# Bromine

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Domestic producers sold or used nearly 434 million pounds of elemental bromine in 1977, a decrease of 6% from that of 1976. Demand for the industry's primary product, ethylene dibromide, as a leaded-gasoline additive was down, but sales of the compound for agricultural use improved. Consumption of other bromine-containing compounds declined. The total value of bromine and bromine compounds sold by producers was $203 million.

Bromine capacity in Arkansas continued to grow as a producer completed an expansion of its bromine production facilities. Several Federal agencies were evaluating some bromine compounds that could possibly be hazardous to consumers and workers.

## DOMESTIC PRODUCTION

The amount of elemental bromine sold or used by domestic producers in 1977 declined 6% to 434 million pounds. Sales of bromine compounds by producers were down 7%. Producers' sales of methyl bromide rose 6%, but the quantities of ethylene dibromide and other bromine compounds sold decreased 6% and 10%, respectively. The total value of elemental bromine and bromine compounds sold dropped $13 million. The unit value of elemental bromine declined, but the average price of manufactured compounds was essentially unchanged.

Six companies operated nine bromine-producing plants in two States, Arkansas and Michigan. Three of these companies combined sold or used 88% of the U.S. total.

The Governor's Brine Study Commission in Arkansas proposed legislation covering unitization and royalty payments. The bill was referred to a joint interim committee of the Arkansas legislature.

Great Lakes Chemical Corp. brought additional brine production and bromine extraction facilities onstream at Marysville, Ark., and acquired Drug Research, Inc., a Michigan-based firm which produces brominated chemicals primarily for swimming pool sanitation. Great Lakes' new research and development laboratories were completed at West Lafayette, Ind.[2]

Emery Industries, Inc., signed an agreement with Dead Sea Bromine Co., Ltd., of Israel to market certain nonagricultural bromine compounds in the United States. A jointly owned U.S. plant for the manufacture of bromine derivatives is being considered. Dead Sea Bromine will continue to market some bromine products in the United States through its subsidiary, Ameribrom.[3]

**Table 1.—Elemental bromine sold as such or used in the preparation of bromine compounds by primary producers in the United States**

(Thousand pounds and thousand dollars)

| | 1976 | | 1977 | |
|---|---|---|---|---|
| | Quantity[r] | Value[r] | Quantity | Value |
| Sold | 57,405 | 12,859 | 59,036 | 12,763 |
| Used | 402,655 | 99,488 | 374,782 | 86,915 |
| Total[1] | 460,061 | 112,348 | 433,818 | 99,678 |

[r]Revised.
[1]Data may not add to totals shown because of independent rounding.

**Table 2.—Bromine compounds sold by primary producers in the United States**

(Thousand pounds and thousand dollars)

| | 1976[r] | | | 1977 | | |
|---|---|---|---|---|---|---|
| | Quantity | | Value | Quantity | | Value |
| | Gross weight | Bromine content | | Gross weight | Bromine content | |
| Ethylene dibromide | 298,752 | 254,149 | 77,286 | 279,581 | 237,840 | 75,061 |
| Methyl bromide | 31,032 | 26,120 | 13,773 | 32,930 | 27,717 | 15,701 |
| Other compounds[1] | 138,417 | 97,191 | 112,007 | 125,066 | 86,650 | 99,200 |
| Total[2] | 468,201 | 377,459 | 203,067 | 437,576 | 352,206 | 189,962 |

[r]Revised.
[1]Includes hydrobromic acid, tetrabromobisphenol-A, ethyl, ammonium, sodium, potassium, and other bromides.
[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

Total demand for ethylene dibromide declined in 1977, primarily because reduced requirements for lead in gasoline necessitated a corresponding reduction in lead-scavenging additives. The decline was tempered by increased consumption of the compound as an agricultural fumigant brought about by the removal of 1,2-dibromo-3-chloropropane from the marketplace. Ethylene dibromide accounted for 55% of bromine sold or used by domestic producers. Results of National Cancer Institute (NCI) carcinogenicity studies have prompted the Environmental Protection Agency (EPA) to examine ethylene dibromide under the rebuttable presumption against registration process. However, preliminary EPA studies have recognized its importance, since elimination could result in losses to grain and other crops, increased pest control costs to farmers for substitute pesticides, and restricted movement of certain fruits and vegetables in interstate and overseas commerce.[4] The Occupational Safety and Health Administration (OSHA) issued guidelines recommending that work-

er exposure in air be limited to the lowest possible concentration.[5] EPA was also considering adding ethylene dibromide and 37 other compounds to a proposed list of 23 hazardous pesticides that can only be applied by trained applicators.[6]

Among the 23 substances on the original list was methyl bromide. Consumption of this fumigant was up in 1977. Methyl bromide's share of bromine sold or used by producers was 6%. Total demand for other bromine compounds, which represented 20% of the total sold or used by producers, declined, although consumption of certain flame retardants, calcium bromide, and other compounds increased.

