dorado	Well brines.
The Dow Chemical Co	Columbia	Magnolia	Do.
Ethyl Corp	do	do	Do.
Great Lakes Chemical Corp	Union	El Dorado	Do.
Do	do	Marysville	Do.
Velsicol Chemical Corp	do	El Dorado	Do.
Michigan:			
The Dow Chemical Co	Mason	Ludington	Do.
Do	Midland	Midland	Do.
Morton Chemical Co	Manistee	Manistee	Do.

CONSUMPTION AND USES

Although demand increased for bromine compounds in general, demand declined for EDB, which has traditionally been the most important bromine chemical, as a constituent in gasoline. This was primarily because reduced requirements for lead in gasoline necessitated a corresponding reduction in lead-scavenging additives. Use of EDB as an insecticide and soil fumigant continued to grow, however, owing to its substitution for another bromine compound (1,2-dibromo-3-chloropropane or DBCP) after EPA banned the use of DBCP in certain agricultural applications.

In view of the decline in traditional markets for some bromine chemicals, producers sought to satisfy growing markets for others, such as methyl bromide, another agricultural fumigant. Rising sales of a variety of bromine compounds in the "other compounds" category were attributed in part to growing demand for certain flame retardants and for calcium bromide.

Calcium bromide is used by the oil- and gas-well drilling industry for high-density, solids-free completion, packer, and workover fluids. As a result of rapid growth in oil industry demand, three of the producers of elemental bromine and its compounds announced plans to expand capacity in 1979 for producing calcium bromide solutions.[18] The Dow Chemical Co., which in 1978 increased capacity at Midland, Mich., to 84 million pounds, announced a further incremental increase that would bring calcium bromide capacity to 120 million pounds per year. Velsicol Chemical Corp.'s plants at Beaumont, Tex., and El Dorado, Ark., will have combined annual capacity of about 13 million pounds. Another plant at El Dorado, Ark., that of Great Lakes Chemical Corp., was expected to increase its annual capacity to almost 100 million pounds.

Expanding in another direction, Great Lakes purchased in 1978 Tesco Chemicals, Inc., of Atlanta, Ga., a manufacturer and distributor of swimming pool sanitation chemicals and dispensing devices.[19] The acquisition was expected to enhance the growth of Great Lakes' bromine-based

swimming pool products, which the firm purchased in 1977. In 1978 Great Lakes also acquired WIL Research Laboratories of Cincinnati, Ohio. WIL is an independent animal testing laboratory with clients in the pharmaceutical, food, cosmetic, and chemical industries, as well as government agencies.

The Dow Chemical Co. announced plans to construct a 30-million-pound-per-year facility to produce bromine chloride for use in disinfecting municipal and industrial waste water.[20] The facility, which is to be located in Houston, Tex., is expected to come on-stream in 1980 (see Technology).

PRICES

The industry-wide base price for elemental bromine in bulk reached 28 cents per pound by yearend 1979; however, discount pricing was prevalent. The average price of bulk elemental bromine, f.o.b. plant, reported by U.S. producers was 21.24 cents per pound in 1978 and 22.03 cents per pound in 1979. Quoted yearend prices for elemental bromine and selected compounds follow.

Table 4.—Prices of elemental bromine and selected compounds

Product	Value per pound (cents) December 31	
	1978	1979
Bromine, purified:		
Carlots, truckloads, delivered	75	75
Drums, carlots, truckloads, delivered east of the Rocky Mountains[1]	55-62	55-69
Bulk tank car, tank trucks (45,000-pound minimum), delivered east of the Rocky Mountains[1]	25-30	26.5-28
Ammonium bromide, national formulary (N.F.), granular, drums, carlots, truckloads, freight equalized	74	74
Bromochloromethane, drums, carlots, f.o.b. Midland, Mich	98	98
Bromoform, pharmaceutical grade, 5-gallon drums, f.o.b. works	270	270
Ethyl bromide, technical, 98%, drums, carlots, freight allowed, East	61.5	61.5
Ethylene dibromide, drums, carlots, freight equalized	37	37
Hydrobromic acid, 48%, drums, carlots, truckloads, f.o.b. works	39-41	39-41
Hydrogen bromide, anhydrous, cylinders, extra, 30,000 pounds, f.o.b. works	65	65
Methyl bromide, distilled, tanks, 140,000-pound minimum, freight allowed	41	41
Potassium bromate, granular, powdered, 200-pound drums, carlots, f.o.b. works	106	106
Potassium bromide, N.F., granular, drums, carlots, f.o.b. works	67	67
Sodium bromide, 99%, granular, 400-pound drums, freight, f.o.b. works	65	65

[1]Delivered prices for drums and bulk shipped west of the Rockies, 1 cent per pound higher. Bulk truck prices 1 cent per pound higher for 30,000-pound minimum and 2 cents per pound higher for 15,000-pound minimum. Price f.o.b. Midland and Ludington, Mich., freight equalized, 1 cent per pound lower.

