Chemistry and Uses of
PESTICIDES

by E. R. deONG

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SECOND EDITION
of "Chemistry and Uses of Insecticides"

by

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To MY WIFE

AND OUR DAUGHTER

GENEVIEVE

IN APPRECIATION OF THEIR ASSISTANCE

PREFACE

The title and scope of this book has been changed from "Insecticides" to "Pesticides." Several years ago, the latter term became the official name for all chemicals used as pest control agents: insecticides, repellents, fungicides, seed protectants, herbicides (weed killers), and rodenticides. Some of the properties and the established uses of the various chemicals are given, together with the more recent advances in research. Many references to important literature are included in each chapter.

The entire text has been rewritten and brought up to date. The chapters on organic pesticides are completely revised and expanded to include the established compounds, many of which show not only increased efficacy but frequently reduced hazard to the operator. The pesticide tolerances established (1955) by the Food and Drug Administration of the U. S. Department of Health, Education and Welfare are listed, as well as the materials requiring no tolerances and those with zero tolerances.

Chemical and physical data, toxicology and compatibility are given for the benefit of the college instructor, manufacturer and research worker. The breadth of coverage makes the book especially useful for the instructor of vocational agriculture. The farmer will find much detailed instruction on the use of both the new and the older compounds. For the general reader there are guides in the index to what may seem a bewildering mass of names. Under the subject headings of "wood preservatives," "weed killers" and "industrial fungicides" are grouped the names of chemicals suitable for such purposes.

The details of pesticide dosage and time of application being extremely variable, the author disclaims any responsibility for the correctness of dosages or use of materials for any specific occasion. Local agricultural officers or experienced operators should be consulted for such information. Proprietary names are given only when their use has been established in the literature on the subject. The inclusion of such names does not constitute an endorsement of same nor does the omission of any well-known name minimize its value.

It is a pleasure to thank Dr. S. A. Hall, Chemist, Pesticide Chemicals Research, U. S. Department of Agriculture for certain data furnished and the criticism of Chapters 9 and 10, and also Allen B. Lemmon, Chief, Bureau of Chemistry of the California State Department of Agriculture, for criticism of the first few chapters.

The following publications have been used as references: "Pesticide Official Publication" (1954, 1955) from the Association of American Pesticide Control Officials, Incorporated; "Guide to Chemicals Used in Crop Protection" by Hubert Martin, Canada Department of Agriculture (1954); and the "Compatibility Chart for Insecticides and Fungicides," published by the American Fruit Grower (1954).

Albany, California
April, 1956

E. R. de Ong

CONTENTS

1: INTRODUCTION

Man is surrounded by enemies: he is fighting constantly against weeds, insects, plant diseases and rodents. Billions of dollars worth of growing crops are lost to these enemies annually. Rodents, insects and molds cause annual losses throughout the world of 33 million tons of stored grain and rice, according to estimates of the United Nations Food and Agriculture Organization. This is a year's supply of food for 150 million people. Losses of stored grain in the United States alone are estimated at 18 million tons. To hunger resulting from food losses must be added the illnesses and deaths caused by disease-carrying insects. This group, including a number of flies, mosquitoes and lice, is being controlled in the United States, and malaria, dysentery and typhus fever are declining. In other parts of the world, however, the fight is only beginning.

Until the middle of the ninteenth century, man was helpless against the mass attack of insects. The early settlements west of the Mississippi were subject to "grasshopper years," when migrating swarms of locusts (grasshoppers) descended from the Colorado foothills in clouds so dense that the sun was darkened. Wherever they touched, every green thing and even the bark on the trees was devoured. The helpless settlers could only stand and watch the destruction. The building of the Panama Canal was delayed 35 years by epidemics of yellow fever. Success came only with the discovery that the *Aedes* mosquito was the carrier of the deadly disease, followed by the development of suitable means for combating it.

