A GUIDE to PESTICIDES Used in PLANT PROTECTION
FOREWORD

Due to the spectacular success achieved by the pesticides in pest control, they are extensively used in plant protection work. As a result, large number of them are available in the market and several new products are being introduced annually by the various commercial firms. It is often experienced that the cultivators find it extremely difficult to select a proper type of pesticide for plant protection work. In fact, a bulletin giving an up-to-date technical information about the various pesticides used in plant protection was a long felt need of the Department for giving guidance to the extension workers and cultivators in selecting a proper type of pesticide to meet their requirements.

This bulletin has been prepared by Dr. S. K. Dorge, Agricultural Entomologist, Agriculture Department, Maharashtra State, Poona, with the help of his staff members Sarvashri D. S. Ajri and T. K. Murti. It is hoped that it will serve as a guide for efficient utilization of pesticides in plant protection work.

POONA-I.
Dated:

GHATGE,
Director of Agriculture,
Maharashtra State.
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### ABBREVIATIONS

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>ppm</td>
<td>Parts per million.</td>
</tr>
<tr>
<td>mg./kg.</td>
<td>Milligrams per kilogram of body weight.</td>
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<tr>
<td>g./kg.</td>
<td>Grams per kilogram of body weight.</td>
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<tr>
<td>LD₅₀</td>
<td>Dose of pesticide enough to kill 50 per cent of the test species.</td>
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<tr>
<td>MLD</td>
<td>Minimum lethal dose.</td>
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<tr>
<td>m.p.</td>
<td>Melting point.</td>
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<tr>
<td>pt.</td>
<td>Pint.</td>
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<td>sp. gr.</td>
<td>Specific gravity.</td>
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A GUIDE TO PESTICIDES USED IN PLANT PROTECTION

Of the various methods of pest control, viz., mechanical, cultural, chemical, biological, etc. the use of chemicals is the most important one, as it gives quick and effective control. As a result, a large number of pesticidal formulations are annually unloaded on the market by various commercial firms. More than 10,000 chemicals have so far been screened for their insecticidal properties and at present about 400 of them are in commercial use. In India, about 50,000 tons of different pesticidal formulations are used annually for pest control work and by 1970-71 the consumption of pesticides is estimated to go up to about 1,00,000 tons which will be enough to treat the entire cropped area in the country.

Due to the introduction of a large number of pesticides in the market, it is often found extremely difficult to select a proper pesticide for pest control work. Information about the commonly used pesticides is given in this bulletin which it is hoped will serve as a guide to those engaged in pest control work.

The chemicals used for pest control work are called ‘pesticides’, which term includes insecticides, acaricides, rodenticides, molluscicides, nematocides, etc. Insecticides are used for the control of insects while acaricides or miticides are used against mites. Similarly, the chemicals used against rodents, nematodes and molluscs are referred to as rodenticides, nematocides and molluscicides respectively. Amongst these however, insecticides are the major ones since a large number of insects are the important pests of crops, stored products, livestock, etc.

I. INSECTICIDES

The earliest use of an insecticide can be traced back to 1,000 B.C. when Homer referred to sulphur as a pest ‘averting’ substance. Subsequently, arsenicals and insecticides of plant origin were used for the control of pests like ants, lace bugs, human lice, etc. Besides, insecticides like rotenoids were used as fish poisons. However, arsenicals were extensively used for the first time in the year 1865 for the control of Colorado potato beetle in U.S.A. Inorganic insecticides like arsenicals and fluoride compounds as well as those of plant origin like nicotine, pyrethrum, rotenone, etc. were in use for quite a long time. With the discovery of DDT insecticide by Paul Muller in 1939, which proved miraculously effective against a wide range of pests, the research work on development of synthetic insecticides received impetus and since then a large number of synthetic chemicals are being screened for their insecticidal properties.

On the basis of action, insecticides have been classified into four groups as follows:

(1) Stomach poisons.—These act on insects when taken internally. They are mostly effective against insects having chewing type of mouth parts like grasshoppers, beetles, caterpillars, etc. but may also be used against those
with sponging, siphoning, lapping or sucking type of mouth parts. They are applied as dusts or sprays or in the form of poison baits, e.g., lead arsenate, cryolite, paris green, BHC, aldrin, dieldrin, etc.

(2) **Contact poisons.**—These chemicals kill insects by entering their bodies, either through their integuments into the blood or by penetrating the respiratory system through spiracles into the trachea, when they come in contact with the treated surface. They may be applied directly over the insects or on the materials to be protected. They are effective against insects having chewing as well as piercing and sucking type of mouth parts. e.g. Nicotine sulphate, pyrethrum extract, rotenone, DDT, BHC, parathion, malathion, carbaryl, etc.

(3) **Systemic poisons.**—These are the chemicals which when applied to plant parts, seeds or to the soil are absorbed by the plants and translocated in different parts thereby rendering them toxic to pests feeding on them. They are found to be promising mostly against pests having sucking type of mouth parts like aphids, jassids, thrips, etc. These insecticides are selective in their action and are toxic only to the harmful species but have no adverse effect on beneficial insects like parasites, predators and pollinators, e.g. Demeton, methyl demeton, thiometon, dimethoate, phosphamidon, phorate, disulfoton, etc.

(4) **Fumigants.**—Gaseous poisons used to kill insects are called fumigants. They kill the insects by entering through their respiratory system. They are available as a dust, a gas under pressure or a liquid. Fumigants are used under air tight conditions obtainable in buildings, storage bins, godowns or burrows, etc. They are usually used for controlling pests infesting stored products, termites and other subterranean species like rats, nematodes, etc. They have penetrating ability and can reach even the minute crevices, e.g. carbon disulphide, ethylene dichloride, ethylene dibromide, ED/CT mixture (Ethylene dichloride + carbon tetrachloride), methyl bromide, ‘Dun-fume’ (ethylene dibromide + methyl bromide), chloropicrin, etc.

Most of the modern synthetic insecticides are found to have stomach and contact toxicity while few of them also have slight fumigant action. Thus the classification on the basis of action may not be proper and the modern trend is to classify the insecticides on the basis of their chemical composition. Accordingly the insecticides are divided into two broad groups viz. (i) Inorganic insecticides and (ii) Organic insecticides

Chemicals acting solely as fumigants, attractants and repellents, chemo- sterilants, etc. have been dealt separately.
(i). Inorganic Insecticides

These are of mineral origin and include arsenicals, fluorine compounds and miscellaneous insecticides like tartar-emetic (Antimony potassium tartrate), boric acid, compounds of mercury, thallium and selenium, barium carbonate, zinc phosphide, etc. These chemicals were extensively used in plant protection work in earlier days. However, due to their toxicity hazards to higher animals and some of them being water soluble hereby proving phytotoxic to several species of plants, they did not become much popular. Besides, they were mostly effective against the pests having chewing type of mouth parts. With the advent of new synthetic insecticides which are more potent, relatively safer to higher animals and effective against large number of pests, these inorganic insecticides are rarely used in plant protection work. Compounds like barium carbonate and zinc phosphide are still used as rodenticides and are described elsewhere.

Brief information on some of the important inorganic insecticides is given below:

A. Arsenicals.—These are the compounds of arsenic and were extensively used for pest control work in the past. They act as stomach poisons and are used against insects having chewing type of mouth parts like grasshoppers, beetles, caterpillars, etc. but are highly toxic to higher animals. Because of the toxic residues left on the treated surfaces, their use on fruit and vegetable crops is discouraged. Besides, some of these are fairly water soluble and cause phytotoxicity. An ideal arsenical is, therefore, one which contains higher percentage of arsenic and is insoluble in water but soluble in the digestive juices of insects.

The commonly used insecticides of this group are described below:

(1) Lead arsenate.—It was first used as an insecticide by Moulton in Massachusetts, U.S.A. in 1892 against gypsy moth. Of the numerous forms, acid orthoarsenate, PbHASO₄, and basic orthoarsenate, Pb₄(PbOH) — (AsO₄)₃, are mainly used as insecticides. The commercial product is a mixture of the two, in which the acid form is predominant.

(a) Acid lead arsenate PbHASO₄.—It is also known as dibasic lead arsenate, diplumbic or dilead orthoarsenate and diplumbic or lead hydrogen arsenate. It is a white crystalline powder, containing 20 per cent. metallic arsenic, about 0·25 per cent. of which is usually soluble in water. It is stable to light, air and water but decomposed by alkalies. It is relatively less toxic, compared to other arsenicals since it contains less arsenic equivalent per unit weight. However, it is almost insoluble in water, stable and adheres well to the treated surfaces for a long time without causing phytotoxicity.
The insecticide is applied either as a dust or spray. As a dust it is usually diluted with 2 to 20 parts of an inert carrier like talc, hydrated lime or gypsum. As a spray, 2-3 lb. of the compound are mixed in 100 gallons of water. It was extensively used to protect fruit and vegetable crops, ornamental plants and forest and shade trees from injury by chewing insects. However, in view of its hazards to higher animals due to toxic residues on treated surfaces, it is rarely used for the control of crop pests.

The acute oral LD$_{50}$ values for rabbits, rats and chickens are 125, 825 and 450 mg./kg. respectively.

(b) Basic lead arsenate.—It contains less arsenic compared to acid salts and is converted to acid lead arsenate in acidic media with pH below 6.5.

Both forms of lead arsenate are of doubtful compatibility with dinitrophenols and TEPP.

(2) Calcium arsenate.—The commercial product is a mixture of tricalcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, and acid or di-calcium arsenate, $\text{CaHAsO}_4$, with lime and calcium carbonate. Basic calcium arsenate, $[\text{Ca}_3(\text{AsO}_4)_2]_n \cdot \text{Ca} (\text{OH})_2$, is the principal constituent of calcium arsenate. It is a white flocculent powder almost insoluble in water but soluble in dilute mineral acids.

Calcium arsenate is more toxic to insects and is cheaper than lead arsenate but is phytotoxic. It is applied in the same way as lead arsenate. As a spray it is mixed in the proportion of 1½ to 3 lb. in 100 gallons of water and an equal quantity of freshly prepared slaked lime or hydrated lime is added to the mixture. Since it has poor adhesive property, it is mainly used as a dust which, however, should contain 20 per cent. metallic arsenic. A colouring matter is usually added to prevent hazards. It is incompatible with soaps, nicotine sulphate (in sprays only), fluosilicates, cryolite, BHC, lime-sulphur and TEPP and of doubtful compatibility with rotenone, pyrethrum, oils, dinitrophenols, chlordane, toxaphene, parathion and dithiocarbarnates. The oral lethal dose for rat and rabbit is 20 and 40 mg./kg. respectively.

(3) Paris green, $\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu} (\text{AsO}_2)_2$.—It is chemically copper acetoarsenite and though prepared in 1814, was first used on a large scale for the control of Colorado potato beetle in U.S.A. in the year 1865. It is a green powder containing about 33 to 39 per cent. metallic arsenic, 2 to 3 per cent. of which is water soluble. It decomposes readily in presence of water and carbon dioxide to give water soluble arsenicals which cause phytotoxicity.
Though it is a good stomach poison, because of its high phytotoxicity and being expensive on account of its high copper content, it is mostly used in poison baits against insects having chewing type of mouth parts. It is a violent poison to man when ingested and also causes suppuration of open wounds. The oral minimum lethal dose to rat is 300 mg./kg.

In addition to the above mentioned important arsenicals sodium arsenite, NaAsO\textsubscript{3} and Na\textsubscript{2}HAsO\textsubscript{4}, basic copper arsenate, Cu\textsubscript{2}O\textsubscript{3}AsO\textsubscript{4}, magnesium arsenate, Mg\textsubscript{3}(AsO\textsubscript{4})\textsubscript{2} and MgHAsO\textsubscript{4}, Zinc arsenate Zn\textsubscript{3}(AsO\textsubscript{4})\textsubscript{2}, etc. are also used for pest control work to some extent.