Preliminary NCI data released in February showed that tris(2,3-dibromopropyl)phosphate, a flame retardant used in textiles including children's sleepwear, was a carcinogen.[7] The Consumer Products Safety Commission (CPSC), after placing an initial ban on the sale and manufacture of "tris"-treated garments, banned tris and all treated fabric, yarn, and fiber in May.[8] However, a U.S. District Court in South Carolina prohibited CPSC from enforcing the ban.[9] CPSC has since voted to propose rules to eliminate the portion of the children's sleepwear standards that necessitated the use of flame retardants.[10]

In August EPA announced that it would regulate the flame retardant polybrominated biphenyl under the Toxic Substances Control Act, by prohibiting its use as a fire retardant, requiring new uses to come under review, and applying quality-control limitations to manufacture for export.[11] Results of a continuing study by a New York medical team on the health effects of polybrominated biphenyl on Michigan residents indicated that the duration of exposure to the compound was as important as the intensity. However, tentative findings of the Michigan Public Health Department showed no significant pattern of immunological problems related to exposure levels.[12]

The agricultural fumigant 1,2-dibromo-3-chloropropane was suspected of causing sterility in male chemical workers at Occidental Chemical Co.'s pesticides plant in Lathrop, Calif., and at the facilities of the two major producers of the compound, The Dow Chemical Co. and Shell Chemical Co.[13] The State of California prohibited the use or manufacture of pesticides containing the compound.[14] Emergency temporary worker exposure limits were announced by OSHA in September, and stringent permanent exposure limits were proposed in November. In addition, the Food and Drug Administration began monitoring foods for residues.[15] EPA ordered a halt to all sales and use of the compound in late October, but may allow limited utilization if producers agree to the application of the compound only by trained personnel.[16] Tests conducted by Dow at yearend indicated that the sterility may be reversible.[17]

Monsanto Co. announced that results of the first year of a 2-year study on vinyl bromide showed that no danger to its plant workers existed at present exposure levels. Although a statistical increase in cancer was observed among rats inhaling 1,250 and 250 parts per million (ppm) vinyl bromide, no adverse effects occurred at levels of 100 and 50 ppm. Monsanto's plant exposure standard is 1 ppm, with actual exposure levels far less. Other firms sponsoring the study are The Dow Chemical Co., Dow-Badische Co., and Ethyl Corp.[18]

## PRICES

The average price of bulk elemental bromine, f.o.b. plant, as reported by producers in 1977 was 21.62 cents per pound, down 3% from the 1976 average price of 22.40 cents per pound. Quoted prices for bromine and selected compounds at yearend follow:

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

Source: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials. V. 213, No. 26, Dec. 26, 1977, pp. 26-37.

## FOREIGN TRADE

The quantity of elemental bromine and bromine contained in compounds that was exported by domestic bromine producers declined 11% in 1977 to 59 million pounds, and represented 14% of total bromine sold or used. The amount of exported elemental bromine rose 21%, but exports of bromine compounds were down 13%. The value of all bromine exports decreased 6%.

Bromine imports amounted to less than 0.2% of domestic consumption. About 95% of U.S. bromine imports were shipped from Israel.

The U.S. Treasury Department initiated a countervailing duty investigation into imports of bromine from Israel. A petition filed in July by Velsicol Chemical Corp. alleged that the Government of Israel made benefits available to Israeli manufacturers and exporters of bromine and bromine compounds which may constitute bounties or grants under U.S. law.[19]

**Table 4.—U.S. exports of bromine and bromine compounds**

(Thousand pounds and thousand dollars)

| Year | Elemental bromine | | Bromine compounds | | |
|---|---|---|---|---|---|
| | Quantity | Value | Gross weight | Contained bromine | Value |
| 1975 | 3,635 | 1,037 | 72,395 | 61,598 | 25,791 |
| 1976 | 4,435 | 944 | 74,063 | 62,589 | 29,244 |
| 1977 | 5,379 | 1,096 | 64,381 | 54,061 | 27,278 |

## WORLD REVIEW

The United States continued as the world leader in bromine production with about two-thirds of the total. Other principal bromine-producing nations included Israel, the United Kingdom, France, the U.S.S.R., and Japan.

