This cylindrical fungus-feeding beetle is admirably suited for living in round tunnels which it bores into forest trees for the propagation of its food.

The Inorganic Insecticides

R. H. Carter

Inorganic insecticides are of mineral origin, mainly compounds of antimony, arsenic, barium, boron, copper, fluorine, mercury, selenium, sulfur, thallium, and zinc, and elemental phosphorus and sulfur.

Antimony potassium tartrate, tartar emetic, $\text{K(SbO)}_3\text{C}_6\text{H}_4\text{O}_6\cdot\text{H}_2\text{O}$, is a white powder soluble in water. It is sometimes used as the toxic agent in ant poisons and for the control of thrips.

Arsenical compounds are among the most widely used inorganic insecticides. Recommendations for their use date from 1681. They were probably used before that. The poisonous properties of arsenic trioxide were well known during the Middle Ages and it was a favorite instrument of murder as practiced by the Borgias. This knowledge of the poisonous properties of arsenic compounds probably led to their use as insecticides.

Arsenic trioxide, $\text{As}_2\text{O}_3$, also called arsenuous oxide, is a white crystalline material sometimes referred to as white or gray arsenic. It is the starting material in the manufacture of arsenical compounds used as plant insecticides and it is sometimes used in weed killers. It is obtained from the flue dust from copper smelters. Our supply comes from domestic and foreign sources. It is sometimes used as the toxic agent in baits to control grasshoppers, cutworms, and other insects.

The calcium arsenate that is sold commercially as an insecticide is not a single chemical compound but a complex mixture of several calcium arsenates and an excess of calcium hydroxide. The material is made from arsenic trioxide by first oxidizing it to arsenic.
pentoxide with nitric acid and then reacting the solution of arsenic pentoxide or arsenic acid with a slurry of calcium hydroxide. The conditions of temperature, concentration, and duration of reaction are important because of their influence on the physical nature of the product. Commercial calcium arsenate generally is colored pink and is alkaline in reaction. It is a finely divided powder. It has been used extensively against certain insects affecting field crops, especially cotton. It cannot be used safely on apples, peaches, beans, and some other crops because of its burning effect on the foliage and fruit.

Calcium arsenate-calcium arsenite mixture is sold under the name London purple. It has some use for poisoning insects on cotton.

Among the insecticidal materials containing copper and arsenic, copper-aceto-arsenite (or Paris green), 3 Cu\((\text{AsO}_2)\_2\cdot\text{Cu(C}_2\text{H}_4\text{O}_2)\_2\), is by far the most important. It has been used as an insecticide since about 1870. For many years it was the most widely used insecticide in the United States for control of Colorado potato beetles. It has largely been supplanted by some of the newer materials, but approximately 4 million pounds are used annually by farmers and gardeners.

Copper arsenite, \(\text{Cu}_3(\text{AsO}_3)_2\cdot\text{xH}_2\text{O}\); copper meta arsenite, \(\text{Cu}(\text{AsO}_3)\_2\cdot\text{H}_2\text{O}\); and basic copper arsenate, \(\text{Cu}_3(\text{AsO}_4)_2\cdot\text{Cu(OH)}\,2\), have all been proposed as insecticides but have not been used to any extent. Compounds similar to Paris green made from organic acids other than acetic have also been tested but have not developed into commercial use.

Several chemically different compounds are known as lead arsenate. Two of them are commonly used as insecticides. Acid lead arsenate (dilead-ortho arsenate), \(\text{PbHAsO}_4\), is formed by the action of arsenic acid on litharge salt. It is a white powder, insoluble in water. Basic lead arsenate (lead hydroxy arsenate), \(\text{Pb}_3(\text{PbOH})_2(\text{AsO}_4)_3\), also is a white insoluble powder.

Both forms should contain very little water-soluble arsenic pentoxide in order to minimize plant damage. Generally they are much less apt to burn plant foliage than is calcium arsenate or Paris green. The basic compound is safer to use on growing plants in some localities (for example, the foggy regions of California) than is the acid compound, but in general it is not so toxic to insects.