Sources: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials. V. 215, No. 1, Jan. 1, 1979, pp. 46-55, and V. 216, No. 27, Dec. 31, 1979, pp. 26-35.

FOREIGN TRADE

Increasing producer exports of elemental bromine and bromine contained in compounds (table 5) were major factors in regaining the sales level that existed prior to Federal restrictions on domestic uses.

In 1978, about 82% of imported bromine and bromine compounds (table 6), which amounted to less than 1% of domestic consumption, were shipped from Israel, and 11% from the Netherlands; however, in 1979 about 99% of imports were from Israel. Other bromine compounds imported by the United States are not easily identified because they are classified in multiproduct categories.

Table 5.—U.S. exports of bromine and bromine compounds by primary producers

(Thousand pounds and thousand dollars)

Year	Elemental bromine		Bromine compounds		
	Quantity	Value	Gross weight	Contained bromine	Value
1976	4,400	900	74,100	62,600	29,200
1977	5,400	1,100	64,400	54,100	27,300
1978	6,400	1,300	106,000	87,900	38,500
1979[p]	10,100	2,100	98,300	83,100	37,500

[p]Preliminary.

Table 6.—U.S. imports of bromine and bromine compounds

(Thousand pounds and thousand dollars)

	1977		1978		1979	
	Quantity	Value	Quantity	Value	Quantity	Value
Elemental bromine	517	102	669	102	34	5
Potassium bromide	89	56	119	84	794	536
Sodium bromide	106	60	320	175	2,190	1,056
Ethylene dibromide	79	22	589	102	193	33

Source: U.S. Bureau of the Census.

WORLD REVIEW

The United States, as world leader in bromine production and consumption, produces annually about two-thirds of the world total. Other principal bromine-producing nations include, in decreasing order, Israel, the United Kingdom, France, the U.S.S.R., and Japan.

China, mainland.—The Ginghai Salt Lake Institute of the Chinese Academy of Sciences completed an evaluation of the mineral resource potential of the Tibetan Plateau.[21] Following a general survey of the multitude of salt lakes in the region, more than 50 in northern and western Tibet were examined in more detail. The brines contain high percentages of bromine, sodium, potassium, boron, magnesium, lithium, rubidium, cesium, uranium and thorium. China produces large tonnages of salt by evaporation of sea and inland brines, as well as by underground mining, and also already obtains bromine, borax, iodine, lithium, potash, sodium sulfates, and other minerals from salt lakes at Chaerhan, Yuncheng, and elsewhere.

Israel.—The Customs Service, U.S. Department of the Treasury, made a final countervailing duty determination involving manufacturers and/or exporters of Israeli bromine and brominated compounds.[22] The final determination reversed the preliminary determination in which the Israeli Government was found to have given two companies benefits considered to be bounties or grants under U.S. law. Although the final results of the Customs investigation confirmed that the two firms, Dead Sea Bromine Co., Ltd. and Bromine Compounds, Ltd., had indeed received partial rebates of property taxes and other kinds of aid, these were considered to be minimal and, therefore, not legally classified as bounties or subsidies.

The Israeli Government was reportedly preparing to take the first step to change the nation's economic system from one of socialism to free-enterprise by either selling outright, or offering shares in as many as 160 Government-owned or Government-controlled companies.[23] One of the largest of these concerns, Israel Chemicals, Ltd. (ICL), is the parent organization of numerous natural resource development and inorganic chemical firms, including Dead Sea Bromine and Bromine Compounds. Ongoing expansion of capacity for producing bromine compounds at the new industrial park at Ramat Hovav may reach 100,000 tons per year by 1984.[24] Production of calcium bromide is part of the expansion plan (see Technology).

Japan.—The Ministry of Health and

Welfare ban of the use of tris (2,3-dibromopropyl) phosphate as a fire retardant in clothes, soft furnishings, paints, household adhesives, and shoe polish went into effect on November 1, 1978.[25] The ruling was aimed at possible imports of consumer goods containing tris since the compound itself is not made in Japan.