**Canada.**—The Department of Fisheries and the Environment has banned the import, manufacture, and use of polybrominated biphenyl fire retardants.[20]

**Israel.**—Dead Sea Bromine Co., Ltd., commissioned a 110-ton-per-day chlorine plant at Sodom which will provide an assured supply of chlorine for existing and future bromine production. Present bromine capacity of 44,000 tons per year at the Sodom plant should reach 66,000 tons per year by yearend 1978, with further additions expected. A new bromine-compounds plant, due onstream at Ramat Hovev in 1978, will

consist of three single-product units—methyl bromide, tetrabromobisphenol-A, and inorganic bromides—plus several smaller multipurpose plants. Production of compounds will increase export value and reduce the transportation and distribution problems associated with the corrosive nature of elemental bromine.[21]

**Japan.**—Daikin Kogyo Co. brought a trifluorobromomethane plant onstream based on Produits Chimiques Ugine Kuhlmann technology. The compound is used as a fire-extinguishing fluid for high-value applications.[22]

**Netherlands.**—A bromine-derivatives plant constructed by Dead Sea Bromine Co., Ltd., of Israel came onstream at Terneuzen in October.[23]

**United Kingdom.**—ISC Chemicals, Ltd., brought a new plant onstream for the production of brominated diphenyl oxides, which are used as flame retardants in plastics.[24] Steetley Chemicals, Ltd., acquired a sodium and potassium bromides and bromates plant located at Gillingham from Akzo Chemie (UK) Ltd.[25]

**Table 5.—Bromine: World production, by country**

(Thousand pounds)

| Country[1] | 1975 | 1976 | 1977[p] |
|---|---|---|---|
| France | 36,971 | 33,466 | [e]35,000 |
| Germany, Federal Republic of | 9,414 | 9,158 | [e]9,000 |
| India[e] | 600 | 600 | 620 |
| Israel | 39,700 | 46,100 | 69,445 |
| Italy[2] | [r]1,477 | [e]1,500 | [e]1,500 |
| Japan[e] | 24,900 | 25,400 | 26,500 |
| Spain | 838 | [e]880 | 900 |
| U.S.S.R. | 28,000 | 30,000 | 33,000 |
| United Kingdom | 62,391 | 65,918 | 66,000 |
| United States[3] | 407,163 | 460,061 | 433,818 |
| Total | [r]611,454 | 673,083 | 675,783 |

[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]Figure for 1975 is from official Italian sources; figures for 1976 and 1977 are U.S. Bureau of Mines estimates. Officially reported figures for years prior to 1975 are as follows, in thousand pounds: 1971—11,515; 1972—9,965; 1973—3,073; 1974—1,512.

[3]Sold or used by producers.

## TECHNOLOGY

Bromine chloride could be an alternative to chlorine for disinfecting secondary waste water treatment plant effluent because of its greater effectiveness and lower toxicity. The rate of hydrolysis is faster than for either bromine or chlorine alone. Bromine chloride reacts with ammonia in waste water to form bromamines which are superior to corresponding chloramines in terms of bactericidal and viricidal activity.[26] Environmental officials of the State of Virginia and Ethyl Corp. were conducting tests with bromine chloride and chlorine at a Newport News sewage treatment plant to compare their effectiveness as well as the toxicity of treated effluent on fish.[27]

The Dow Chemical Co. introduced 2,2-dibromo-nitrilopropionamide as a fast-acting, broad-spectrum, industrial antimicrobial for water-cooling towers, paper mills, and aqueous metalworking fluids. The liquid rapidly decomposes in water to produce ammonia, carbon dioxide, and bromide ions.[28]

Researchers at the University of Illinois have found that perfluorooctyl bromide can effectively coat the gastrointestinal tract, temporarily blocking food absorption. In conjunction with a program of diet and exercise, the chemical may provide treatment for obesity. Apparently none of the perfluorooctyl bromide is absorbed into the bloodstream, but further tests are needed to determine the safety of the compound and whether it accumulates in any of the body tissues.[29]

[1]Physical scientist, Division of Nonmetallic Minerals.

[2]Chemical Marketing Reporter. Bromine Chemical Firm Bought by Great Lakes. V. 211, No. 25, June 20, 1977, pp. 7, 20.

