

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

Mirex is not known to occur in the environment as a natural product (IARC 1979c; Waters et al. 1977b). Although it was originally synthesized in 1946, mirex was not commercially introduced in the United States until 1959, when it was produced by the Allied Chemical Company under the name GC-1283 for use in pesticide formulations and as an industrial fire retardant under the trade name Dechlorane® (EPA 1978b; IARC 1979c; Waters et al. 1977b). Mirex was produced as a result of the dimerization of hexachlorocyclopentadiene in the presence of an aluminum chloride catalyst (IARC 1979c; Sittig 1980).

The technical grade of mirex consisted of a white crystalline solid in two particle size ranges, 5-10 and 40-70 microns (IARC 1979c). Technical grade preparations of mirex contained 95.18% mirex, with 2.58 mg/kg chlordecone as a contaminant (EPA 1978b; WHO 1984a). Several formulations of mirex have been prepared in the past for various pesticide uses. Some of the more commonly used formulations of mirex used as baits were made from corn cob grit impregnated with vegetable oil and various concentrations of mirex. Insect bait formulations for aerial or ground applications contained 0.3-0.5% mirex, and fire ant formulations contained 0.075-0.3% mirex (IARC 1979c).

Mirex is no longer produced commercially in the United States. Hooker Chemical Company (Niagara Falls, New York) manufactured and processed mirex from 1957 to 1976 (Lewis and Makarewicz 1988). An estimated 3.3 million pounds (1.5×10^6 kg) of mirex were produced by Hooker Chemical Company between 1959 and 1975, with peak production occurring between 1963 and 1968 (EPA 1978b). About 25% of the mirex produced was used as a pesticide and the remaining 75% was used as an industrial fire retardant additive (EPA 1978b). Hooker Chemical Company reported purchasing 1.5 million pounds of mirex (680,400 kg) from Nease Chemical Company during this period. The Nease Chemical Company of State College, Pennsylvania, manufactured mirex from 1966 to 1974 (EPA 1978b). Allied Chemical Company also manufactured technical grade mirex and mirex bait in Aberdeen, Mississippi (EPA 1978b), but Allied Chemical formally transferred all registrations on mirex, along with the right to manufacture and sell mirex bait, to the Mississippi Department of Agriculture on May 7, 1976 (IARC 1979c; Waters et al. 1977a, 1977b).

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Chlordecone is not known to occur in the environment as a natural product (IARC 1979a).

Chlordecone has been produced by reacting hexachlorocyclopentadiene and sulfur trioxide under heat and pressure in the presence of antimony pentachloride as a catalyst. The reaction product is hydrolyzed with aqueous alkali, neutralized with acid; chlordecone is recovered via centrifugation or filtration and hot air drying (Epstein 1978). Chlordecone was produced in 1951, patented in 1952, and introduced commercially in the United States by Allied Chemical in 1958 under the trade names Kepone® and GC-1189 (Epstein 1978; Huff and Gerstner 1978). The technical grade of chlordecone, which typically contained 94.5% chlordecone, was available in the United States until 1976 (IARC 1979a). Chlordecone was also found to be present in technical grade mirex at concentrations of up to 2.58 mg/kg and in mirex bait formulations at concentrations of up to 0.25 mg/kg (EPA 1978b; IARC 1979a).

Approximately 55 different commercial formulations of chlordecone have been prepared since its introduction in 1958 (Epstein 1978). The major form of chlordecone, which was used as a pesticide on food products, was a wettable powder (50% chlordecone) (Epstein 1978). Formulations of chlordecone commonly used for nonfood products were in the form of granules and dusts containing 5% or 10% active ingredient (Epstein 1978). Other formulations of chlordecone contained the following percentages of active ingredient: 0.125% (used in the United States in ant and roach traps), 5% (exported for banana and potato dusting), 25% (used in the United States in ant and roach bait), 50% (used to control mole crickets in Florida), and 90% (exported to Europe for conversion to kelevan for use on Colorado potato beetles in eastern European countries) (Epstein 1978).