B. **Fluorine compounds.**—Fluorine is a highly active element and combines readily with metals as well as non-metals to give a variety of compounds most of which have insecticidal properties. These compounds were developed to replace arsenicals which leave toxic residues on treated surfaces. Fluorine is derived from the naturally occurring minerals like fluor spar, CaF\textsubscript{2} and Cryolite, Na\textsubscript{3}AlF\textsubscript{6}. Fluorine compounds are generally more effective and cheaper compared to arsenicals and are less toxic to higher animals. They act mostly as stomach poisons but also have contact toxicity to some extent. They produce irritation of appendages when insects come in contact with the treated surface and the poison is ingested although they may not feed on the treated foliage. Some of these compounds also act as repellents. The important fluorine compounds employed in pest control work are sodium fluosilicate and sodium fluooaluminate or cryolite.

(i) **Sodium fluosilicate**, Na\textsubscript{2}SiF\textsubscript{6}.—This compound was used as a substitute for sodium fluoride, which on account of its water solubility was found unsuitable for the control of crop pests. Marcovitch used it for the first time against the Mexican bean beetle in the year 1924 and found it to be quite useful.

It is a white, granular, odourless powder containing about 60.6 per cent. fluorine. It is hydrolysed by water to form sodium fluoride and hydrogen fluoride while its reaction with alkalies also yields sodium fluoride, which is relatively more water soluble and causes phytotoxicity. Therefore sodium fluosilicate is not suitable for application on plants. It however, has been used extensively in the form of poison baits or as a dust against grasshoppers, crickets, cutworms, etc.

The acute oral LD\textsubscript{50} value to rabbit is about 125 mg./kg.

(ii) **Sodium fluooaluminate** (cryolite), Na\textsubscript{3}AlF\textsubscript{6}.—This substance occurring as a mineral in Greenland was first used by Marcovitch in the year 1929. In nature it occurs as monoclinic crystals, while the synthetic product is white amorphous powder, practically insoluble in water but is soluble in dilute alkales and acids and contains about 54.2 per cent. fluorine. It reacts with alkali and lime to form soluble fluorides which may cause foliage
Cryolite is non-phytotoxic and is used as stomach and contact insecticide against insects having chewing type of mouth parts like flea beetles, pumpkin beetles, etc.

It is usually used with inert diluents like clays, talc and sulphur. As a spray, 3 to 8 lb. of the insecticide are mixed in 100 gallons of water. It is also available as 20 to 80 per cent. dust and is diluted with inert carriers like clay and talc in the proportion of 1:2. It is incompatible with lime, lime-sulphur, bordeaux mixture, nicotine, paris green and calcium arsenate and of doubtful compatibility with dormant oils, dinitrophenols, TEPP and parathion.

Cryolite has an advantage of being relatively less toxic to mammals, the oral LD_{50} value for rats being 15.5 g./kg.

Besides these, other fluorine compounds like sodium fluoride, NaF, barium fluosilicate, BaSiF_{6}, etc. were also used in the past on a small scale for pest control work.

C. Miscellaneous inorganic insecticides—(i) Potassium antimonyl tartrate or tartar emetic, OSbOOC-(CHOH)_{2} COOK.—It occurs as colourless, transparent, rhombic crystals or as a white powder soluble in water to the extent of 5.26 per cent. It has been found to be effective against thrips on onion and citrus and is also used as bait in molasses or sugar against fruit flies and ants.

The acute oral LD_{50} to rabbit is 115 to 120 mg./kg.

In addition to these, several other inorganic insecticides were also used in the past for pest control work. These include white or yellow phosphorus used as baits against cockroaches, mice and rats, thallium sulphate (Tl_{2}SO_{4}) against ants, borax (Na_{2}B_{4}O_{7}) against housefly maggots and mosquitoes, boric acid (H_{3}BO_{3}) against cockroaches, mercuric chloride (HgCl_{2}) and mercurous chloride (Hg_{2}Cl_{2}) against root infesting insects, sodium selenate (Na_{2}SeO_{4}) against aphids and other sucking insects, etc.

(ii) Organic Insecticides

This vast group of insecticides can be conveniently divided into (i) Oils and soaps, (ii) Insecticides of plant origin and (iii) Synthetic insecticides.

A. Oils and Soaps

1. Oils.—Although a number of petroleum products were used as insecticides as early as 1763, they were extensively used for pest control work only in the 19th century. Initially they were applied as such or by mixing with water but proved phytotoxic. In the year 1870 kerosene oil emulsion was prepared by adding soap as an emulsifier and was found satisfactory for the plant protection work. Since then, various commercial preparations are in use.
By about 1930, highly refined neutral or white oils, free from unsaturated hydrocarbons, acids and volatile elements came into use which were found to be relatively safe for treating the foliage. Kerosene, diesel and crude oil emulsions were used in past in India. In addition to petroleum products, pine-tar and creosote oils have also been used to some extent in pest control work. Pine-tar oils, on account of their repellent properties have been employed as sprays against pests of live-stock, while creosote oil has been used for the protection of wood. Some of the vegetable oils also possess, insecticidal properties. However, due to their high cost and phytotoxic effects, they have not become popular for pest control work, and with the advent of new synthetic insecticides which are more potent and safe, they have almost gone out of use. In countries like U.S.A., oils and oil emulsions are still being used mostly as dormant sprays in orchards.

2. Soaps.—These have been used against insects since 1787. They are mostly used in emulsions as emulsifiers or as spreaders, wetting agents and stabilisers for nicotine and pyrethrum compounds. However, some soaps also act as insecticides, e.g., fish oil rosin soap, which is used at 1 per cent. concentration mostly against soft bodied insects like aphids, mealybugs, whiteflies, etc.

B. Insecticides of plant origin

It is wellknown that several species of plants possess insecticidal properties. In earlier days extracts of different parts of these plants were used as fish poisons, arrow tip poisons and for the control of louse. These compounds have quick knockdown effect on insects and are relatively less toxic to mammals. They however, have short residual effect and as such frequent applications are necessary. Some of the commonly used insecticides are described below :-

(i) Nicotine (C\textsubscript{10}H\textsubscript{14}N\textsubscript{2}).—Nicotine in crude form was used as an insecticide as early as 1763. However, the pure alkaloid was synthesized in 1904 by Pictet and Rotachy. Commercially it is obtained from tobacco, *Nicotiana tabacum* and *N. rustica*, where it occurs in leaves to the extent of 2 to 5 per cent. and 5 to 14 per cent. respectively. Of the 12 alkaloids isolated from tabacco, nicotine constitutes a major portion of about 97 per cent. while in the remaining alkaloids only nornicotine and anabasine have insecticidal properties. Pure nicotine is a colourless liquid but darkens slowly and becomes viscous on exposure to air and light. It is readily miscible with water and forms salts with acids and metals.

Nicotine alkaloid, nicotine sulphate and several nicotine compounds have been used as contact and stomach poisons and fumigants. Of these nicotine sulphate, which is available as 40 per cent. emulsion with sp. gr. 1.188, is widely employed in pest control work. It has marked contact action with a short residual property. For quick liberation of nicotine from this compound,
soap, hydrated lime, lime-sulphur or ammonium hydroxide is usually added. Diluted nicotine sprays should contain 0.05 to 0.06 per cent. nicotine. It is generally used for the control of soft bodied insects like aphids, jassids, thrips, etc.

Nicotine is incompatible with calcium cyanide dust, barium fluosilicate and cryolite and of doubtful compatibility with chlordane, BHC, dinitrophenols and TEPP. It is highly toxic to warm blooded animals when taken orally or absorbed through skin. The acute oral LD₅₀ to rat is 30 mg./kg. while acute dermal LD₅₀ to rabbit is 50 mg./kg.

(ii) Pyrethroids.—Pyrethrum was used as an insecticide in the Transcaucasus regions of Asia in the 18th century. However, its source was kept secret for many years and the product was sold extensively as flea and louse powder at exhorbitant prices. Following the publication on its chemical nature and source, its use became worldwide. Until World War I, Japan was the leading producer of pyrethrum. Later the industry began to flourish in Kenya and by 1940 it became the principal source of the product.

Pyrethrum occurs in flowers of the plants belonging to the genus Chrysanthemum of family Compositae. The species of commercial importance is Chrysanthemum cinerariaefolium. The flowers of Kenya strain contain on an average 1.3 per cent. pyrethrins, reaching upto 3 per cent. in selected strains. Pyrethrum derives its toxicity from 4 esters, viz., pyrethrin I and II and cinerin I and II. It is highly unstable in presence of air, light and moisture and is hydrolysed by alkali thereby losing its insecticidal properties. Ground flowers and the other formulations lose their toxicity in storage. The efficacy of the insecticide increases with the addition of certain synergists, like piperonyl butoxide, sesamin, etc.

It is a powerful contact poison having quick knockdown effect on insects, but lacks persistance. It is available as emulsion and dust and applied at 0.0-30.1 per cent. sprays especially for the control of the pests infesting vegetable and fruit crops. It is also used for treating the warehouses or for mixing with grains, as cattle or live-stock sprays and as household insecticide against flies, mosquitoes, bed bugs, ants, clothes moths, cockroaches, etc.

Pyrethrum is incompatible with lime and soaps. It is quite safe to mammals. However, persons handling it are occasionally subjected to dermatitis caused by the volatile oil present in flowers. The acute oral LD₅₀ to guinea pig is 1500 mg./kg.

Besides pyrethrum, its synthetic analogues like allethrin, cyclethrin, barthrin, etc. have also been found to be useful as insecticides but are not in commercial use.

(iii) Rotenoids.—These substances of plant origin were used as fish poisons for many centuries in the past. They occur in a large number of plants like Derris, Tephrosia, Lonchocarpus, Milletia and Mundulea which belong to the
family Leguminosae. A number of toxic substances have been isolated from the roots and seeds of these plants, the most important amongst them is rotenone \((\text{C}_{23}\text{H}_{22}\text{O}_{6})\). It was used as an insecticide for the first time in 1848 against leaf-eating caterpillars. Nagai isolated rotenone from Derris roots in 1902 and the structure of the compound was first determined by La Forge et al. in 1932-33.

It exists in the form of colourless crystals, m.p. 163°C, practically insoluble in water (15 ppm at 100°C), slightly soluble in petroleum oils and carbon tetrachloride and soluble in polar organic solvent. It is readily oxidised to less toxic compounds in presence of alkali or light. The change occurs in about 10 days in insecticidal residue on treated plant. These preparations should therefore be protected from light during storage.

Rotenone is used in the form of dusts, where ground roots are used with non-alkaline carrier, water dispersible powder containing 25 to 35 per cent. rotenone. It is also available as emulsifiable concentrates and aerosols.

It is a selective insecticide with some acaricidal action and has short residual effect. The insecticide is mainly effective against the insects having piercing, and sucking and chewing type of mouth parts. It is also used for the control of ectoparasites of animals.

The compound is incompatible with lime, other alkaline materials and paris green and of doubtful compatibility with calcium arsenate, dinitrophenols and TEPP. It is relatively harmless to warm blooded animal. The acute oral LD_{50} values for rat and guinea pig are 25 to 75 and 50 to 200 mg./kg. respectively.

In addition to the insecticides of plant origin mentioned above there are several others of minor importance which include sabadilla, hellebore, ryania, quassia, etc.

C. Organic synthetic insecticides

On the basis of chemical composition, these insecticides have been further divided into chlorinated, hydrocarbons organophosphous compounds, carba-mates, organothiocyanates and dinitrophenol.

(a) Chlorinated hydrocarbons

These are the compounds having molecules made up of chlorine, hydrogen, carbon and occasionally, oxygen. They are potent insecticides having fairly long residual property. They act as stimulants of central nervous system. As a result, the insects exhibit symptoms like hyperactivity, tremors and unco-ordinated movements and are ultimately killed. They have a wide spectrum of pest control and some of them have been found to be effective even against internal
feeders like bollworms, borers, etc. Use of these insecticides has certain limitations too. Due to longer residual property, they cannot be applied on crops shortly prior to harvest. As most of these compounds are liposoluble, they have a tendency of getting accumulated in the body fat and produce ill effects on kidney, liver, etc. When milk animals are fed with the fodder treated with these insecticides, they are excreted through milk. Most of them are not so promising against phytophagous mites but on the contrary some of them destroy their natural enemies which results in increased population of mites. Besides, some of the chemicals are phytotoxic to certain species of plants, especially the cucurbits.

Some of the important insecticides commonly used in pest control work are given below:

1. DDT (Dichlorodiphenyl trichloroethane) \( \text{C}_{14}\text{H}_{9}\text{Cl}_3 \) 2, 2—Bis (P-chlorophenyl)—1, 1, 1—trichloroethane.