Acid lead arsenate is used extensively to control chewing insects on fruits, such as apple and pear, on flowers, trees, and shrubs, and on vegetables, such as potato and tomato. It also has extensive use in treating soil to control Japanese beetle and Asiatic garden beetle larvae and related soil-infesting forms.

A number of United States patents cover processes for the manufacture of magnesium arsenates for use as insecticides. The magnesium arsenates tested as insecticides consisted generally of the dimagnesium arsenate, \(\text{MgHAsO}_4\), the trimagnesium arsenate, \(\text{Mg}_3(\text{AsO}_4)_2\), or the pyroarsenate, \(\text{Mg}_5\text{As}_2\text{O}_7\), with varying amounts of water of crystallization and excess magnesium oxide or hydroxide.

Magnesium arsenate has been tested against a large number of insects affecting fruits and vegetables and at one time was recommended for the control of the Mexican bean beetle, but its use has declined.

A crude manganese arsenate once was proposed as an insecticide for combating caterpillars on tobacco because its brown color made it less conspicuous on cured tobacco leaves than the white lead arsenate.

Sodium arsenite is formed by dissolving arsenic trioxide in sodium hydroxide solution. Depending on the ratios of the reacting materials, the products range from the monosodium compound, \(\text{NaAsO}_2\), to the trisodium arsenite, \(\text{Na}_3\text{AsO}_3\). A standard formula for making so-called liquid sodium arsenite requires 4 pounds of white arsenic and 1 pound of sodium hydroxide per gallon of solution.
Sodium arsenite is not used as an insecticide on field crops because of its corrosive action. It is used as an ingredient in poison baits for grasshoppers, crickets, roaches, ants, and other insects, and in stock dips. It has been used extensively as a weed killer.

Zinc meta arsenite, \( \text{Zn(AsO}_2\text{)}_2 \), is formed when a soluble zinc salt is reacted with arsenious acid or white arsenic under carefully controlled conditions, as it is soluble in either acid or alkaline solutions.

Zinc arsenite is used in wood preservation but is not used in household insecticides or as a constituent of formulations to be used on field crops.

Zinc arsenate, \( \text{Zn}_3(\text{AsO}_4\text{)}_2 \), has been proposed in place of lead arsenate in codling moth control, principally because it avoids lead residues.

Arsenates and arsenites of many of the other elements have been investigated for insecticidal use but none has been developed into satisfactory materials. Organic arsenicals have likewise failed to find a place as insecticides.

Barium carbonate, \( \text{BaCO}_3 \), is a white, finely divided powder which is sometimes used as the toxic agent in rat poisons.

Borax, \( \text{Na}_2\text{B}_4\text{O}_7 \), and boric acid, \( \text{H}_3\text{BO}_3 \), have been used in roach powders, but more effective compounds, such as sodium fluoride, DDT, and chlordane, are available now.

Bordeaux, or bordeaux mixture, is the name applied to the compounds formed by reacting dilute solutions of copper sulfate with calcium hydroxide suspensions. If equivalent amounts of the two materials are used, an intimate mixture of the copper hydroxide, \( \text{Cu(OH)}_2 \), and calcium sulfate, \( \text{CaSO}_4 \), is formed. This suspension has a blue color and leaves a bluish-white deposit on sprayed surfaces.

Bordeaux mixture is primarily a fungicide but is often used in connection with insecticides such as nicotine, lead arsenate, and calcium arsenate. It is sometimes used to control the potato leafhopper and as a repellent for flea beetles on various vegetables and flowering plants. It is sometimes used also as an emulsifier for lubricating-oil sprays applied to fruit trees, such as apple, pear, quince, and peach, when they are dormant.

Several other copper compounds, including the oxide, oxychloride, phosphate, quinolinolate, silicate, basic sulfate, and cyanide are used as spray materials. They have little insecticidal value but are potent fungicides.