Many forms of combat are used in the warfare against pests: sanitation, building devices, plant breeding, natural control by growing beneficial insects, and of course chemicals. The most practical approach to pest control is often that of sanitation: the removal of breeding places of insects and rodents, draining pools of water where mosquitoes breed, careful building to exclude termites, other insects and rodents. Resistant types of grain and vegetables are being developed, but this is a slow approach. The growing of insects that feed on injurious forms has been successful in a limited way but as yet has not been widely developed. All these methods have value, but for immediate protection in many fields, dependence must first be placed on the use of chemicals.

To be effective as a control agent, the chemical must first of all be toxic. Only after many years was it recognized that the chemical itself must also be one that could be used without being harmful to man. The first use of toxic chemicals was to kill insects; thus the term "insecticide" has to a greater or less degree been applied to all materials used as control agents The Federal Insecticide Act of 1910 includes both insecticides and fungicides. The Federal Insecticide, Fungicide and Rodenticide Act (1947) uses "economic poison" to apply to all three groups, and in addition includes herbicides. The term "pesticide" is now used officially to cover all toxic chemicals, whether used against insects, fungi, weeds or rodents and other specified animals.

Early Uses of Insecticides

In the 1860's the invasion of the potato fields of the Mississippi by the Colorado potato beetle, *Leptinotarsa decemlineata*, gave rise to the first general use of an insecticide. An arsenical known as Paris green, an imported dye, was used so successfully as a plant protectant that orchardists next adopted it in their fight against the codling moth, *Carpocapsa pomonella*, whose larvae mine apples and pears. Paris green became so popular that by 1900 its purity became the basis for the first State insecticide laws. Six of the orchard-growing states passed laws designed to give protection against adulteration and poorly made stocks of Paris green that might be ineffective or injurious to plants (Haywood, 1903). None of these acts, however, made provision for public health, either in regulating the amounts applied or the possible danger of minute amounts (residues) remaining on the marketed fruit. This lack of care in protecting the operator and the public against the dangerous qualities of the insecticide is the chief difference between the early laws and present ones.

The state laws were gradually extended to cover a wide range of compounds almost all of which are dangerous unless carefully handled. Arsenic, combined with copper, lead and calcium, heads the list; but in addition there were phosphorus pastes for ants, roaches and rodents; strychnine in rodent baits; thallium in ant and rodent baits and selenium for certain plant-feeding mites. Mercury, both as corrosive sublimate and calomel, was recommended both as an insect repellent and later as a seed disinfectant. Sodium fluoride was the common ant poison and sodium and calcium cyanide the universal fumigants. Concentrated nicotine was in wide use both on the farm and in the suburban garden. These materials were sold generally with but little regulation or safety warning.

The Beginning of Safety Regulations

The trend toward the safer use of insecticides and concern for public health began about 1925. It was started in 1919 by the embargo of a shipment of western pears. Illness had been reported in England as being caused by eating apples from the United States. To meet this difficulty, the Federal Food and Drug Administration ruled in 1927 that fruit in interstate shipments should not show more than 0.025 grain of arsenic trioxide per pound of fruit (3.57 parts per million). Food exceeding established tolerances is subject to seizure. To meet this requirement, the growers were compelled to use chemical washes in cleaning their fruit. This practice has now become quite general and adds to the attractiveness of the marketed apples and pears. The remarkable success attained from this practice is shown in five annual reports of the Food and Drug Administration (1945 to 1950 inclusive). During this period there were only 34 seizures recorded as due to insecticidal residues, all being for lead arsenate. There were no seizures in 1950. During this same period there were hundreds of seizures for decomposition or insect, rodent or other filth contamination of food (Decker, 1951).