The compound was first synthesised by a German chemist Zeidler in the year 1874. Its insecticidal properties however, were discovered by Paul Muller in 1939 in Switzerland, for which he was awarded a Nobel Prize in medicine and physiology in the year 1948 “in recognition of the importance of DDT insecticide in hygiene”. Technical DDT is a white to cream-coloured amorphous powder containing 9.5 to 11 per cent. hydrolysable chlorine and less than one per cent. volatile and alcohol insoluble material. It is composed of 14 compounds of which \( pp' \) isomer is responsible for insecticidal action. It is practically insoluble in water, but soluble in most organic solvents. Normally, the pure \( pp' \) isomer is stable and inert and is not attacked by ordinary acids. However, it is dehydrochlorinated at temperature above melting point and also in solution in organic solvents by alkalis or organic bases to form non-insecticidal compound like DDE.

DDT acts as stomach as well as contact poison and has fairly long residual property. In out-door applications it remains effective up to one month, while in-door sprays are reported to remain effective up to one year. It is available as 2–10 per cent. dust, 50 to 95 per cent. wettable powder, 15 to 30 per cent. emulifiable concentrate, 0.5 to 20 per cent. solution and also as granules and aerosols.
It is one of the most extensively used insecticides and is effective against a variety of pests like thrips, jassids, leaf eating caterpillars, pod borers, etc. However, it is less effective against most Orthoptera, flea beetles and aphids. It is generally used at 1 to 3 lb. toxicant per acre. It has also been used for the control of pests of live-stock and household pests.

It is compatible with sulphur and most of the commonly used pesticides but is incompatible with too strong alkaline substances like lime-sulphur. The acute oral and dermal LD₅₀ to female rat is 118 mg./kg. and 2510 mg./kg. respectively.

(2) BHC (C₆H₆Cl₆)—
1, 2, 3, 4, 5, 6.—Hexachloro cyclohexane or Benzene hexachloride.

The insecticide was first synthesised by Faraday in 1825. However, its insecticidal properties were not discovered until 1940-42 when both British and French workers developed the material independently.

The crude product is a greyish or brownish amorphous powder with a characteristic musty odour. It is a mixture of several isomers. The important amongst these is a gamma isomer (m.p. 112°C) which has an insecticidal property. It constitutes about 10-18 per cent. of the technical material. Other isomers present are the alpha, beta, delta, and epsilon. BHC is stable to light, air, heat and carbon-di-oxide. It is also resistant to strong acids but is dehydrochlorinated by alkali, with the exception of beta isomer.

It is a good stomach and contact poison with slight fumigant action and generally more toxic than DDT. The insecticide is non-phytotoxic except to cucurbits and causes tainting in crops like potato.

BHC is available as 5-10 per cent. dust, 50 per cent. wettable powder, 20 per cent. emulsifiable concentrate, 5 % granules and aerosols.

It is used for the control of grass-hoppers, flea beetles, army worms, etc. at 1–3 lb. per acre. It is also used for mosquito and fly control work and against the subterranean pests like wire worms, termites, root grubs, etc. Though it is compatible with most of the pesticides, it is incompatible with calcium arsenate, lime, lime-sulphur and bordeaux mixture.
BHC is toxic to mammals, the acute oral LD$_{50}$ to rats being 125 to 200 mg./kg.

(3) Lindane (C$_6$H$_8$Cl$_6$)—

Gamma—1, 2, 3, 4, 5, 6 Hexachloro-cyclohexane.

It is a colourless, crystalline substance, m.p. 120°C and contains not less than 99 per cent. gamma isomer. It is practically insoluble (10 ppm) in water but soluble in organic solvents. It is stable to air, light, heat and carbon dioxide and unattacked by strong acids but is dehydrochlorinated to trichlorobenzene in presence of alkali. It is available as 0.5-2 per cent. dust, 15-20 per cent. wettable powder, 20 per cent. emulsifiable concentrate and 5-10 per cent. granules. It is used especially against pests of vegetables as it has less tainting effect than BHC and found promising against subterranean pests at 0.5 to 2 lb. toxicant per acre. Its compatibility and mamalian toxicity are same as in case of BHC.

**Cyclodiene Insecticides**

The compounds of this group, viz., chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan and isobenzan are chlorinated cyclic hydrocarbons with characteristic 'endomethylene bridged' structure. These are produced by the wellknown Diels-Alder diene reaction.

(4) Chlordane (C$_{10}$H$_8$Cl$_8$)

1, 2, 4, 5, 6, 7, 8, 8—Octachloro—2, 3, 3a, 4, 7, 7a—hexahydro—4, 7 methanoindene.
The compound was first synthesised by Julius Hyman in U.S.A. and by Riemscheneider in Germany and its insecticidal properties were described by Kearns et al. in the year 1945. The technical material is a viscous brown liquid with cedar-like odour and a sp. gr. of 1.61. It contains about 60-75 per cent. alpha and beta isomers (both melting at about 105°C) and 25 to 40 per cent. heptachlor, hexachlor and trichlor. It is insoluble in water but soluble in most organic solvents and is dehydrochlorinated in presence of alkali.

Chlordane is a stomach and contact poison with a good residual property. It is formulated as 5 to 10 per cent. dust and granules, 40 to 50 per cent. wettable powder, 2 to 20 per cent. oil solution and 45 to 75 per cent. emulsifiable concentrate. It has been extensively used for the control of pests like beetles, grasshoppers, weevils and soil inhabiting pests at 0.5 to 3 lb. toxicant per acre. It has also proved useful against the species harmful to domestic animals and man such as lice, ticks, fleas, biting flies etc. and household pests like ants, cockroaches, flies, silver fish, clothes moths, etc. The insecticide is compatible with most of the pesticides but of doubtful compatibility with lime, lime sulphur, bordeaux mixture, nicotine, calcium arsenate, basic lead-arsenate and dithiocarbamates.

It has low acute toxicity to mammals, the oral and dermal LD₅₀ to female rats being 430 to 590 and 690 mg./kg. respectively.

(5) Heptachlor (C₁₀H₈Cl₇)

1, 4, 5, 6, 7, 8, 8—heptachloro—3a, 4, 7, 7a—tetrahydro—4, 7—endomethanoindene (U.S.A.).

This compound is usually present in technical chlordane. However, it is synthesised by chlorination of hexachlorodicyclopentadiene.

The pure material is a white crystalline solid melting at 95 to 96°C and has mild camphor or cedar-like odour. The technical material contains about 62-72 per cent. heptachlor and 28 to 33 per cent. alpha chlordane and is a soft waxy solid having a melting point ranging between 46-74°C. It is practically insoluble in water but is soluble in ethyl alcohol (4-5 g./100 ml.) and kerosene (18.9 g./100ml.).
Heptachlor has strong insecticidal properties with some fumigant action. It is available as 2·5 to 25 per cent. dust, 15 per cent. wettable powder, 25 per cent. emulsifiable concentrate and 2·5 to 20 per cent. granules. The insecticide is 3 to 4 times more toxic compared to chlordane and found to be effective against several beetles, flies, grasshoppers and soil insects at 0·5 to 3 lb. toxicant per acre. It is compatible with the most commonly used pesticide. The compound is toxic to mammals. The acute oral LD$_{50}$ to rat ranges between 130 to 135 mg./kg. In plant and animal tissues and in soil, heptachlor is converted to heptachlor epoxide which has the same mammalian toxicity as heptachlor.

(6) Aldrin (C$_{12}$H$_8$Cl$_6$)

1, 2, 3, 4, 10, 10—hexachloro—1, 4, 4a—5, 8, 8a—hexahydro-endo—1, 4-Exo—5, 8—dimethanonaphthalene (U.S.A.).

The insecticide was developed by Julius Hyman and Co. and first described by Kearns et al. in 1948.

It is a white, crystalline, odourless compound having a m.p. 104°C. It is stable to the action of alkali. The technical material is a brown waxy solid containing about 78 per cent. aldrin. The impurities present may slowly form hydrochloric acid in storage and therefore addition of an acid inhibitor such as epichlorohydrin as a stabilizer is usually necessary. It is insoluble in water, moderately soluble in mineral oils but readily soluble in acetone, benzene and xylene.

Aldrin is a potent insecticide and acts as a stomach and contact poison with fairly good residual property. It is especially effective against soil insects and used at the rate of 0·5 to 5 lb. per acre. It is also found useful for the control of grasshoppers, ants, termites, etc. at the dosage of 0·25 to 5 lb. per acre. It is formulated as 2·5 to 5 per cent. dust, 25 per cent. wettable powder, 25 to 50 per cent. emulsifiable concentrate, 5 to 20 per cent. granules and 75 per cent. wettable powder for seed dressing and is compatible with most of the pesticides and fertilizers.

Aldrin is toxic to mammals. The acute oral LD$_{50}$ to rat is 50 mg./kg. while acute dermal LD$_{50}$ value for rabbit is 150 mg./kg.
(7) Dieldrin (C\(_{12}\)H\(_{8}\)Cl\(_6\)O)

1, 2, 3, 4, 10, 10—hexachloro—exo—6, 7—epoxy—1, 4, 4a, 5, 6, 7, 8, 8a—octahydro—1, 4, endo, exo—5, 8—dimethanonaphthalene (U.S.A.).

This compound was also developed by Julius Hyman and was first described by Kearns et. al. in 1948. Dieldrin is an epoxide of aldrin. Technical material is a light tan, flaky solid containing about 76 per cent. dieldrin and 13 per cent. other insecticidally active substances. It is insoluble in water, slightly soluble in mineral oils, moderately soluble in acetone and soluble in aromatic solvents. It is completely stable to the action of alkali, mild acids and light.

It is a good contact and stomach poison, highly persistent and is effective against pests like thrips, grasshoppers, leafhoppers, etc. at 4 to 8 oz. per acre. It has also been extensively used as a seed protectant and against soil inhabiting pests. It is formulated as 50 per cent. wettable powder, 18 per cent. emulsifiable concentrate, 2 per cent. dust and is also available as granules. It is compatible with most of the commonly used pesticides.

The acute oral LD\(_{50}\) to rat is 100 mg./kg. while the acute dermal LD\(_{50}\) to rabbit is 150 mg./kg. Aldrin is converted to dieldrin in living tissues and in soil.

(8) Endrin (C\(_{12}\)H\(_{8}\)Cl\(_4\)O)

1, 2, 3, 4, 10, 10—hexachloro—6, 7—epoxy—1, 4, 4a, 5, 6, 7, 8, 8a—octahydro—endo—1, 4—endo—5, 8—dimethanonaphthalene (U.S.A.).
This compound was introduced in the year 1951 by Julius Hyman. It is an epoxide of isodrin and stereoisomer of dieldrin. Technical endrin is a light tan coloured powder, m.p. 200°C and contains about 85 per cent. of the insecticide. It is practically insoluble in water, sparingly soluble in alcohol and petroleum hydrocarbons and moderately soluble in benzene and xylene. The compound is relatively less stable to alkals compared to dieldrin. Hexamethylene tetramine is added to formulations as a stabiliser. It is non-phytotoxic but reported to be harmful to corn and cucumbers. It is highly toxic to insects and extensively used for the control of pests infesting cotton, cabbage, tobacco, sugarcane, jowar, paddy, etc. including tissue borers at 0·25 to 0·5 lb. per acre.

It is available as 25 per cent. wettable powder, 20 per cent. emulsifiable concentrate, 1 per cent. dust and 2 per cent. granules. It is compatible with most of the commonly used pesticides.

Endrin is the most toxic amongst the chlorinated hydrocarbons to warm blooded animals. The acute oral and dermal LD₅₀ values to rats are 10 to 12 and 15 mg./kg. respectively.

(9) Endosulfan (C₉H₆Cl₆O₃S)

6, 7, 8, 9, 10—hexachloro—1, 5, 5a, 6, 9, 9a—hexahydro—6, 9—methano—2, 4, 3—benzodixathiepin—3-Oxide.

The chemical was introduced in 1956 as an experimental insecticide by Farbwerke Hoechst in Germany and first described by Finkenbirnk in the same year. Commercially it is known as 'Thiodan'.

The technical material is a brownish crystalline solid and has a faint smell of sulphur dioxide. It is a mixture of two stereoisomers with a melting range of 70 to 100°C and is practically insoluble in water but moderately soluble in most organic solvents. The compound is stable to sunlight but hydrolyses slowly in presence of water.