Hydrated lime, or calcium hydroxide \( \text{Ca(OH)}_2 \), is used in the manufacture of lime-sulfur, calcium arsenate, and bordeaux mixture. When limestone, \( \text{CaCO}_3 \), is heated, the carbon dioxide is driven off, leaving the product known as quicklime, \( \text{CaO} \). When quicklime reacts with water, heat is evolved and the resulting product is hydrated lime, \( \text{Ca(OH)}_2 \). Hydrated lime is not primarily an insecticide but is used as a safener with some of the arsenical sprays.

Calcium cyanide, \( \text{Ca(CN)}_2 \), reacts slowly with moisture in the air to liberate hydrocyanic acid gas, a highly toxic organic compound used as an insecticidal fumigant.

Compounds that contain fluorine have been in use as insecticides since about 1890. Barium fluosilicate, \( \text{BaSiF}_6 \), a white, finely divided powder, has been tested extensively as a substitute for arsenicals in the control of fruit and vegetable crop insects. It has some value in the control of flea beetles, blister beetles, Mexican bean beetle, and others.

Cryolite, or sodium fluoaluminate, \( \text{Na}_3\text{AlF}_6 \), is a white crystalline material. Natural cryolite (ice-stone) is mined in Greenland and imported into this country. Synthetic cryolite, of similar composition, has been manufactured and sold for insecticidal use. For most uses there is little difference in their effectiveness. Large quantities have been used on codling moth in the Pacific Northwest and on the tomato pinworm, tomato fruitworm, lima-bean pod borer, corn earworm, Mexican bean beetle, walnut husk fly, pepper weevil, cabbage caterpillars, blister
beetles, and flea beetles. It is generally used as a spray but may be diluted with talc, pyrophyllite, or other diluents to form a dust.

Sodium fluoride, NaF, is a white powder. Sometimes it is colored green or blue so it will not be mistaken for baking soda. It is used extensively as a roach powder and is effective against chicken and animal lice of various kinds. It causes serious damage on plants.

Sodium fluosilicate, \(\text{Na}_2\text{SiF}_6\), is a white crystalline powder much less soluble than sodium fluoride in water. It has been used as a dust and spray in the control of some insects on field crops, as a poison in cutworm, mole cricket, and grasshopper baits and is effective as a mothproofing agent for woollen fabrics. A large number of fluorine compounds, both inorganic and organic, have been patented for use as mothproofing agents.

Some compounds of mercury are used as insecticides. Mercuric chloride (corrosive sublimate), HgCl₂, and mercurous chloride (calomel), HgCl, are used against fungus gnats, earthworms, cabbage maggotts, and onion maggotts. Mercuric chloride is also used for the treatment of dormant gladiolus corms and as a fungicide and germicide. Formulations containing mercury compounds are sometimes used to control insects affecting man and animals.

Pastes containing elemental phosphorus are made by grinding yellow phosphorus in the presence of water and then mixing with flour. Glycerin is sometimes used as an ingredient. Such pastes are effective against the American cockroach.

Selenium compounds have been tested as insecticides, but because of their toxicity to man their use is not recommended on crops intended for human or animal consumption.

Sodium selenate, \(\text{Na}_2\text{SeO}_4\), is a water-soluble salt. Plants can take it up from the soil in sufficient amounts to kill aphids feeding on the plants. A product containing selenium and sulfur of the formula \((\text{KNH}_2\text{S})_2\text{Se}\) has been used in the Pacific Northwest to combat mites on apples and grapes.

The use of elemental sulfur and alkaline sulfides as insecticides and fungicides on field crops and in greenhouses dates back many years. The materials are elemental sulfur, sulfides, polysulfides or salts of some of the oxygen acids of sulfur. Elemental sulfur is used alone as a dust or in combination with other insecticides with many of which it is compatible. The sulfur is reduced to a very fine state of subdivision by grinding, precipitation, or sublimation.