Jordan.—The Arab Potash Co., owned by the Jordanian Government (51%), the Arab Mining Co. (44%), and the Libyan Government (5%), has reportedly raised $231 million to finance the Dead Sea potash project.[26] In addition, plans were announced for expanding the project to construction of facilities to produce bromine and refractory magnesia. The bromine project, which is expected to cost $60 million, will employ U.S. technology provided by Great Lakes Chemical Corp. (25% interest). The proposed annual production of 33,000 short tons of bromine would have potential to rival in world markets the growing importance of Israel's Dead Sea Bromine operation.[27]

Netherlands.—Broomchemie, the bromine compounds producer that opened a new plant at Terneuzen in 1977, was accused of failure to comply with agreed upon safety regulations.[28] Broomchemie is the production company of Eurobroom in The Hague, which is a subsidiary of the Dead Sea Bromine Group of Israel. Elemental bromine from Israel serves as the raw material for manufacture at Terneuzen of sodium, potassium, and ammonium bromides, carbon tetrabromide, and other bromine products. Reports that plant workers were experiencing symptoms caused by high bromide concentrations in the workplace environment prompted a governmental inquiry that resulted in a fine of $1,200.[29] The environmental inspector's recommendation for closing the tetrabromobisphenol-A (TBBA) plant was overruled by provincial authorities after Broomchemie installed new environmental control equipment.[30]

United Kingdom.—Following the lead of the United States and other countries, the United Kingdom banned the supply of tris-treated nightwear for children.[31] The ban will go into effect throughout the European Community on January 1, 1980.[32]

Table 7.—Bromine: World production, by country

(Thousand pounds)

Country[1]	1976	1977	1978[p]	1979[e]
France	33,466	34,326	[e]35,000	35,000
Germany, Federal Republic of	9,158	8,236	8,583	8,600
India[e]	600	620	660	600
Israel	46,100	69,450	76,170	100,000
Italy	[r]1,230	[e]1,300	[e]1,300	1,300
Japan[e]	26,500	26,500	26,500	26,000
Spain[e]	[r]900	900	900	900
United Kingdom	[r]65,928	54,500	55,000	55,000
United States[2]	[r]468,000	433,900	446,500	502,000
U.S.S.R.[e]	30,000	33,000	33,000	33,000
Total[3]	682,000	663,000	684,000	762,000

[e]Estimate. [p]Preliminary. [r]Revised.

[1]In addition to the countries listed, several other nations produce bromine, but output data are not reported and available general information is inadequate for formulation of reliable estimates of output levels.

[2]Sold or used by producers.

[3]Data may not add to totals shown because of independent rounding.

TECHNOLOGY

A new process for producing calcium bromide directly has been developed by TAMI, the research arm of Israel Chemicals Ltd.[33] TAMI developers say the method uses less energy and is more economical than conventional processes that must produce elemental bromine first. The direct route takes advantage of the high bromine content (up to 10,000 parts per million) of the Dead Sea. Calcium bromide is selectively extracted out of sea brine by means of an undisclosed solvent, which is subsequently removed, and the calcium bromide is concentrated to 52% by evaporation. The compound can be used to make other bromides, and is finding increased usage in oil-well drilling muds.

Exxon Research and Engineering demonstrated a laboratory prototype of a zinc-bromine battery at the Electric Vehicle

Expo II in Philadelphia.[34] The battery, being developed for use in electric vehicles and for utility load leveling, has a projected energy density two to three times that of conventional lead-acid batteries, or 35 watt-hours per pound. Design estimates place the cost of the battery at $30 per kilowatt-hour. Among the advantages of the prototype (a 6-volt, 80-ampere-hour system that has been under development for 3 years) are operation at ordinary temperatures and low-cost components.

Research into the structure and function of hemoglobin, the oxygen-carrying molecule in blood, and into what goes wrong with hemoglobin in sickle cell anemia patients, has led to investigation of several types of chemicals that show potential to treat the disease.[35] A research group at Northwestern University is exploring the use of a brominated aspirin derivative (acetyl-3,5-dibromosalicylic acid) that can enter red blood cells to react with the hemoglobin inside, and thereby prevent the cell deformation known as sickling. Although toxicity studies have not yet been conducted, it is generally believed that derivatives of well-known drugs such as aspirin stand a good chance of being approved for therapeutic use in humans.

An experimental drug therapy for workers poisoned by the pesticide Kepone appears to have potential for detoxifying the systems of persons afflicted with dangerous levels of other halogenated hydrocarbons.[36] Successful preliminary research at Virginia Medical College using cholestyramine, a bulky anion-exchange resin, could possibly be expanded to detoxification studies of such potential carcinogens as PBB, polychlorinated biphenyls (PCB), mirex, aldrin, dieldrin, and DDT. Future research would include studies of the mechanism of halogenated hydrocarbon excretion from the body, and the safety of using cholestyramine and similar agents for eliminating these compounds.

Field trials at two waste-water treatment plants have convinced the Dow Chemical Co. that bromine chloride has greater efficacy in killing bacteria and viruses than chlorine.[37] Although more expensive than chlorine, bromine chloride offers the advantages of use at lower vapor pressures, shorter retention time, and avoidance of formation of chemical compounds that may be toxic to fish.

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