This compound containing both sulphur and oxygen is effective as insecticide as well as acaricide and is reported to be safe to beneficial species.
It is found to be promising against the pests infesting potato, cotton, etc. at 0.5 to 1 lb. per acre. It is available in the form of 25 and 50 per cent. wettable powders, 25 and 35 per cent. emulsifiable concentrates, 3 to 4 per cent. dusts and 5 per cent. granules.

The acute LD$_{50}$ to rat is about 110 mg./kg. while the dermal LD$_{50}$ to rabbit is about 360 mg./kg.

(10) Isobenzan (C$_9$H$_8$Cl$_8$O$_2$)

1, 3, 4, 5, 6, 7, 8—Octachloro—3a, 4, 7, 7a—tetrahydro—4—7—methanophthalan.

The insecticide is commercially known as 'Telodrin' and was synthesised in the year 1953. Technical material is a white crystalline powder, m.p. of 120°C. It is insoluble in water but soluble in organic solvents and is reported to be stable in storage.

It is a potent insecticide having a wide spectrum of pest control and is effective against soil borne insects as well as against those infesting the aerial plant parts. Besides, it does not cause tainting of crops. It is formulated as 1 per cent. dust, 50 per cent. wettable powder and 15 per cent. emulsifiable concentrate. It is compatible with many commonly used pesticides and fertilizers. The compound is highly toxic to mammals, the acute oral LD$_{50}$ to rat being 6.3 mg./kg. as emulsion but is 10 mg./kg. in groundnut oil.

(11) Toxaphene (C$_{10}$H$_{10}$Cl$_9$)

This compound which is a chlorinated terpene was discovered by George Buntin and later described by LeRoy Park and Beach.,
It is a yellow, waxy solid having mild smell of terpene with a m.p. of 65 to 90°C. It is insoluble in water, but readily soluble in organic solvents. The product is broken down by heat, strong alkali and sunlight.

It is a good contact and stomach poison and has proved useful especially in the control of grass-hoppers, cotton insects, cutworms, etc. at 0.5 to 2 lb. per acre. Besides, it is also useful against pests of live-stock. Generally it is safe on most plants but exhibits phytotoxicity to cucurbits. It is formulated as 40 per cent. wettable powder, 5 to 10 per cent. dust and granules.

It has somewhat less residual action than DDT and is of doubtful compatibility with calcium arsenate, bordeaux mixture, lime and lime-sulphur.

This product is about four times more toxic to mammals than DDT but has low chronic toxicity. The acute oral LD₅₀ value to rat is 69 mg./kg.

Besides the important chlorinated hydrocarbon insecticides mentioned above, there are a few other compounds like methoxychlor, TDE or DDD, DFDT and 'Kepone' which have also been used as insecticides on small scale. Methoxychlor needs special mention for its use against pests of live-stock being less accumulated in body fat and excreted through milk to a very small extent.

(b) Organophosphorous Compounds

These are mostly the esters of phosphoric, phosphorothioic or phosphorodithioic acids with the only exception of 'EPN' which is an ester of phenylphosphoric acid. They contain one or more phosphorus atoms chemically bounded either directly to the carbon atoms of organic radicals or indirectly through nitrogen, oxygen or sulphur. The German chemist, Dr. Gerhard Schrader was the pioneer worker who synthesised the first organophosphorous insecticide, HETP (Hexaethyl tetraphosphate) in the year 1942. Since then, several new compounds have been developed which are extensively used in pest control work all over the world. These compounds are effective against a wide range of pests. Unlike chlorinated hydrocarbons, they have acaricidal property too. Besides, they possess systemic property to some extent, while a few are truly systemic and are highly selective in their action.

These insecticides act as inhibitors of cholinesterase, an ester hydrolysing enzyme involved in the normal transmission of nerve impulses through nerve tissues and this action is irreversible. Due to the inhibition of activities of cholinesterase, the acetyl choline gets accumulated in the nerve tissues and the insects get killed. Besides cholinesterase, other enzymes are also reported to be responsible for causing death of insects.

The organophosphorous compounds have certain limitations also. Since they do not have residual effect, frequent applications are found necessary. Besides, some of these compounds are highly toxic to warm blooded animals, both by ingestion and contact and hence are required to be used with care and
under expert supervision. Unlike chlorinated hydrocarbons, however, these compounds are rapidly detoxified and not stored in body fat. It is also interesting to note that most of these compounds on enzymatic oxidation in living tissues yield more toxic metabolites while on hydrolysis non-toxic substances are formed. For the sake of convenience, this vast group of insecticides is divided into two sub-groups viz., (a) surface-active poisons and (b) systemic poisons.

A. Surface-active poisons

(1) TEPP (Tetraethyl pyrophosphate) \((C_8H_{20}O_7P_2)\)
Bis-\(O\), \(O\)-diethylphosphoric anhydride.

\[
\begin{array}{c}
\text{O} \\
\text{P} \\
\text{O} \\
\text{P} \\
\end{array}
\]

\((C_2H_5O)_2\) \(\text{P} \rightarrow \text{O} \rightarrow \text{P} \) \((OC_2H_5)_2\)

Although the compound was first synthesised by Clermont in 1854, apparently nothing was known about its insecticidal properties until Schrader in 1942 produced a phosphorous insecticide as a substitute for nicotine which he described as HETP (Hexaethyl tetraphosphate). It, however, was observed that TEPP was the active ingredient in HETP.

Pure TEPP is a colourless, odourless, and hygroscopic liquid, b.p. of 135-138°C at 1 mm. The commercial product contains about 40 per cent. TEEP and is a dark, amber coloured liquid. It is miscible with water and most organic solvents but is practically insoluble in petroleum oils and is hydrolysed by water to form diethyl phosphoric acid which is non-toxic to insects. It decomposes at 170°C and is corrosive to metals.

The insecticide is useful as an aphicide or acaricide. Being rapidly decomposed by water, it has a very short residual property. It is available as 1 per cent. dust and 20-40 per cent. emulsifiable concentrate and is compatible with DDT and sulphur. Its use on tomatoes should be avoided.

TEPP is extremely toxic to mammals. The acute oral \(LD_{50}\) to rat is 1.4-2 mg./kg. while the dermal \(LD_{50}\) to rabbit is 48 mg./kg.

(2) Parathion \((C_{20}H_{14}NO_8PS)\)

\(O\), \(O\)-Diethyl \(O\)-\(P\)-nitrophenyl phosphorothioate.

\((C_2H_5O)2\) \(\text{PS} \rightarrow \langle \text{NO}_2 \rangle \)
The insecticide was first developed by Schrader in 1944. Parathion is a nearly odorless, pale yellow liquid with b.p. of 157-162°C/0.6 mm. The technical material is a dark brown liquid with a garlic odour. It is sparingly soluble in water (20-25 ppm.) but is miscible with most organic solvents and gets hydrolysed in presence of alkali yielding p-nitrophenol and diethyl orthothiophosphoric acid. On heating, it is converted to form a less toxic compound.

It is one of the most extensively used insecticides having an excellent contact toxicity. In the animal body, parathion is oxidised by enzyme to paraoxon which is an active anticholinesterase. Its residual property on plant surface, however, is only 5-12 days. It has been found to be effective against a very wide range of pests like aphids, mites, caterpillars, scales, mealybugs, beetles, leaf-miners, etc. at a dosage of 0.2 to 1 lb. toxicant per acre. It is also claimed to be effective against some internal feeders like stem borer and gall fly on paddy. It is formulated as 1-2 per cent, dust, 15-20 per cent. wettable powder, 20-50 per cent. emulsifiable concentrate and 5 per cent. granules.

It is compatible with most of the insecticides and fungicides except bordeaux mixture, lime and lime-sulphur.

The compound has high mammalian toxicity. The acute oral LD₅₀ to rat is 5-9 mg./kg. while the dermal LD₅₀ to rabbit is 420-870 mg./kg.

(3) Methyl parathion (C₆H₁₀NO₅PS)

O,O-Dimethyl, O-P—nitrophenyl phosphorothioate,

\[
\left(\text{CH}_3\text{O}\right)_2\text{PS}·\text{O}·\text{NO}_2
\]

This chemical is the dimethyl analogue of parathion. Pure methyl parathion is a white crystalline solid, m.p. 35-36°C and sp. gr. 1.358. The commercial product is a light to dark tan liquid and is slightly soluble in water but soluble in most organic solvents. It readily gets hydrolysed and isomerized and is therefore less stable in storage and when applied on crops.

It is used against pests like bugs, leaf eating caterpillars, thrips, etc. but is found to be more promising against aphids and beetles at 0.25 to 0.5 lb. per acre. It persists on foliage for 4-8 days after application. Usually a mixture of methyl and ethyl parathion is used. It is less toxic to mammals than parathion. The acute oral LD₅₀ to rat is 30 mg./kg. The dermal lethal dose to rabbit of the pure material is 1.27 mg./kg. but when applied in corn oil, it is 0.42 g./kg.
(4) Diazinon \((C_{12}H_{21}N_{2}O_{3}PS)\)

O, O-Diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate.

The compound was synthesized by H. Gysin and introduced in 1952 as a experimental insecticide by J. R. Geigy, Switzerland. In pure form it is a colourless liquid with a b.p. of 83-84°C/0·0002 mm. The technical material (about 90 per cent. purity) is pale to dark brown in colour and is slightly soluble in water (0·004 per cent. at room temperature) but soluble in organic solvents. It is relatively stable in dilute alkalies but slowly hydrolyses in dilute acids.

Diazinon is mostly used at 0·25–2 lb. per acre against the pests of vegetable and fruit crops. It is also found to be effective against houseflies and other household and livestock pests. It is formulated as 10–40 per cent. wettable powder, 20 per cent. emulifiable concentrate and 5 per cent. granules. It is compatible with most of the pesticides except copper fungicides.

The chemical has a moderate mammalian toxicity, the acute oral LD\(_{50}\) to rats being 100–150 mg./kg.

(5) Azinphos \((C_{10}H_{12}N_{3}O_{2}PS)\)

O, O-Dimethyl S-4-oxobenzotriazino-3-methyl phosphorodithioate.

This chemical was introduced in 1954 as an experimental insecticide by Farbenfabriken Bayer, in Germany and was first described by Ivy \etal\ during the same year and is commercially known as ‘Guthion’.
It is a white, crystalline material with a m.p. of 73–74°C. It is practically insoluble in water but soluble in many organic solvents. It is however, unstable in alkaline media.

The insecticide has been used against pests infesting cotton, fruit crops, vegetables, etc. at 0.5 to 1 lb. actual toxicant per acre. It is available as 2.5 per cent. dust, 15 per cent. wettable powder and 20 to 50 per cent. emulsifiable concentrate.

It is highly toxic to mammals the acute oral LD$_{50}$ to rat being 16.4 mg./kg.

(6) Malathion (C$_{10}$H$_{19}$O$_{6}$PS$_{2}$)
O–O–Dimethyl S–1, 2-di (ethoxycarbamyl) ethyl phosphorodithioate.

\[
\text{CH}_3\text{O} \quad \text{P} \quad \text{S} - \text{CH} - \text{CO}_2 \text{C}_2\text{H}_5
\]
\[
\quad \text{CH}_3\text{O} \quad \text{S} - \text{C}_2\text{H}_5
\]

The compound was introduced in the year 1950 as an experimental insecticide by the American Cyanamid Company.

The pure compound is a yellow to dark brown liquid with a b.p. of 156–157°C/0.7 mm. and sp. gr. of 1.23 at 25°C. The technical material is about 95 per cent. pure and has an unpleasant odour. It is slightly soluble in water (145 ppm) but soluble in most organic solvents. It is hydrolysed both in acidic and alkaline media but more so in the latter. It is however, stable at pH between 5–7. It reacts with heavy metals like iron and hence containers with polythene lining are used.

It is one of the safest general purpose insecticides used for the control of the pests having sucking type of mouth parts like aphids, jassids, scale insects, mealy bugs, white flies, mites, etc. It is especially suited for the control of the pests infesting vegetables and fruit crops and household and live-stock pests. It is usually used at 0.25 to 2 lb. toxicant per acre and remains effective on treated crops for 3–10 days. It is available as 4–5 per cent. dust, 25 per cent. wettable powder, 50–95 per cent. emulsifiable concentrate and 2–20 per cent. aerosol.