Another progressive step in the safety campaign was the development of two plant extracts which are effective insecticides but only slightly toxic to man. Both materials are safe to apply to growing crops up to within a few days of harvest, since they quickly break down into harmless compounds. The first, marketed as "pyrethrins I and II," is derived from a chrysanthemum-like flower. The extracts have been standardized and are now used in many forms of commercial extracts, including both fly sprays and others for garden use. The second material, known as "rotenone," is derived from certain tropical plants, *Derris*, *Lonchocarpus*, *Tephrosia* and others. Both the ground root, unextracted, and standardized extractives are used as garden applications and for the cattle grub, *Hypoderma*.

Synthetic Organic Pesticides

Prior to World War II, pest control in the United States, Canada and much of Europe had almost reached a stalemate. Success in one field was met with failure in another. Malaria, yellow fever and typhus fever had been checked in the more progressive communities, but lurked beyond their boundaries always ready to strike. Bubonic plague flared occasionally in the western United States, held in check only by a continuous fight against the flea-carrying rat and ground squirrel, while millions in parts of Asia, Africa and the Island Empires sickened and died. Our farmers, gardeners and housekeepers fought unending, expensive and almost hopeless campaigns against their enemy pests. The codling moth not only took a heavy toll of apples and pears but extended its field to the English walnut, the apricot and other fruits. Grasshopper plagues may be checked, but the corn borer, introduced from Europe, has spread through the corn belt, lowering yields and increasing the growing expense. The Texas cattle fever tick has been controlled, but swarms of flies, wherever livestock was kept, reduced the yield of milk and meat. Potato and tomato blight wiped out thousands of acres of promising fields with diastrous results to the grower and higher prices to the consumer. Brown rot takes its annual toll of peaches, plums and apricots. Weeds spread over some of our best farm land.

The war years brought two new synthetic organic compounds, the insecticide DDT and the herbicide 2,4-D which with related compounds have revolutionized pest control and brought new hope in the war against pests. DDT, first used in this country by the military for delousing as a preventive of typhus fever, is now found on almost every farm and home garden. The house fly, apparently conquered by DDT but later developing resistance to it, is being controlled by phosphate insecticides used in baits. Mosquitoes have been proved more susceptible to DDT, and malaria—one of the curses of mankind—has been checked, not only in the United States but in many of the malarial regions of the world. Since the introduction of DDT in 1943, many other very effective pesticides are being marketed or are now in the developmental stage, and these have broadened the field of pest control. There are new types of organic fungicides that are more effective in specific fields than the old standard ones of copper and sulfur. New rodenticides are now available that are more effective for some purposes than strychnine, and safer to handle.

What DDT and related compounds have done in the control of insects, 2,4-D has done to the undesired plants known as "weeds." This compound will kill or check the growth of many of the braod-leaved plants, such as dandelion and wild mustard. Rice and grain growers are using it increasingly to check weedy growth in the fields. Thickets of brush and brambles are cleared with one or two timely applications of 2,4-D and related compounds.

Safety Requirements

Despite the increased efficiency of the new synthetic organic pesticides, there has been a striking reduction in the hazards of chemical pest control as shown in Tables 1, 2 and 3. These are records of accidental deaths in the United States from 1933 to 1950, according to various methods of segregation. All records of deaths are from the published reports of the United States Public Health Service of the Department of Health, Education and Public Welfare (Anonymous, 1949, 1952) to which the Department kindly added the records for 1947, 1948 and 1950. The data in Table 1 contain only three items used chiefly as pesticides, namely arsenic, strychnine, and nicotine. As these were not segregated as pesticides, the data include other usage, but this may balance data for other pesticides not given under any of the headings. A healthy downward trend in the number of fatalities due to arsenic, strychnine and nicotine is seen for the period of 1933 to 1950. This is due in part to the cooperative efforts of state officials and the manu-

