

Bromine

By Charles L. Klingman ¹

The bromine industry displayed surprising vitality in 1972. In spite of efforts to reduce atmospheric pollution from automobile exhausts, the predicted reduction in use of tetraethyl lead as an antiknock and ethylene dibromide as a lead scavenger in gasoline did not occur. There was, in fact, an increase of more than 13% in ethylene dibromide production in the United States, compared with that of 1971.

The increase was caused, to some extent, by increased exports of antiknock compounds, which include ethylene dibromide particularly to the United Kingdom and Brazil.² In 1972 total bromine production increased by 30,918,000 pounds over 1971 production. It is probable, however, that the large 1972 gain will not be maintained in 1973 and subsequent years.

DOMESTIC PRODUCTION

The State of Arkansas continued to gain in bromine production, with 1972 output about 17% above that of 1971. Michigan had a 6.6% reduction in output. The high bromine concentration and large reserves of Arkansas underground brine makes this State a logical location for future expansion. The brine wells of Michigan, by comparison, were not as free-flowing and had lower bromine content. Therefore, more wells had to be drilled and more brine had to be handled in Michigan per pound of bromine produced.

About 10% of the total bromine produced was sold in the elemental state to nonmanufacturers of bromine compounds. The fraction of the bromine production not used in the manufacture of compounds had remained relatively constant over the years.

The rate of bromine production in 1972 was 9% higher than that of 1971. The historic growth rate for the industry was about 7% per annum.

Table 1 presents data only on elemental bromine. The bromine classified as "used" in table 1 is the same bromine that appears in table 2 as the "bromine content" of manufactured compounds, except for processing losses and variations in stocks on hand. Table 2 deals exclusively with bromine compounds manufactured for the end use market.

In 1972 there were 10 bromine producing plants in three States operated by

¹ Physical scientist, Division of Nonmetallic Minerals.

² Chemical Engineering News, Surprise Comeback for Antiknock Compounds. V. 50, No. 47, Nov. 20, 1972, p. 6.

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)

	1971		1972	
	Quantity	Value	Quantity	Value
Sold.....	33,295	6,074	37,402	6,343
Used.....	322,651	55,676	349,462	57,346
Total.....	355,946	61,750	386,864	63,689

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

(Thousand pounds and thousand dollars)

	1971			1972		
	Quantity		Value	Quantity		Value
	Gross weight	Bromine content		Gross weight	Bromine content	
Ethylene dibromide.....	279,191	237,508	44,126	316,603	269,334	49,325
Methyl bromide.....	W	W	W	24,683	20,768	8,381
Other compounds ¹	105,132	75,804	45,926	84,962	58,934	39,770
Total.....	384,323	313,312	90,052	426,248	349,036	97,476

W Withheld to avoid disclosing individual company confidential data; included with "Other compounds."

¹ Includes ammonium, sodium, potassium, ethyl, and other bromides.

Table 3.—Domestic bromine producers

State	Company	County	Plant	Production source
Arkansas.....	Arkansas Chemicals, Inc.	Union.....	El Dorado.....	Well brines.
	Bromet Co.....	Columbia.....	Magnolia.....	Do.
	The Dow Chemical Co..	do.....	do.....	Do.
	Great Lakes Chemical Corp.	Union.....	El Dorado.....	Do.
California.....	Michigan Chemical Corp	do.....	do.....	Do.
	Kerr-McGee Chemical Corp.	San Bernardino..	Trona.....	Searles Lake brines.
Michigan.....	The Dow Chemical Co..	Mason.....	Ludington.....	Well brines.
	do.....	Midland.....	Midland.....	Do.
	Michigan Chemical Corp	Gratiot.....	St. Louis.....	Do.
	Morton Chemical Co...	Manistee.....	Manistee.....	Do.

seven companies. Two of these plants extracted elemental bromine only for sale and did not produce compounds. In addition,

other plants, not shown in table 3, made compounds only from purchased bromine.

CONSUMPTION AND USES

The Bureau of Mines has not surveyed the consumers of bromine and bromine compounds for many years and therefore does not have 1972 data on the final disposition of these products. It was known, however, that over 74% of U.S. production in 1972 went to the manufacture of ethylene dibromide. Most of this production was used in gasoline additives, but the compound was also used in agriculture and as a solvent. In 1971 there was great pessimism over the future of ethylene dibromide because of the Clean Air Act of 1970, which required a 90% reduction in harmful emissions from automobile exhausts by the year 1975. This pessimism, however, was apparently not justified by actual conditions because, in 1972, the industry rebuilt depleted inventories and de-

veloped new markets for bromine compounds.