Malathion is compatible with most of the commonly used pesticides except bordeaux mixture and should be used with caution with zinc and calcium arsenate, cryolite, organo-mercury compounds, fixed coppers, lime-sulphur and lime.

It is one of the safest insecticides and is relatively less toxic to mammals. The acute oral LD$_{50}$ to rats is about 1400 mg./kg.
Carbophenothion \( (C_{11}H_{16}ClO_2PS_3) \) ·
\[ \text{O, O—Diethyl S—P—Chlorophenylthiomethyl phosphorodithioate} \]
\[ (C_2H_5O)_2 \cdot \text{PSCH}_{2}S \cdot \bigcirc \cdot \text{Cl.} \]

The chemical was introduced (as an insecticide and acaricide) by the Stauffer Chemical Company in the year 1955 and is commercially known as 'Trithion'. Technical material (95 per cent. purity) is an amber coloured liquid with a sp. gr. of 1·265 to 1·285. It has low vapour pressure and is practically insoluble in water (less than 2 ppm at 20°C) but is miscible with most organic solvents. It is relatively stable in water, acidic and basic media, soils and in storage.

Carbophenothion possesses insecticidal and acaricidal properties and has been found to be quite promising against several species of mites, homopterous and dipterous insects and pests of livestock. It is used at the dosage of 0·25 to 1 lb. actual toxicant per acre. It is formulated as 1 to 5 per cent. dust, 25 per cent. wettable powder, 20 per cent. emulsifiable concentrate and 5 to 10 per cent. granules.

The acute oral LD\(_{50}\) to rat is 28 mg./kg. while the acute dermal toxicity to rabbit is 1,250 mg./kg.

Trichlorphon \( (C_4H_8Cl_3O_4P) \)
\[ \text{O, O—Dimethyl (1—hydroxv—2, 2, 2—trichloroethyl) phosphate.} \]
\[ (CH_3O)_2 P \cdot \text{CH (OH)} \cdot \text{CCl}_3 \]

The compound was first synthesized by W. Lorenz and introduced in 1952 by Farbenfabriken Bayer as an experimental insecticide. Commercially it is known as 'Dipterex'.
It is available as 5 and 10 per cent. dusts, 50 and 80 per cent. wettable powder and as 1 per cent. sugar bait. It is relatively less toxic to mammals, the acute oral LD$_{50}$ value for rats being 450–500 mg./kg. while the dermal lethal dose to rabbit is 5,000 mg./kg.

(9) Dichlorvos (C$_4$H$_7$Cl$_2$O$_4$P)

Dimethyl—2, 2—dichlorovinyl phosphate.

\[ \text{(CH}_3\text{O})_2\text{POCH} = \text{CCl}_2 \]

The compound was discovered as a highly insecticidal impurity of trichlorphon (Dipterex) by Mattson et al. in 1955 and is commonly known as DDVP, ‘Nuvan’ or ‘Vapona’. It is a liquid with a b.p. 120°C/14 mm. and sp. gr. of 1.45 at 25°C. It is produced by the dehydrochlorination of trichlorphon. The chemical acts as a good stomach and contact poison and also as a fumigant. It rapidly kills insects at concentrations harmless to mammals. It has been used for the control of flies and mosquitoes in houses, dairy barns, etc. and also against pests infesting stored products. It is available as a 100 per cent. emulsifiable concentrate.

It is moderately toxic to mammals. The acute oral LD$_{50}$ to rat is 80 mg./kg.

In addition to the important insecticides described above few other compounds like 'EPN', Sulfotepp, fenthion, ethion, etc. have also been found to possess insecticidal properties but have not been used on large scale in this country.

B. Systemic Poisons

As defined earlier these insecticides are absorbed by plants and translocated to different parts thereby rendering them toxic to the pests feeding on them. Although inorganic compounds like selenium and those of plant origin like sodium fluoroacetate and extracts of derris roots were reported to possess some systemic properties, they did not become popular in pest control work probably because of their prohibitive prices and high toxicity to mammals. The real research on systemic insecticides began in 1947 when Schrader and his coworkers found that some of the organophosphorous insecticides possess systemic properties. Since then hundreds of chemicals were screened for their systemic properties and at present more than a dozen are commercially available for pest control work.

Systemic insecticides have certain advantages over others. Being absorbed in plants they are only toxic to the phytophagous species and have no adverse effect on the beneficial species like parasites, predators and pollinators. In recent years, method of integrated control of pests is becoming popular which combines chemical and biological control methods wherein systemic insecticides
play a major role. Being less subjected to the environmental conditions, they remain persistent for a longer period compared to other insecticides. These chemicals, however, are found to be promising mostly against the insects having sucking type of mouth parts and have not shown much promise against internal feeders like bollworms and tissue borers. Besides, most of them are highly toxic to warm blooded animals. It is necessary to avoid their use at least a fortnight prior to harvest to prevent toxicity hazards due to their residues.

Some of the commonly used systemic insecticides are described below:

1. Schradan (Octamethylpyrophosphoramide)
   
   \((\text{C}_8\text{H}_{24}\text{N}_4\text{O}_9\text{P}_2)\)

   Bis—\(\text{N}, \text{N}, \text{N'}, \text{N'}\)—tetramethylphosphorodiamidic anhydride.

   
   \[
   \begin{array}{c}
   \text{O} \\
   \parallel \parallel \\
   [(\text{CH}_3)_2\text{N}]_2 \text{P—O—P [N (CH)_3]_2} \\
   \end{array}
   \]

   This was the first organic systemic insecticide discovered by Schrader and Kukenthal in the year 1941-42. The pure compound is a colourless, viscous liquid b.p. 154°C, sp. gr. 1.13 at 25°C and contains 40 per cent. active ingredient. It is completely miscible with water and most organic solvents but not with paraffinic hydrocarbons. The commercial product is a dark brown viscous liquid. Unlike most organophosphorous compounds it is stable to water and alkalis but hydrolysed in acidic media to form dimethyl amine and orthophosphoric acid.

   The insecticide has very little, contact action. It is converted to methyl derivative, monoemide oxide, in plant or animal tissues which is the actual toxicant. It gives control of many sucking insects and mites for several months. It is usually used at 0.5 to 1 lb. actual toxicant per acre. It is available as 30 per cent. aqueous solution, or 75 to 80 per cent. anhydrous material and is compatible with most of the commonly used insecticides and fungicides. The compound is highly toxic to mammals, the acute oral LD\(_{50}\) value to rats being 18 to 35 mg./kg.

2. Demeton \((\text{C}_8\text{H}_{19}\text{O}_3\text{PS})\)

   \(\text{O, O—Diethyl O—2 (ethylthio) ethyl phosphorothioate.}\)

   \((\text{C}_2\text{H}_5)_2 \text{PS \cdot OCH}_2\text{CH}_2 \cdot \text{SCH}_2\text{CH}_3\)

   The compound was developed for insecticidal use by G. Schrader. It is a mixture of thiono (65 per cent.) and thiol (35 per cent.) isomers. The technical material is a yellow liquid with a b.p. 134°C/2 mm. and sp. gr. 1.19 at 21°C. It is slightly soluble in water but readily soluble in most organic solvents and is readily hydrolysed by alkali. On oxidation in the plant tissues it yields toxic metabolites, viz., sulphone and sulphone.
It acts as a contact insecticide with slight fumigant action and marked systemic activity in plants. It is found to be quite effective against aphids, mites and other sucking pests. Residual effect of the sprays lasts for 1–2 weeks. It is usually used at 0·125 to 0·5 lbs. per acre. The insecticide has also proved promising as a seed-dresser (1–3 per cent. by weight of seed) against aphids, thrips, mites, etc. Demeton is usually marketed as 26 per cent. emulsifiable concentrate and 50 per cent. seed-dresser on activated charcoal. It is compatible with most non-alkaline spray materials except water soluble mercurial compounds.

The compound is highly toxic to mammals, the acute oral LD₅₀ to rats being 15 mg./kg. Thiol isomer is more toxic than the thiono isomer.

(3) Methyl demeton (C₆H₁₆O₃PS₂)

O, O—Dimethyl O—2 (ethylthio) ethyl phosphorothioate.

(CH₃O)₂ PS · OCH₂CH₂ · SCH₂CH₃

The compound was first prepared by Schrader and introduced in 1954 as an insecticide by Farbenfabriken Bayer in Germany.

It is a methyl analogue of demeton and is commonly known as 'Metasystox'. The technical material is yellowish brown with a garlic odour and is slightly soluble in water but soluble in most organic solvents. The insecticide is a mixture of thiono and thiol isomers (60 : 40), the latter being more toxic than the former.

Methyl demeton is a promising systemic insecticide and reported to be very effective especially against aphids. It remains effective for a period of 10–14 days, when used at 0·25 to 0·5 lb. per acre. It is formulated as 15 per cent. thiol isomer (known as Metasystox I or demeton-S-methyl) and 35 per cent. thiono isomer (known as Metasystox II or demeton-O-methyl). The sulfoxide of thiol isomer is marketed under the trade name of 'Metasystox R'. The sulfoxide is stable in acidic media but is rapidly hydrolysed by alkalies. The insecticide is compatible with colloidal sulphur and many other fungicides.

The acute oral LD₅₀ to rats of the thiono isomer is approximately 180 mg./kg., of thiol isomer is 65 mg./kg. and that of sulfoxide of thiol isomer is 75 mg./kg. The acute dermal LD₅₀ of thiono isomer is 100 mg./kg. while that of sulfoxide is 250 mg./kg. to rats.

(4) Dimethoate (C₅H₁₂NO₃PS₂)

O, O—Dimethyl S—(N—methylcarbamoylmethyl) phosphorodithioate.
The insecticide was introduced in 1956 independently by American Cyanamid Company in U.S.A., Fisons in U.K. and Montecatini in Italy. It is marketed as 'Rogor' in India.

The pure compound is a white, crystalline solid having a melting point of 51-52°C. It is slightly soluble in water but is soluble in most organic solvents except saturated hydrocarbons. It is stable to sunlight and in aqueous solution at room temperature but is readily hydrolysed in alkaline media and is decomposed slowly at higher temperatures.

It has been found to be effective against aphids, mites, larvae of fruit flies, etc. at 0.5 to 3 lb./acre. The compound is available as 50 per cent. wettable powder, 40 per cent. emulsifiable concentrate and 8 per cent. granules.

It is moderately toxic to mammals, the acute oral LD₅₀ to rats being 245 mg./kg.

(5) Thiometon (C₉H₁₅O₂PS₃)

O₂O—dimethyl S—2 (ethylthio)—ethyl phosphorodithioate.

S

(CH₃O)₂ PSCH₂CH₂SC₂H₅

The compound is bluish liquid with disagreeable odour and has a sp. gr. of 1.208 at 20°C. It is sparingly soluble in water but miscible with most organic solvents.

Thiometon is found to be quite promising against aphids, mites and sawfly larvae at 0.5 to 1 lb. actual toxicant per acre. It however, lacks ovicidal property. It is rapidly absorbed by the plants within 2 to 6 hours after application and is oxidised to thiometon sulphoxide and thiometon sulphone in the plant tissues. It is formulated as 25 per cent. emulsifiable concentrate. It being relatively less toxic to mammals, is used against pests of livestock at doses ranging from 5 to 25 mg./kg. body weight of the animal. Its acute oral LD₅₀ to rats is 225 mg./kg.

(6) Mevinphos (C₇H₁₃O₆P)

Dimethyl 2—carbomethoxycarbonyl—1—methylvinyl phosphate.

O

O

(CH₃O)₂ POC (CH₂) = CHCOCH₃

The compound was first introduced in the year 1953 and is commercially known as 'Phosdrin'.

The technical material is a light yellowish orange coloured liquid, b.p. 106 to 107°C/1 mm. and sp. gr. 1.25 at 20°C. It is miscible with water, xylene and acetone, slightly soluble (about 5 per cent.) in kerosene but insoluble in...
hexane. The insecticide is a mixture of two stereoisomers, the alpha or cis and beta or trans (2 : 1). Technical material contains about 60 to 70 per cent. of the cis isomer which is about 100 times more toxic than the trans isomer but the latter is more persistent. It is stable under neutral conditions but is rapidly hydrolysed by alkalies.