TABLE 1. NUMBER OF DEATHS FROM ACUTE ACCIDENTAL POISONING BY SPECIFIED SOLIDS OR LIQUIDS: UNITED STATES 1933–1950

Cause of Death	1950	1949	1948	1947	1946	1945	1944	1943	1942
Total	1584	1634	1436	1504	1536	1532	1381	1254	1193
Arsenic and antimony*	58	57	63	48	63	58	77	85	71
Strychnine	23	22	30	37	45	52	54	54	50
Nicotine	—	7	8	10	11	9	12	6	12
Alcohol	466	239	140	178	139	188	152	96	74
Aspirin & other salicylates	99	70	—	—	—	—	—	—	—
Barbituric acid & derivatives	409	466	419	418	436	392	270	226	197
Lye and potash	—	—	74	72	90	79	74	88	87
All other and unspecified substances (solids, liquids)	749	773	702	741	752	754	742	699	702

Cause of Death	1941	1940	1939	1938	1937	1936	1935	1934	1933
Total	1191	1324	1371	1437	1482	1465	1411	1417	1490
Arsenic and compounds	70	73	109	87	78	90	89	73	67
Strychnine	40	67	82	92	124	108	82	113	113
Nicotine	7	7	7	10	16	10	14	41	35
Alcohol	132	139	127	154	105	99	149	142	198
Barbituric acid and derivatives	232	246	201	199	195	165	133	145	107
Lye and potash	94	111	120	113	147	139	59	64	69
All other and unspecified substances	616	681	725	782	817	854	885	839	901

* Data for antimony is combined with arsenical compounds for 1948, 1949.

TABLE 2. DEATHS FROM ACCIDENTAL POISONING BY SPECIFIED GASES AND VAPORS: UNITED STATES, 1949 AND 1950

Cause of Death	1949	1950
Utility (illuminating) gas	967	1,012
Motor-vehicle exhaust gas	244	351
Other carbon monoxide gas	263	251
Cyanide gas	5	9
Other specified gases and vapors	109	105
Unspecified gases and vapors	29	41
Total	1,617	1,769

TABLE 3. DEATHS FROM ACCIDENTAL POISONING BY OTHER AND UNSPECIFED SOLID AND LIQUID SUBSTANCES: UNITED STATES, 1949

Cause of Death	Number
Chlordane	1
Copper (Paris green)	2
DDT	6
Nicotine	7
Parathion (tetraethyl pyrophosphate)	6
Rat poison*	17
Roach powder	3
Toxaphene (chlorinated camphene)	2
Weed poison	1
Alcohol and barbiturates	8
Chlorine (bleaching solutions)	6
Furniture polish (cedar oil)	12
Home permanent wave solutions	4
Poison, chemical (unspecified)	55
Other and unspecified	37
Total	167

* Four of these were reported to contain phosphorus.

facturers in developing greater care in the handling and use of dangerous compounds and to the agitation over spray residues on treated fruit. The impact of the Federal Insecticide, Fungicide and Rodenticide Act of 1947 and the substitution of organic for inorganic compounds is evident.

In contrast to the downward trend of fatalities in the use of pesticides is the rapid increase of accidental deaths due to barbiturates and aspirin. Note also the tremendous difference in mortality rates between utility (illuminating) gas and the fumigant cyanide gas. Sodium and potassium cyanide are not listed as pesticides because of their wide use in industry.

As a further aid toward safeguarding the user of pesticides, plans are developing for a central laboratory, approved by the American Medical Association, to furnish first aid treatment and follow-up treatment advice to the medical profession throughout the United States on a 24-hour day service. This would be available for call from all physicians and hospitals for advice on the treatment of accidental exposure (Gardner, 1954).

The radical changes in the requirements under which pesticides may be marketed as incorporated in the Insecticide, Fungicide and Rodenticide Act of 1947 have led to even further improvements in the safety situation. All products offered for sale in the interstate trade must be registered with the United States Department of Agriculture at Washington with a fully warranted statement of active and inert ingredients. Materials that have years of safe and effective usage behind them are registered without question. New materials must furnish satisfactory evidence of effectiveness for the purpose sold, and if there is any question as to safety in its use, confirmatory data are required. Such tests include both short and long term exposures to varying amounts of residues. The label must give directions for use, with safety warnings if necessary, and the highly dangerous ones must be appropriately marked and the antidote given. Toxic white powders must be colored or discolored so they may be readily recognized.