Chlordecone is no longer produced commercially in the United States. Between 1951 and 1975, approximately 3.6 million pounds (1.6 million kg) of chlordecone were produced in the United States (Epstein 1978). During this period, Allied Chemical Company produced approximately 1.8 million pounds (816,500 kg) of chlordecone at plants in Claymont, Delaware; Marcus Hook, Pennsylvania; and Hopewell, Virginia. In 1974, because of increasing demand for chlordecone and a need to use their facility in Hopewell, Virginia, for other purposes, Allied Chemical transferred its chlordecone manufacturing to Life Sciences Products Company (EPA 1978b). Life Sciences Products produced an estimated 1.7 million pounds (771,000 kg) of chlordecone from November 1974 through July 1975 in Hopewell, Virginia (Epstein 1978). Hooker Chemical Company also produced approximately 49,680 (22,500 kg) pounds of chlordecone in the period from 1965 to 1967 at a plant at Niagara Falls, New York. Nease Chemical Company produced approximately 65,780 pounds (30,000 kg) of chlordecone between 1959 and 1966 at a plant in State College, Pennsylvania (Epstein 1978).

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4.2 IMPORT/EXPORT

No current data are available regarding import volumes of mirex. Mirex has reportedly been imported to the United States from Brazil, but data on the amounts of mirex imported are not available (DHHS 1985; IARC 1979c).

No current data are available regarding import volumes of chlordane.

Technical mirex and technical chlordane are not exported since these substances are no longer produced in the United States.

Over 90% of the mirex produced from the 1950s until 1975 was exported to Latin America, Europe, and Africa (Sterret and Boss 1977). No other historic data regarding the export of mirex were located.

Diluted technical grade chlordane (80% active ingredient) was exported to Europe, particularly Germany, in great quantities from 1951 to 1975 by the Allied Chemical Company (Epstein 1978) where the diluted technical product was converted to an adduct, kelevan. Approximately 90-99% of the total volume of chlordane produced during this time was exported to Europe, Asia, Latin America, and Africa (DHHS 1985; EPA 1978b).

4.3 USE

Because it is nonflammable, mirex was marketed primarily as a flame retardant additive in the United States from 1959 to 1972 under the trade name Dechlorane® for use in various coatings, plastics, rubber, paint, paper, and electrical goods (EPA 1978b; IARC 1979c; Kutz et al. 1985; Merck 1989; Verschueren 1983). Mirex was most commonly used in the 1960s as an insecticide to control the imported fire ants (*Solenopsis invicta* and *S. richteri*) in Alabama, Arkansas, Florida, Georgia, Louisiana, Mississippi, North Carolina, South Carolina, and Texas (Carlson et al. 1976; EPA 1978b; IARC 1979c; Waters et al. 1977a, 1977b). From 1962 to 1976, approximately 132 million acres (53.4 million hectares) in 9 states were treated with approximately 485,000 pounds (226,000 kg) of mirex at a rate of 4.2 g/hectare (later reduced to 1.16 g/hectare) (IARC 1979c). Mirex was chosen for fire ant eradication programs because of its effectiveness and selectiveness for ants (Carlson et al. 1976; Waters et al. 1977a, 1977b). It was originally applied aerially at concentrations of 0.3-0.5%.

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However, aerial application of mirex was replaced by mound application because of suspected toxicity to estuarine species and because the goal of the fire ant program was changed from eradication to selective control. Mirex was also used successfully in controlling populations of leaf cutter ants in South America, harvester termites in South Africa, Western harvester ants in the United States, mealybugs in pineapples in Hawaii, and yellowjacket wasps in the United States (EPA 1978b; IARC 1979c; Waters et al. 1977b). All registered products containing mirex were effectively canceled on December 1, 1977 (Sittig 1980). However, selected ground application was allowed until June 30 1978, at which time the product was banned in the United States with the exception of continued use in Hawaii on pineapples until stocks on hand were exhausted (EPA 1976; Holden 1976; Sittig 1980; Waters et al. 1977a).