Mevinphos is especially suited for the control of pests infesting vegetables and fruit crops even at harvest, as it is rapidly dissipated by volatilization and enzymatic decomposition in the plant tissues. Vegetables treated with it can be used for consumption within 3 to 4 days after application. It is reported to be effective against aphids, mites, lepidopterous pests, houseflies, etc. at 0·125 to 0·25 lb. of toxicant per acre. It is available as 10 per cent. wettable powder, 1 to 5 per cent. granules and also as emulsifiable concentrates. It is marketed as technical grade material also, which is used after diluting with water.

The insecticide is highly toxic to warm blooded animals, the acute oral LD$_{50}$ to rats being 6·8 mg./kg.

(7) Phorate (C$_7$H$_{15}$O$_2$PS$_3$)

O, O—Diethyl S—2—(ethylthio) methyl phosphorodithioate.

S

\[
\frac{\text{O}_2\text{PSCH}_2\cdot\text{SC}_2\text{H}_5}{(\text{C}_2\text{H}_5\text{O})_2}\]

This compound commercially known as 'Thimet' was introduced by the American Cyanamid Co. in 1954 as an experimental insecticide. The pure compound is a yellowish liquid b.p. 118–120°C/0·8 mm. and sp. gr. 1·15 at 20°C. The technical material has over 90 per cent. purity and sp. gr. 1·167 at 25°C. It is almost insoluble in water (0·0085 per cent.) but is readily soluble in organic solvents. In plant tissues it is oxidised to Sulphoxide and sulphone metabolites which are responsible for the systemic action of the compound. The metabolites are more soluble and less stable than the parent material and are decomposed in plants to non-toxic hydrolysed products.

Phorate is a contact insecticide with marked systemic action. It is specially used as a seed-dresser to protect crops from the attack of pests like root-maggots, aphids, laflhoppers, thrips, mites, etc. When used at 4 to 6 per cent. by weight of seed, it is reported to have given protection against these pests upto a period of two months after sowing. Similar results have also been obtained with the soil application of phorate granules at 0·5 to 4 lb. toxicant per acre. The treatment has been reported to be promising even against stemflies on jowar and certain species of leaf miners. Due to high mammalian toxicity it is not used as a spray.

It is formulated as 8·0, 47·5 and 90 per cent. emulsifiable concentrate, 44 per cent. carbon powder for seed dressing and 2 to 10 per cent. granules.
The insecticide is highly toxic to mammals, the acute oral LD₅₀ to rats being 1 to 5 mg./kg.

(8) Disulfoton (C₁₉H₁₉O₂PS₃)
O, O—Diethyl S—2 (ethylthio) ethyl phosphorodithioate,

\[
\text{(C}_2\text{H}_₅\text{O})₂ \text{PSCH}_₂\text{CH}_₂\text{SC}_₂\text{H}_₅
\]

This dithio analogue of demeton was first synthesized by G. Schrader and introduced in 1956 as an experimental insecticide by Farbenfabriken Bayer, in Germany. It is commercially known as 'Di-Syston' or 'Thiodemeton'.

The pure material is a colourless liquid but the technical product is a dark yellowish oily liquid with an aromatic odour, b.p. 60°C/1.01 mm. and sp. gr. 1.44 at 20°C. It is slightly soluble in water (1 : 40,000) but soluble in most organic solvents and fatty oils. It is stable in water below pH₈ but is hydrolyzed in alkaline media. On oxidation it yields sulfoxide and sulphone metabolites.

Disulfoton is an excellent systemic insecticide which is effective against a wide range of insects and mites. It is usually applied in the form of granules at the time of sowing or as a side dressing giving protection up to 1-3 months. Promising results have also been obtained with the top dressing or the foliar application of the granules in case of crops like beet, beans, etc. It is usually used at 0.5 to 2 lb. actual toxicant per acre. It is available as 2 to 20 per cent. granules.

The insecticide is highly toxic to mammals. The acute oral LD₅₀ to male rat is 12.5 mg./kg. while to female rat it is 2.6 mg./kg.

(9) Phosphamidon (C₁₀H₁₉ClNO₅P)

Dimethyl 2—chloro—2—diethylcarbamoyl—1—methyl vinyl phosphate.

\[
\text{(CH}_₃\text{O})₂ \text{POC (CH₃)} = \text{CClCN (C}_₂\text{H}_₅\text{)}₂
\]

The compound was discovered by the chemists of Ciba Ltd., Basle, Switzerland in the year 1957.

Phosphamidon is a colourless, odourless oil, b.p. 160°C/1.5 mm. It is readily soluble in water and many organic solvents. It decomposes above 160°C. It is stable under neutral conditions but is hydrolysed in the presence of alkalies into acetoacetic acid derivatives.

It is a systemic and contact insecticide of medium persistence. It is claimed to be effective against the insects having chewing as well as sucking type of mouth parts like aphids, mites, thrips, leafhoppers, leaf miners and
stemflies. The usual concentration used for spray applications is 0.018 per cent. Since, it is regarded as harmful to bees, it is advisable not to spray the blossoming plants. It is marketed as 3 per cent. dust, 50 per cent. wettable powder and 20 and 100 per cent. emulsifiable concentrates.

It is compatible with most of the commonly used pesticides except bordeaux mixture, lime sulphur and other alkaline materials.

The acute oral LD$_{50}$ of the compound to rats is 16.8 mg./kg.

(10) Menazon (C$_9$H$_{15}$N$_5$O$_2$PS)

O, O-Dimethyl S-(4-6-diamino-1, 3, 5-triazin-2-yl) methyl phosphorothiolothionate).

\[
(C\_3H\_2O\_2)\_S\_SCH\_2-\left<\begin{array}{c}N \\ ONH\_2 \end{array}\right> N
\]

The insecticide was introduced in 1959 by the Plant Protection Ltd., United Kingdom.

The technical material contains 90 per cent. of active ingredient and has slight mercaptan odour. It decomposes with partial melting at 160 to 162°C, and is soluble in water to the extent of 0.1 per cent. It is also decomposed under strong acidic or alkaline conditions.

The insecticide has fairly good contact and systemic property. It has been recommended for the control of pests infesting vegetable crops. It is usually used at 1 to 4 lb. per acre. It is available as 4 per cent. dust, 70 per cent. wettable powder and 5 per cent. granules.

Menazon has low mammalian toxicity. The acute oral and dermal LD$_{50}$ values to rats are 430 and 1100 mg./kg. respectively.

In addition to the systemic insecticides mentioned earlier some new insecticides have been put forth in the market which are claimed to have systemic properties. These include 'Bidrin', 'Vamidothion', 'Aphidan', etc. Some systemic insecticides like 'Ronnel' and 'Coral' are used as systemic insecticides for animals.

(c) Carbamate Insecticides

These chemicals are the esters of methyl or dimethyl carbamic acids and were known since 19th century. The first known carbamate ester was an alkaloid of plant origin derived from the seeds of the calabar or ordeal bean, Phytostigma venenosum Balfour.
Like organophosphorous compounds they affect the cholinesterase system. However, they are competitive inhibitors of the enzymes with reversible action. Although they have been found to be effective against several insect pests, they do not possess acaricidal properties and have a short residual effect. Some of them exhibit systemic action. They are highly toxic to warm-blooded animals. However, unlike the chlorinated hydrocarbons, they are not stored in body fat.

Carbaryl is the only insecticide of this group used in pest control work in India:

(1) Carbaryl \( (C_{12}H_{11}O_{2}N) \)

\[
\begin{align*}
1-\text{Naphthyl N-methylcarbamate.} & \quad \text{OCNHCH}_3 \\
\end{align*}
\]

The compound, commercially known as 'Sevin,' was first synthesised by Lambrench (1956) of Union Carbide Company, U.S.A. and its insecticidal properties were described by Haynes et al. in 1957.

It is a white crystalline solid, m.p. 145°C. The technical material is 95 per cent. pure. It is slightly soluble in water (less than 0.1 per cent.) but is soluble in polar organic solvents. The compound is stable to light and heat but under alkaline conditions, it is hydrolysed to form 1-naphthol, carbon dioxide and methylamine.

It is a good contact insecticide of medium persistence with slight systemic action and is found to be quite effective in controlling pests infesting cotton, vegetables, fruit crops, etc. at 0.5 to 4 lb. per acre. It is formulated as 5 and 10 per cent. dusts, 50 and 85 per cent. wettable powders, 13 per cent. emulsifiable concentrate and 5 per cent. granules. It is compatible with most of the pesticides except those which are strongly alkaline like Bordeaux mixture and lime-sulphur.

The insecticide has relatively low mammalian toxicity, the acute oral LD\textsubscript{50} to rats being 500 to 700 mg./kg., while the acute dermal LD\textsubscript{50} to rabbits is above 2,000 mg./kg.

Although few other carbamates like Isolan, Pyrolan, Pyramet, Dimetan and 'Zectran' have also been claimed to be potent insecticides, they are not commercially available in this country.
(d) Dinitrophenols

The earliest record of the use of dinitrophenols as insecticides was in 1892 in Germany. They, however, were extensively used only after 1925, as acaricides, dormant sprays against mites, scale insects, etc. and as poison baits for grasshoppers. Because of their high phytotoxicity, they are mostly used as herbicides and as dormant sprays.

The important chemicals belonging to this group are DNC or DNOC (nitroortho-cresol) and DNOCHP (Cyclohexyl-dinitrophenol). Due to the availability of other more promising and safer insecticides they are rarely used in India.

(e) Organic Thiocyanates

These compounds were developed in U.S.A. to replace insecticides of plant origin like pyrethrum and rotenone which were required to be imported from other countries. Insecticides like Lethane and Thanite were used during World War II. They however, are rarely used in plant protection work these days.

FUMIGANTS

As mentioned earlier these are the chemicals which in gaseous or vapour state kill the pests by entering their respiratory system. Fumigants were known to the Greeks and Romans even before the Christian era. Almost all these compounds have low molecular weight and are often simple derivatives of methane, ethane and propane gases. They are generally used in confined places like ware-houses, bins and several other air tight containers and are found useful in controlling pests of stored products, some internal feeders like mango stem borer, bark eating caterpillar, etc. and subterranean pests. They, however, are deadly toxic to higher animals, while some are highly inflammable and are therefore required to be used with great care and under expert supervision.

Some of the important fumigants commonly used in this country are described below:

(1) Hydrocyanic acid (HCN) or Hydrogen cyanide.

It was discovered by Scheele in 1783, but was used for the first time in 1886 against scale insects, Icerya purchasi Mask, on citrus in U.S.A. It is a colourless gas with almondlike odour b.p. 26°C, sp. gr. 0.699 at 20°C and vapour density almost equal to that of air. It is soluble in water, alcohol and ether.

It was extensively used for fumigating citrus trees for controlling scale insects and for the destruction of pests infesting stored products. For treating 1000—1500 cu. ft. of space, a mixture of sodium cyanide (98 per cent. pure)
1 lb., sulphuric acid (sp. gr. 1.83) 1½ pt. and water 3 pt. is used. Initially the gas was obtained by action of sulphuric acid on potassium cyanide which was later substituted by a cheaper chemical, sodium cyanide, (NaCN). Calcium cyanide or 'Cyanogas' Ca(CN)₂ also liberates this gas on coming in contact with moisture. HCN is available in liquid form which is stored under pressure in iron cylinders. It is safe for the fumigation of dry products but has adverse effect on vegetables, unripe fruits, etc. Its use on trees treated with copper compounds should be avoided.

It is highly toxic to mammals. A concentration of 200 ppm. is fatal to human beings.

(2) Carbon disulphide (CS₂)

The insecticidal properties of the compound were discovered by Garreau in France in 1854. It is a yellowish liquid and the commercial product has a highly offensive odour. The purified compound has a b.p. 46.3°C, m.p. 108°C, sp. gr. 1.263 at 20°C and a vapour pressure of 357 mm. at 25°C. It is highly inflammable and slightly soluble in water but miscible with alcohol, ether and chloroform.

The compound has been widely used as a fumigant for nursery stocks, stored grains and potatoes at 1 lb./100 cu. ft. It is also used against soil pests. A mixture of two parts of carbon disulphide and one part each of chloroform and creosote oil is used as a borer solution for controlling stem and bark borers. Being highly inflammable it is often mixed with carbon tetrachloride but the efficiency of the mixture is reduced. It is also reported to have harmful effect on some plants and seeds.