The chlorinated hydrocarbon insecticides have been largely restricted in their use on dairy animals and for cattle being fed for the market. Milk showing detectable signs of these chemicals is not allowed to be marketed. These measures are purely precautionary for to date no injury is known to have occurred to any persons consuming such milk or the meat from animals showing DDT or similar compounds absorbed in the body fat. In a recent world review of the Toxic Hazards of Certain Pesticides to Man, Barnes (1953) states that "There is a possible risk to health from the ingestion of small quantities of pesticides in food, but there is no evidence that anyone has suffered illness from this cause." There are instances of illness to those working in recently treated crops but "no fatal cases of poisoning have yet occurred from contact in this way."

In 1954 the Federal Food, Drugs and Cosmetic Act was amended (Miller bill) to provide methods for controlling the amount of residues of pesticides on raw agricultural products, such tolerance to be established within 90 days after the Secretary of Agriculture has filed a certificate of usefulness for the product. There will thus be a dual system of control over chemicals used for pest control on food or growing food crops. The United States Department of Agriculture is to be responsible for maintaining warranted standards of purity, requiring demonstrable proof of the value for purposes claimed, and harmlessness when used as directed, both to the operator and the effect on plants. The Food and Drug Administration shall then pass on the safety to human beings of any residual chemicals in food products and shall establish tolerances for safe amounts, if any. The establishment of such dual control over the development and use of pesticidal chemicals will do much to further the present supervision. Such regulation, wisely administered, will avoid undue restrictions on the expense of research in the development of needed chemical products.

Chemical and Physical Properties of Pesticide Formulations

The value of a toxic chemical as a pesticide is influenced by its chemical and physical properties, the diluent in which it is dissolved or suspended, its reaction with water, if present, and the compatibility with other pesticides with which it may be combined. These complex factors are being recognized as worthy of careful study, not only as a means of greater efficiency but of explaining reports of failure in control. Ebeling and Pence (1953) showed a difference in the effectiveness of an insecticide between insects (fruit flies) that do not feed on the substrate of the leaf and the sucking phytophagous species (mites) that contact the surface residues and also obtain the toxicant by sucking up the contaminated sap. The former contact the residue only through the tarsi and efficiency is determined by the length of the period of contact and the activity of the insect. The sucking forms (mites) not only contact the surface residue but also suck up the contaminated sap beneath the plant cuticle. The residual type of application was found to be superior to the topical (directly to the mite) treatment, the former having both surface and subcuticular effects. Emulsions were more effective than suspensions as topical treatments. Suspensions tended to give longer residual values. Acaricides (miticides) were quite effective when applied to but one surface of the leaf, apparently owing to the absorption of the toxicant.

Selz (1953) in a study of emulsifiable concentrates shows the importance of toxicant solubility at low temperatures, a high flash point of the solvent and a low order of phytotoxicity. Concentrate emulsions are tested for spontaneity, stability, re-emulsification and the effect of natural waters.

Hilborn (1953) in discussing the formulation of fungicides, stresses the need of specialized requirements for the control of certain diseases. The importance of particle size of the toxicant, wetting agent, spreader-stickers, safety agents, deposit builders and antifoaming agents is pointed out for some fungicide sprays. In other types of formulations only one or two spray supplements may be desirable. Since most fungicides are applied as wettable powders the particle size is important, especially in regards tenacity.

Harry (1953) shows the need of uniformity in particle size measurement of the toxicant together with the various additives to wettable powder fungicides. Confusion is also noted in the current dust formulation of fungicides. A satisfactory formula should wet easily and without foaming; store for varying lengths of time; show moderate safety to the formulator or applicator and as a residue; and have an acceptable odor and color. A toxicant must not be weakened by the diluent; must show plant tolerance and be without an unsightly residue; must be noninjurious to application machinery; must be compatible with other common pesticides; must have a low production and user cost; and must be satisfactory to customers of varying needs.