Dusting sulfur, or conditioned sulfur, is finely divided elemental sulfur made into a free-flowing powder by the admixture of 1 to 5 percent of clay, talc, gypsum, tri-calcium phosphate, or similar materials. Flotation sulfur, colloidal sulfur, and precipitated sulfur refer to finely divided sulfur formed as a result of chemical reactions of sulfur-containing compounds with other compounds. Wettable sulfur is finely divided sulfur that has been treated with wetting agents of various kinds to render it wettable by water and thus susceptible to suspension in spray formulations. The alkaline sulfides and polysulfides, sometimes referred to as soluble sulfurs, are prepared by the reduction of the salts of some of the oxygen acids of sulfur or by the action of alkaline solutions on elemental sulfur. The most important compounds of this class are the polysulfides of calcium, ammonium, barium, and sodium.

Calcium monosulfide, CaS, has been used to a limited extent. It is formed by the reduction of calcium sulfate. Liquid lime-sulfur or calcium polysulfide, \(\text{CaS}_x\), is formed by the reactions between calcium hydroxide and elemental sulfur when they are boiled together in water. It is assumed to contain a mixture of the sulfides up to and including the pentasulfide, \(\text{CaS}_5\). The theoretical reaction between 3 moles of hydrated lime, \(\text{Ca(OH)}_2\), and 12 moles of sulfur results in the formation of 2 moles of calcium pentasulfide, \(\text{CaS}_5\), 1 mole of calcium thiosulfate, \(\text{CaS}_2\text{O}_3\), and 3 moles of water, \(\text{H}_2\text{O}\).
Dry lime-sulfur is made by adding a stabilizer such as cane sugar to liquid lime-sulfur and evaporating to dryness. Self-boiled lime-sulfur is made by utilizing the heat of hydration or slaking of quicklime, CaO, to carry on the reactions with sulfur.

Ammonium polysulfide and sodium polysulfide are made by passing hydrogen sulfide gas, H₂S, into ammonium or sodium hydroxide containing excess sulfur. It is supposed that the chemical reactions are similar to those taking place in the preparation of lime-sulfur.

Sulfur is used under some conditions for the control of potato leafhopper, the cotton fleahopper, tomato psyllid, mites, and plant bugs.

Organic sulfur compounds, including thiocyanates, xanthates, and thiram disulfides, have some insecticidal properties although they are used largely as fungicides.

Sulfur dioxide, SO₂, made by burning sulfur, is sometimes used to kill insects in closed spaces.

Thallium sulfate, Tl₂SO₄, sometimes is used as the toxic agent in ant poisons.

Several zinc compounds are in limited use as insecticides. Zinc sulfate, ZnSO₄, is sometimes used in place of copper sulfate in reactions with hydrated lime to form a zinc bordeaux mixture that has special uses. Zinc chloride, ZnCl₂, is used to protect against termites.

**Insecticides From Plants**

**Louis Feinstein**

More than 2,000 species of plants are said to have some value as insect killers. They belong to 170-odd families. Commercial insecticides of plant origin are found in five families: Nicotine in the Solanaceae family; pyrethrum in Compositae; derris, cube, and timbo in Leguminosae; hellebore in Liliaceae; and anabasine in Chenopodiaceae. Anabasine is also found in Solanaceae.

Who first discovered the insecticidal value of plants is not known. The Romans divided poisons into three groups, animal, plant, and mineral. They used two species of false hellebore in medicines and in rat and mice powders and insecticides. The Chinese discovered the insecticidal value of derris.

Chemists in the Bureau of Entomology and Plant Quarantine since 1927 have conducted research on the principal insecticides of plant origin, such as nicotine, nornicotine, anabasine, rotenone, deguelin and related rotenoids, quassin, and the pyrethrins. They also have worked on more than 450 plants in an effort to discover new sources of these and other insecticides, as well as attractants, repellents, and adjuvants. They have learned that many of the species in the 170 families do not warrant further investigation and that botanical classification is not a dependable guide in the search for insecticidal plants.

Plant insecticides are only a small fraction of the insecticidal material used each year. Yet in the development of new insecticides they deserve careful consideration: Often they are highly effective against many insect enemies that are not successfully controlled by inorganic insecticides. The plant insecticides often are relatively nontoxic to