The vapours of the chemical are highly poisonous to warm blooded animals and concentration as low as 70 ppm. is reported to be dangerous on repeated exposures.

(3) Ethylene dichloride (C₂H₄Cl₂)

The compound was introduced by Cotton and Roark in 1927. It is a colourless liquid with a smell of chloroform, b.p. 83·5°C, m.p.—36°C, and sp. gr. of 1.257 at 20°C. It is practically insoluble in water but soluble in organic solvents and is stable in presence of water, alkalies and acids. It is resistant to oxidation and is non-corrosive to metals. However, being highly inflammable, it is mixed with carbon tetrachloride and is commonly available as a ED/CT mixture (3 : 1) which is used for fumigating the stored grains at 8·14 lb./1,000 cu. ft. spec. It is quite safe for the fumigation of seeds. Though it is less toxic to human beings, repeated exposures lead to anaesthesia.

(4) Ethylene dibromide or EDBR (C₂H₄Br₂)

It was developed by the DOW Chemical Co. U.S.A. and reported as an effective fumigant by Neifert et al. in 1925.
It is a colourless liquid with a chloroform like odour, b.p. 131°C, sp. gr. 2.172 at 25°C and the vapour pressure of 110 mm. at 25°C. Though slightly soluble in water, it is soluble in most organic solvents and is stable and non-inflammable.

It is extensively used for fumigation of grains. Impregnation of gunny bags with EDBR and insecticide mixture is reported to have given complete protection against stored grain pests. A mixture of EDBR and methyl bromide (Durofume) has also been found to be effective against stored grain pests. Its vapours are poisonous while the contact with liquid causes irritation of the skin.

(5) Methyl bromide (CH₃Br)

The insecticidal properties of the chemical were first reported by Le Goupil in 1932. At ordinary temperature, it is a gas about 3.3 times heavier than air and therefore has a good penetrating property. The liquid form is colourless, b.p. 3.6°C and a sp. gr. 1.73 at 0°C. The vapours are odourless but can be detected by halide leak detector. It is slightly soluble in water, but soluble in most organic solvents. It is stable and non-corrosive to metals. Being non-inflammable it is widely used as a fire extinguisher. The chemical is extensively used for the fumigation of flour mills, warehouses, termitoria and soil to destroy nematodes. It is usually used at 1 lb. per 1,000 cu. ft. for 48 hours, exposure. Since it adversely affects germination, its use for fumigation of seeds is discouraged.

It is highly toxic to mammals at concentrations above 17 ppm.

(6) Chloropicrin (CCl₃NO₂)

Although the compound was synthesized in 1848, it was used as a ‘war gas’ in the first World War by the Russians. It is a colourless liquid, b.p. 112°C, sp. gr. 1.69 at 0°C and a vapour density of 5.7. It is non-inflammable and is insoluble in water but is miscible with organic solvents.

It is used for the fumigation of soil against nematodes, stored grains etc. at 2 to 5 lb. per 1,000 cu. ft. Since it causes irritation of mucous membrane, it has been used as a warning agent in other fumigants.

It is toxic to mammals and proves fatal at 0.8 mg./litre of 30 minutes exposure.

(7) Hydrogen phosphide (PH₃)

It is a colourless, poisonous, inflammable gas which is slightly heavier than the air and has been used as a fumigant for many years. Recently however, a product known as ‘phostoxin’ tablets containing a mixture of aluminium phosphide (65 per cent.) ammonium carbamate (40 per cent.) and aluminium oxide (5 per cent.) is available. These tablets in presence of moisture, release hydrogen phosphide or phosphine, ammonia and carbon dioxide gases
leaving behind a non-toxic residue of aluminium hydroxide. Each 3 gramme tablet produces 1 gramme of hydrogen phosphide. It is extensively used for fumigation of grains, but is highly poisonous to warm blooded animals and should be handled with care.

(8) Dichloropropene and dichloropropane (C\textsubscript{6}H\textsubscript{10}Cl\textsubscript{4})

The compound commercially known as ‘D-D’ fumigant was first used as a soil fumigant by Carter in 1943. It is a black volatile liquid, practically insoluble in water but soluble in most organic solvents and is inflammable.

It is extensively used as a soil fumigant especially for the control of nematodes by injecting it into the soil at the rate of 200–400 lb. per acre. Since it is phytotoxic and causes tainting, it should be applied 6-8 weeks before planting. As the compound causes irritation of skin and eyes, protective clothing should be used.

(9) Dibromochloropropane (C\textsubscript{6}H\textsubscript{5}Br\textsubscript{2}Cl)

1-2-Dibromo-3-3-chloropropane

CH\textsubscript{2}Br—CHBr—CH\textsubscript{2}Cl

The compound commercially known as ‘Nemagon’ or ‘Fumazone’ was first described as a nematocide by McBeth and Bergeson in 1955. It is a dark brown liquid with pungent odour, b.p. 196°C and sp. gr. 1.55 at 25°C. It is sparingly soluble in water but miscible with hydrocarbon oils, isopropane, alcohols, etc.

It is a soil fumigant especially useful against nematodes. It is less phytotoxic and is more effective than ‘D-D’ or ethylene dibromide. It is available as liquid or granules. The former is injected into the soil while the latter are worked into the soil. It is usually used at 0.5 to 4 imperial gallons of actual toxicant per acre.

It is moderately toxic to mammals. The acute oral LD\textsubscript{50} to male rat is 172 mg./kg.

In addition to the fumigants mentioned above, a few others like ethylene oxide (C\textsubscript{2}H\textsubscript{4}O), acrylonitrile (C\textsubscript{2}H\textsubscript{3}N), methallyl chloride, trichloracetonitrile (Cl\textsubscript{3}C CN), paradichlorobenzene, sulphuryl fluoride, etc. have also been found to be useful as fumigants but are not commonly used in this country. Mixtures of some of these fumigants are also commonly used and found to be more effective and safer than their components.

(IV) MICROBIAL INSECTICIDES

Like human beings and other animals, insects also suffer from diseases caused by protozoa, bacteria, fungi or viruses. Due to the toxicity hazards associated with the use of pesticides, the method of using the microorganisms for pest control work has attracted attention in recent years. Being specific to insects,
they are becoming popular in plant protection work. Promising results have been obtained by using microbial cultures, e.g., larvae of Japanese beetle the most destructive pest of fruit trees, lawns and pastures is effectively controlled by the preparations containing the spores of Bacillus popillae which cause milky disease. Similarly, the formulations containing spores of Bacillus thuringiensis Berliner are also found to be promising against the several species of lepidopterous larvae. Besides bacteria, viruses have also been used in controlling certain pests, important amongst these are the nuclear polyhedroses and granuloses. In India, however, the only microbial insecticide tried in pest control work is the preparation of Bacillus thuringiensis commercially known as ‘Thuricide’. It is available as dust and wettable powder and is reported to be effective against lepidopterous larvae at 35-50 lb. of dust or 0.25 to 4 lb. of wettable powder per acre.

(V) ATTRACTIONS AND REPELLENTS

These chemicals act on insects as olfactory stimulants:

1) Attractants.—Are the chemicals which attract insects either for feeding, oviposition or mating. They are commonly used for controlling insects either by attracting them to the traps or poison baits containing insecticides or chemosterilants and for studying the population density of pests. The outstanding examples of success, obtained with this method are the use of geranoil and methyl eugenol against Japanese beetle and oriental fruit fly respectively. A synthetic sex attractant ‘gyplure’ or ‘gyptol’ (d-12-acetoxy cis-g-octadeceno-1-101) is used in bait traps for controlling the gypsy moth by attracting males. Similarly, butyl esters, like ‘medlure’ and ‘trimedlure’ for Mediterranean fruit fly, ‘cue-lime’ [(4-cp-acetoxyphenyl)-2-butanone] for melon fruit flies, etc. have also been found to be effective synthetic attractants. Besides, fermenting sugars and syrups, essential oils, protein hydrolysates, etc. are also used as attractants for controlling different pests.

2) Repellents.—These are the chemicals which repel the insects by making their food or living conditions unattractive or offensive to them and thus prevent damage to the host. They may act as repellents against crawling insects, e.g. trichlorobenzene against termites, to feeding insects, e.g. bordeaux mixtures against leafhoppers, or to prevent egg layings by insects, e.g., pine tar oil and diphenylamine. Repellents are mostly used against the pests attacking man and domestic animals.

(VI) CHEMOSTERILANTS

These chemicals by their action render insects sterile. Most of the aziridinyl compounds used in cancer therapy or in textile industries as anti-crease compounds have been found to act as chemosterilants. They render insects sterile by inhibiting the production of ova or sperms or destroying them if they are already formed or producing multiple lethal genes and preventing further multiplication.
Though these compounds are in experimental stage, a few like ‘Tepa’, ‘Metapa’, Apholate, Aphamide, etc. have been found to be promising against houseflies, fruit flies, etc.

II. ACARICIDES

As defined earlier, these are the chemicals which kill mites. They are highly stable compounds with a comparatively prolonged residual action and low mammalian toxicity. Since these chemicals act purely as acaricides, they have little or no effect on insects and are thus not harmful to beneficial insects. Some of the important and commonly used acaricides are described below:

(1) Sulphur (S).—It is extensively used as a fungicide but has acaricidal properties also. Originally it was used in the form of ‘Flowers of Sulphur’ obtained by the sublimation of crude sulphur. However, since there is a direct relationship between the degree of toxicity and particle size, finely ground powder or colloidal formulations are used in plant protection work.

It is a yellow powder melting at 115°C to yellow mobile liquid which darkens and becomes viscous at 160°C. It is insoluble in water but slightly soluble in alcohol and ether. Only the crystalline form is soluble in carbon disulphide. It is slowly hydrolysed by water.

It is a good acaricide and is used alone or in combination with insecticides at 1-2 lb. per acre. It is generally non-phytotoxic but reported to cause damage to ‘sulphur shy’ varieties of crops. At higher temperatures (above 30°C) it also causes damage known as ‘sulphur scald’.

It is available as 300 mesh dust, 40-80 per cent. wettable powder and as 50 per cent. colloidal sulphur. It is nontoxic to man and other higher animals.

(2) Lime-sulphur.—The compound was developed as a substitute for sulphur and was used against San Jose scale for the first time in 1886 in California by Dusey. It is prepared by boiling fresh lime and sulphur but should have a sp. gr. of 1.28 at 60°F. It is an orange coloured liquid with a bad odour and is a mixture of calcium pentasulphide (CaS₅), calcium tetrasulphide (CaS₄), calcium thiosulphate (Ca₅S₈O₃) and calcium sulphite (CaS₂O₃). The first three are soluble in water while calcium sulphite is almost insoluble. Of these, calcium pentasulphide and tetrasulphide are called as polysulphides which have acaricidal property.

It is used for the control of mites. Like sulphur, it also causes ‘sulphur scald’ at higher temperature (above 30°C) and is phytotoxic to ‘sulphur shy’ varieties of crops. It is compatible with calcium arsenate but is of doubtful compatibility with most of the commonly used pesticides.
(3) Chlorobenzilate (C₁₄H₁₄Cl₂O₉)
Ethyl P, P′—dichlorobenzilate.

It was first synthesised by Hafliger and Girod in 1951 while its acaridal properties were described by Gasser in 1952. It is commercially known as 'Akar'.

It is a yellowish viscous liquid, b.p. 141-142°C at 0.06 mm. Hg. The technical material contains about 90 per cent. active ingredient and is slightly soluble in water but freely soluble in most organic solvents. It is decomposed by strong acids and alkalies to give inactive p, p′ dichlorobenzilic acid and ethanol.

The compound is toxic to all stages of mites but less toxic to eggs. It is used at 0.25 to 1 lb. toxicant per acre. The chemical is compatible with most of the insecticides and fungicides except alkaline materials. It is formulated as 25 per cent. wettable powder and 25 per cent. emulsifiable concentrate.

The compound has a low mammalian toxicity, the acute oral LD₅₀ to rats being 700 mg./kg.

(4) Dicofol (C₁₄H₉Cl₃O)
1, 1—bis—(p—chlorophenyl)—2, 2, 2—trichloroethanol.