Isenhour and Brown (1954) show the need of correlating particle size with the actual surface to be covered. Cropland surfaces may be four or five times that of the soil surface area. Orchard crops may exceed this figure. Such coverage by spray application may be met in part by the spreading action of the droplet, which ranges from three to fifteen times the droplet size, while the dry particle, lacking the spreading action, may by contrast show a poor coverage. The latter difficulty can be met by the use of a proper-sized particle, preferably one in excess of 30 microns. Increased efficiency may be achieved where volatile toxicants such as tetraethyl pyrophosphate are used. The type of diluent used with powders will influence both absorption and release of the toxicant as well as the stickiness of the finished formulation. High water solubility of a toxicant may lead to plant injury and also such deposits are easily removed by heavy rains. A low water solubility of 2 to 10 parts per million may be desirable, however, for surface-residual toxicants, as this distributes the toxic action and brings it into contact with spores. Chemical stability is very desirable in the formulation, for changes may lower the efficiency of the toxicant or develop materials injurious to the host. Stability may be affected through hydrolysis in water, chemical or enzymatic reactions, absorption of oxygen or by irradiation.

Application Equipment

The development of new types of insecticides, fungicides, herbicides and defoliants is forcing changes in application equipment. Increased use of low gallonage concentrates at 5 and 10 times the usual concentration makes it necessary to develop new types of nozzles, especially for water suspensions. Air-blast sprayers with their lighter loads and lower costs are taking precedence over the conventional hydraulic sprayer for many types of work.

Airplane application continues to gain in popularity; in 1952 about 40 million acres were treated with dusts or sprays in this manner. The principal crops for which aerial application is used are cotton, wheat, rice, barley, tobacco and alfalfa. Orchard acreage under aerial application is also increasing. Aircraft application is almost entirely in the hands of small operators specializing in this type of work, each group operating three or more planes or helicopters. The number of these operating firms has now reached several thousand.

Agricultural aviation was first developed with surplus airplanes from World War II. A biplane, the Stearman Trainer SNJ-3, is the type of plane most commonly used, but with an increased horsepower for rapid climbing. The Piper Cub is another type in common use. New Types of planes designed for agricultural work are now being developed. The Aviation Center at the Agricultural and Mechanical College, College Station, Texas is one of the leaders (Anonymous, 1954) in this development.

Data on the dispersion and settling rates of aerosol particles is given by Yeomans (1953). Aerosol particles should be less than 50 microns in diameter and 80 percent by weight should be less than 30 microns. Particles that are too small are deflected from a flying insect but will settle on the insect when at rest. If they are too large, they settle rapidly and with poor dispersion. Aerosol particles do not enter dead-end cracks or into materials through which air does not circulate. Dispersion is poor in large unheated buildings but will be improved by heating or the use of blowers.

Approximately 95 percent of an aerosol settles on the top of horizontal surfaces, the remainder on the walls and ceilings. The particle-size range for industrial use should be chosen with regard to the factors involved, the most important being the time required for distribution and settling. Small particles are the best for rooms that will be closed for several hours. The time of exposure can be adjusted to the type of particle produced by available equipment. A list of publications on liquefied-gas aerosols has been compiled by Fulton and Gelardo (1953).

Explosions have resulted from the use of large thermal aerosol machines for indoor treatment (Yeomans and Van Leeuven, 1954). These are caused by the solvents and oils used in aerosol formulations and are influenced by the particle size. The proportion of oxygen in relation to that of the flammable material is also important. The addition of nonexplosive solvents to the explosive solvents in a 50–50 proportion reduces flammability. The common solvents and oils used in aerosol formulations are not explosive when properly dispersed at the rate of one gallon of formulation per 50 thousand cubic feet of free air space.

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