The use of bromine in the manufacture of flame retardants was also believed to be on the increase. It was estimated that between 3% and 4% of total bromine production went into the manufacture of flame retardants in 1972.

Agricultural chemicals also increased, but the extent of the increase was not known. Methyl bromide was classed primarily as an agricultural chemical because of its extended use as a soil sterilant and insect fumigant. Many of the agricultural chemicals were proprietary, and their exact composition was not widely known.

Elemental bromine was utilized as a disinfectant, algacide, and as an oxidizing intermediate in the manufacture of other chemicals.

PRICES

Prices quoted at yearend for bromine marketing Reporter were as follows: and bromine compounds in Chemical Mar-

	Cents per pound
Bromine, purified:	
Cases, carlots, truckloads, delivered east of Rocky Mountains.....	49
Zone I: ¹	
Returnable drums, carlots, truckloads, delivered.....	30
Bulk tank car, tanktrucks (45,000-pound minimum), delivered.....	17
Ammonium bromide, national formulary (N.F.), granular drums, carlots, truckload, freight equalized.....	48.5
Bromochloromethane, drums, carlots, freight equalized.....	54.5
Tanks, same basis.....	53
Ethyl bromide, technical, 98% drums, carlots, freight allowed, East.....	68
Ethylene dibromide, drums, carlots, freight equalized.....	25
Tanks, freight equalized.....	20
Methyl bromide, distilled, tanks, 140,000-pound minimum, freight allowed.....	34
Potassium bromate, granular, powdered, 200-pound drums, carlots, freight allowed.....	64-77
Potassium bromide, N.F., granular, drums, carlots.....	49.5
Sodium bromide, N.F., granular, 400-pound drums, freight equalized.....	40

¹ Delivered prices for drums and bulk shipped west of Rockies, 1 cent per pound higher. Bulk tanktruck 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.

The average unit price of bromine made lower than the 1971 price. by manufacturers in 1972 was about 5%

FOREIGN TRADE

Exports of bromine and bromine compounds from the United States were not separately tabulated. Scattered reports in the press indicated that bromine exports increased in 1972, but few quantitative data were given.

There was only slight incentive to im-

port any bromine or bromine compounds into the United States in competition with the vast domestic supply and competitive price situation. The actual import figures for 1972 consisted mostly of potassium bromide from France and the United Kingdom. Its total valuation was under \$14,000.

WORLD REVIEW

The United States produced and consumed three-fourths of the world production of bromine in 1972.

Israel.—Israel has an enormous resource of bromine estimated at 1 billion tons, in the brine of the Dead Sea. This is a virtually inexhaustible supply when compared to the 1972 production of 30 million pounds of bromine. About one-third of this bromine was converted into compounds within the country, and over one-half of it was exported as elemental bromine to European countries. Elemental bromine was exported in lead-lined steel tanks that held 3.5 tons of bromine each.

Italy.—The bromine industry of Italy

was reported to be producing about 6 million pounds of bromine per year. A bromine plant of Margherita di Savoia Apulia, enlarged its production capacity. This plant extracted bromine from local saltbeds.

Japan.—Japan obtained more than 95% of its bromine from sea water and was reported to have produced about 27 million pounds in 1972. One company, Toyo Soda, produced more than 90% of the bromine in Japan and it recently increased its production capacity by 6.6 million pounds per year. Bromine exports from Japan were small, and total imports, mostly from the United States and from Israel were less than 5% of the Japanese consumption.

TECHNOLOGY

The mechanism by which brominated flame retardants and fire extinguishers op-

erate was explained clearly in a recent article by Walter M. Haessler of Florida

State Fire College.³ A bromide chemical such as bromotrifluoromethane, CF_3Br , interrupts the flame-combustion chain reaction in a dramatic fashion without removal of fuel or air. Under the heat of the flame, CF_3Br is partially ionized and the resultant bromine ion combines with a hydrogen ion of the flame to form hydrobromic acid. This compound, in turn, reacts with a hydroxyl ion of the flame to form

water and leaves a bromine ion ready for recycling through the same series. A single bromide ion may thus remove several of the combustion-chain-carrier ions, namely the hydrogen, H^+ , and the hydroxyl, OH^- ions. Other bromine-bearing chemicals react in a similar manner.

³ Chemical Engineering. Deskbook Issue. V. 80, No. 5, Feb. 26, 1973, pp. 95-100.