Kampen, E. Progress Report From Great Lakes Chemical Corp. Oct. 28, 1977, 2 pp.

[3]Chemical Marketing Reporter. Emery, Dead Sea Group Sign a Marketing Pact. V. 211, No. 11, Mar. 14, 1977, pp. 3, 53.

[4]Chemical Marketing Reporter. EDB Review Ordered by Environmental Unit; Risks, Benefits Assessed. V. 212, No. 25, Dec. 19, 1977, pp. 5, 53.

Chemical Week. EPA Says: "Prove It!" V. 121, No. 25, Dec. 21, 1977, p. 17.

[5]Chemical & Engineering News. OSHA Issues Guidelines on EDB Exposure. V. 55, No. 51, Dec. 19, 1977, p. 13.

[6]Chemical & Engineering News. EPA Proposes List of Hazardous Pesticides. V. 55, No. 37, Sept. 12, 1977, p. 8.

[7]Chemical Marketing Reporter. Tris Ban Demanded by EDF. V. 211, No. 7, Feb. 14, 1977, pp. 3, 53.

[8]Chemical & Engineering News. Concentrates. Government. V. 55, No. 19, May 9, 1977, p. 7.

[9]Chemical Week. Tris Ban Nullified. V. 121, No. 1, July 6, 1977, p. 14.

[10]Chemical Marketing Reporter. CPSC Votes Rule for Child Sleepwear. V. 212, No. 12, Sept. 19, 1977, p. 68.

[11]Chemical Week. PBB Effects Cited. V. 121, No. 6, Aug. 10, 1977, p. 20.

[12]Chemical Week. Two Views on PBB. V. 121, No. 22, Nov. 30, 1977, p. 22

[13]Chemical & Engineering News. More Tests Link DBCP to Worker Sterility. V. 55, No. 36, Sept. 5, 1977, pp. 5-6.

Chemical Week. Workers Found Sterile. V. 121, No. 6, Aug. 10, 1977, p. 21.

[14]Chemical Week. More DBCP Problems. V. 121, No. 8, Aug. 24, 1977, p. 20.

[15]Chemical Marketing Reporter. OSHA Sets Workplace Rules for DBCP Worker Exposure. V. 212, No. 19, Nov. 7, 1977, pp. 7, 37.

Chemical Week. Crackdown on DBCP. V. 121, No. 11, Sept. 14, 1977, p. 19.

[16]Chemical & Engineering News. EPA Puts the Lid on DBCP. V. 55, No. 45, Nov. 7, 1977, p. 24.

[17]Chemical Marketing Reporter. DBCP Comparison Run by Dow Chemical Turns Up Reassuring Statistics on Workers. V. 212, No. 21, Nov. 21, 1977, p. 15.

[18]Chemical Marketing Reporter. Monsanto Reports Result of Vinyl Bromide Studies. V. 212, No. 20, Nov. 14, 1977, pp. 4, 42.

[19]Chemical Marketing Reporter. Bromine Probe Launched. V. 212, No. 15, Oct. 10, 1977, p. 7.

[20]European Chemical News. Technology. In Brief. V. 31, No. 813, Nov. 25, 1977, p. 26.

[21]European Chemical News. Israel Set To Expand Stake in World Bromines Market. V. 31, No. 800, Aug. 19/26, 1977, p. 21.

European Chemical News. Section II. Israel Chemical Industry Ready for New Export Drive. V. 31, No. 815, Dec. 9, 1977, p. 28.

[22]Chemical Age. New Daikin Plant. V. 115, No. 3047, Dec. 9, 1977, p. 3.

[23]Work cited in footnote 21.

[24]European Chemical News. New Flame Retardant Plant. V. 30, No. 772, Feb. 4, 1977, p. 16.

[25]European Chemical News. Akzo Sells to Steetley. V. 30, No. 786, May 13, 1977, p. 6.

[26]Chemical & Engineering News. Bromine Chloride Looks Good As Disinfectant. V. 55, No. 41, Oct. 10, 1977, p. 8.

[27]Chemical Week. Testing Disinfectant. V. 121, No. 1, July 6, 1977, p. 13.

[28]European Chemical News. Technology. In Brief. V. 30, No. 787, May 20, 1977, p. 36.

[29] Chemical Week. Chemical May Gain As Weight-Loss Aid. V. 121, No. 5, Aug. 3, 1977, pp. 33-34.