Until August 1, 1976, chlordecone was registered in the United States for use on banana root borer (in the U.S. territory of Puerto Rico); this was its only registered food use. Additional registered formulations included non-food use on non-fruit bearing citrus trees to control rust mites; on tobacco to control tobacco and potato wireworms; and for control of the grass mole cricket, and various slugs, snails, and fire ants in buildings, lawns, and on ornamental shrubs (EPA 1978b; Epstein 1978; IARC 1979a). The highest reported concentration of chlordecone in a commercial product was 50%, which was used to control the grass mole cricket in Florida (Epstein 1978). Chlordecone has also been used in household products such as ant and roach traps at concentrations of approximately 0.125% (IARC 1979a). The concentration used in ant and roach bait was approximately 25% (Epstein 1978). All registered products containing chlordecone were effectively canceled as of May 1, 1978 (Sittig 1980).

4.4 DISPOSAL

Since mirex and chlordecone are not flammable and are very stable in the environment, many disposal methods investigated for these chemicals have proven unsuccessful (Sullivan and Krieger 1992; Tabaeiet al. 1991; Waters et al. 1977b).

Mirex is unaffected by hydrochloric, sulfuric, and nitric acids, and would be expected to be extremely resistant to oxidation except at the high temperatures of an efficient incinerator (EPA 1978b; Sittig 1980; WHO 1984a). Mirex is not identified as an EPA hazardous substance under SARA Title III (EPA 1993). A recommended method of disposal for mirex is incineration or long-term storage (Holloman et al. 1975; IARC 1979c). Polyethylene glycol or tetraethylene glycol and potassium

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hydroxide when used in combination with sodium borohydride or alkoxyborohydrides, produce a powerful reducing media which quantitatively destroys mirex at 70 °C. The reduction rate is further increased by using tetrahydrofuran and catalytic quantities of $\text{Bu}_3\text{SnH/AIBN}$ which produce 100% destruction of mirex to hexahydromirex within 1 hour at 58 °C (Tabaei et al. 1991).

Chlordecone is considered an EPA hazardous waste and must be disposed of according to EPA regulations (EPA 1980c). For more information on disposal regulations applicable to chlordecone, see Chapter 7. Degradation of chlordecone has been evaluated in the presence of molten sodium (Greer and Griwatz 1980). Addition of chlordecone to molten sodium at a temperature of 250 °C resulted in significant degradation of chlordecone with small quantities of <12 ppm observed in the reaction products. Microwave plasma has also been investigated as a potential disposal mechanism for chlordecone (DeZearn and Oberacker 1980). An estimated 99% decomposition was observed in a 5-kw microwave plasma system for 80% chlordecone solution, slurry, or solid. Another recommended disposal method for chlordecone is destruction in an incinerator at approximately 850 °C followed by off-gas scrubbing to absorb hydrogen chloride (IRPTC 1985).

Activated carbon adsorption has been investigated for the treatment of waste waters contaminated with chlordecone (EPA 1982b). The discharge of chlordecone in sewage disposal systems is not recommended, as it may destroy the bacteriological system (IRPTC 1985). Chlordecone as a waste product in water may be dehalogenated by a process involving ultraviolet light and hydrogen as a reductant. The reaction is pH dependent, and degradation is best when the system contains 5% sodium hydroxide. Using this method, 95-99% of chlordecone is removed within 90 minutes. The degradation products are the mono-, di-, tri-, tetra-, and pentahydro derivatives of chlordecone. This degradation method is applicable to chlordecone in hazardous wastes at concentrations in the ppm (mg/L) range and lower (Reimers et al. 1989; Sittig 1980).