The compound, commercially known as 'Kelthane' was introduced by Rohm and Hass Co., U.S.A. as an experimental acaricide in 1955.
It is a white solid with m.p. 78.5–79.5°C and b.p. 225°C at 5 mm. It is insoluble in water but soluble in most organic solvents. Though stable to the action of acids, it is hydrolysed by alkalies to yield inactive compounds like p-p′-dichlorobenzophenone and chloroform. The compound is effective against different species of mites when used at 1 to 2 lb. toxicant per acre. It is formulated as 30 per cent. dust, 25 per cent. wettable powder and 50 per cent. emulsifiable concentrate. It is compatible with most of the pesticides except alkaline materials and has low mammalian toxicity. The acute oral LD₅₀ to rats is 700 mg./kg.

(5) Aramite (C₁₆H₂₃ClO₄S)
2—(p—tert—butylphenoxy)—isopropyl 2′—Chloroethyl sulphite.

\[
\begin{align*}
(CH_3)_3 C & \quad O \\
& \quad OCH_2-CH-O\text{SOCH}_2\text{CH}_2\text{Cl.}
\end{align*}
\]

It was discovered by Harris and Zukel of United States Rubber Co., U.S.A. in 1948.

The pure chemical is a colourless liquid, b.p. 175°C at 0.1 mm. while the technical material is a dark amber coloured liquid sp. gr. 1.145–162 at 20°C. It is miscible with most organic solvents but is insoluble in water. The compound is hydrolysed by alkalies while it is decomposed in presence of light and in storage giving sulphur dioxide and/or ethylene oxide.

It is effective against several species of mites at 0.25 to 1.5 lb. toxicant per acre and is mostly recommended on non-edible crops like cotton where there is no residue problem as it is reported to be responsible for causing cancer. It is available as 3 per cent. dust, 15 per cent. wettable powder and 85 per cent. emulsifiable concentrate. It has low mammalian toxicity, the acute oral LD₅₀ to rats and guinea pigs is 3.9 g./kg.

(6) Tetradiforn (C₁₂H₇Cl₄O₂S)
2, 4, 5, 4′—tetrachlorodiphenyl sulphone.

\[
\begin{align*}
\text{Cl} & \quad \text{S} \\
\text{Cl} \quad \text{O} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]
The compound commercially known as 'Tedion' was discovered by N. V. Philipe—Dulphur of Netherland in 1954.

It is a white crystalline solid, m.p. 148—149°C, sp. gr. 1.515 at 20°C, practically insoluble in water, slightly soluble in dioxane, chloroform and aromatic hydrocarbons but is stable to dilute alkalies and strong acids.

It is a promising miticide and is effective against eggs and nymphs of several species of mites when used at 0.5 to 1.5 lb. toxicant per acre. It is available as 2 and 3 per cent. dusts, 20, 50 and 90 per cent. wettable powders and 8 and 13 per cent. emulsifiable concentrates. It is compatible with almost all commonly used pesticides and has low mammalian toxicity. The acute oral LD₅₀ to rat is 14,700 mg./kg.

Besides, the commonly used acaricides mentioned above, few others like chlorobenside, 'Ovex' or 'Ovotran,' 'Neotran,' 'Azobenzene,' 'Florbenside,' 'Dimite,' etc. have also been reported to be promising miticides but are rarely used in this country.

III. RODENTICIDES

These are the chemicals which kill the rodents like rats and bandicoots. They act as stomach poisons and are used in the form of poison baits. Being highly toxic to man and other warm blooded animals they are required to be handled with great care. Some of the important rodenticides used in India are described below:

(1) Zinc phosphide (Zn₃P₂). The compound was used for the first time by Grandi in 1912 in Italy to combat field rats. It is a dark grey or blackish powder with a strong pungent odour. It is practically insoluble in water and alcohol but soluble in benzene and carbon disulphide. It reacts with acids and gets decomposed to form an inflammable phosphine gas. It is stable under normal conditions but decomposes slowly on exposure to moist air. Due to the action of hydro-chloric acid present in the gastric juice of rodents, the phosphine gas is evolved from the chemical which is rapidly absorbed into the system causing death of the animal.

Zinc phosphide is highly toxic to rodents and has become popular due to its quick lethal action. It is used as 5 to 10 per cent. poison bait with carriers like wheat, barley or grain flour or crushed millets and water just sufficient to moisten the bait is added. A little quantity of mustard or groundnut oil is also usually added which, besides being useful in preparing pills, accelerates the absorption of poison in the body. Since rats are suspicious creatures, pre baiting with non-poisonous material is necessary. The chemical is known to develop bait shyness in rats and, therefore, the interval between two successive ba tings should be at least 15 days.

The compound is highly toxic to mammals, the acute oral LD₅₀ to rats being 45 mg./kg.
(2) Barium carbonate (BaCO₃).

The chemical was first used by Nessler and Crampe in 1878 for the control of field mice in Germany.

It is a white, tastelers and odourless powder, insoluble in water and alcohol but soluble in mineral acids and ammonium chloride solutions. The technical material is 98 per cent. pure and is used in the preparation of poison baits. It is less toxic to rats compared to zinc phosphide. Generally 16 to 20 per cent. concentration of the toxicant is used in baits. It is mixed with carriers like cereals moistened with water and a little jaggery or molasses is added for taste. Rats prefer wet baits. They develop bait shyness more quickly than in case of zinc phosphide.

The compound is relatively less toxic to mammals, the acute oral LD₅₀ to rats is about 1,100 to 1,700 mg./kg.

(3) Warfarin (C₁₉H₁₈O₄)
3-{a-acetonylbenzyl}-4-hydroxcoumarin.

It is a coumarin derivative which inhibits the synthesis of prothrombin, responsible for the coagulation of blood. The anticoagulant properties of the compound were discovered by Link et al. in 1944. It is an odourless, colourless, tasteless, crystalline, chemical with m.p. 1959-161°C. It is insoluble in water and benzene, moderately soluble in alcohol and freely soluble in acetone and dioxan. It is acidic in nature and forms salts with metals.

It is a slow acting anti-blood coagulant and when ingested by rat, it damages the blood vessels and causes internal haemorrhages as a result of which the animal collapses. It is less toxic and therefore repeated applications are necessary which increase the cost of treatment. It is marketed as 0.5 per cent. powder, or as ready-to-use paste containing 0.02 per cent. of the active ingredient. The bait is prepared by mixing powder with whole gram or crushed maize or rice to which a little vegetable oil is added. The concentration of the bait is usually 0.025 per cent. The compound does not develop bait shyness in rats and pre-baiting is not necessary.

The chemical is toxic to mammals. The acute oral LD₅₀ value to female rats is about 60 mg./kg.
In addition to the compounds mentioned above, a few others like strychnine hydrochloride, sodium fluoroacetate, pindone (Pival), ‘ANTU’, coumachlor (Tomorin), Fumarin, etc. are also used in rodent control work.

IV. NEMATOCIDES

Chemicals which kill nematodes are known as nematocides. These are mostly fumigants and are applied to the soil. The fumigants commonly used as nematocides are chloropicrin, Nemagon (Dibromochloropropane) D-D (Dichloropropene and dichloropropane), methyl bromide, ethylene dibromide, etc. which have already been discussed under fumigants.

V. MOLLUSCICIDES

These are the chemicals which kill soft bodied animals like snails and slugs belonging to the phylum Mollusca. They act either as stomach or contact poisons. The only chemical used as molluscicide is Metaldehyde which is described below.

Metaldehyde (C\textsubscript{4}H\textsubscript{4}O\textsubscript{4}).

The molluscicidal properties of the compound were reported in 1936. It is a crystalline polymer of acetaldehyde and is a colourless and odourless powder with m.p. 246°C. It is practically insoluble in water but soluble in benzene or chloroform and gets depolymerised in storage.

It is quite promising against slugs and snails, causing paralysis and dehydration due to excessive secretion of slime or mucous. It is used as 2-4 per cent. dry poison bait with wheat bran and also as dust and spray which however are phytotoxic. The treatment is rendered ineffective if rains follow the application.

It is relatively less toxic to warm blooded animals. The acute oral LD\textsubscript{50} to dogs is 600–1000 mg./kg.

In addition to metaldehyde, carbamates like ‘Zectran’ dimetilan, dimetan, organophosphates like phorate and ‘Zinophos’ are also known to possess molluscicidal properties.

VI. PESTICIDAL FORMULATIONS

Most of the pesticides cannot be applied as such, as they are likely to cause phytotoxicity and uneven distribution on treated surfaces. Suitable formulations are therefore prepared. In fact, the success of pest control work depends much on the type of formulation used. The commonly used pesticidal formulations are as follows:

- (1) Dusts.—In these formulations the insecticide is mixed with a dry inert carrier. In contains 0·1 to 20 per cent. toxicant and the rest is inert carrier which helps in uniform distribution. The commonly used carriers are talc, gypsum, clays, flours, etc. which are thoroughly mixed with the toxicant.
While choosing a carrier, factors like particle size, abrasiveness, inertness, etc., are taken into consideration since they have direct bearing on the efficacy of the insecticide. Usually the particle size ranges from 5 to 50 microns.

Dusts are usually used for the control of the pests infesting unirrigated crops or in areas where due to the scarcity of water liquid formulations cannot be used. Dusting is usually carried in calm weather and preferably in the morning when the plants are wet with dew which helps in deposition of dusts. They are applied at 15-20 lb. per acre on crops and 50 to 200 lb. per acre to the soil.

(2) Wettable powders.—These are the powders containing higher percentages of toxicant (15 to 95 per cent.) to which wetting agents are added. In addition, other adjuvants like spreaders and stickers are also incorporated to keep them in suspension when mixed with water and spread and adhere well to the treated surfaces. Because of their longer persistence on the treated surfaces, they are better compared to dusts. They however, are not suited for use in concentrated sprays, as the small nozzle orifices, necessary for atomization of concentrated material, get plugged with the particles of the powder.

(3) Granules.—In this formulation the toxicant is impregnated, into or on to the granulated carriers such as clays, highly absorptive clays (attapulgites and vermiculites), bentonite, tobacco waste, etc. The particle size ranges from 0.3 to 1.5 mm. Most granules are of 30/60 grade i.e. they can pass through 30 mesh but are retained on 60 mesh sieve. Because of their weight, loss of chemical and hazards due to drifts are minimized. Besides, they lodge in leaf whorls and slowly release chemicals and as such, are found to be useful against tissue borers.

The granulated systemics as soil or foliar application have been found to be effective mostly against the pests having sucking type of mouth parts. Soil application, however, is desirable as it is not harmful to beneficial species.

(4) Seed-dressers.—These are usually the wettable powders containing carriers like activated carbon or carbowax and are generally used for treatment of seeds to protect them from the damage due to subterranean species and the crops from the pest infestation in early stages of their growth.

(5) Emulsions.—In this formulation, the insecticide is dissolved in an organic solvent and is to be mixed with water at the time of application. In order to ensure the stability of emulsion, surface active substances known as emulsifiers are usually incorporated which form the interphase between the water and oil droplets and give stability to the emulsion. A water soluble emulsifier is generally used where emulsion is to be produced in a spray tank by mixing but for preparing an emulsifiable concentrate, oil soluble emulsifiers are used. Besides, other adjuvants like wetting and spreading agents, stickers, etc. are also added. At the time of application,
the emulsion breaks or separates into its immiscible constituents. Quick-breaking emulsions are generally preferred for treatment of crops as they produce heavy deposits while for residual spraying on residential buildings, cloth impregnation, etc., stable emulsions are useful. These formulations are suited for low volume spraying. Besides, since they contain solvents, they are superior to wettable powders. If the emulsion is not properly prepared, it causes phytotoxicity.

(6) Solutions.—In these, the insecticides are dissolved in organic solvents. Because of the solvents used in the preparation, they often prove phytotoxic and are therefore not used for treating the plants but against household pests.

(7) Aerosols.—These are ready-for-use preparations containing the toxicant dissolved in an organic solvent. The solvent evaporates rapidly leaving fine concentrated particles of the toxicant dispersed in air. They are also available as aerosol bombs. The most effective particle size is 0.30 microns. They are usually used in enclosed areas such as green houses, dairy barns, etc., mostly against flying insects.

(8) Fumigants.—These are already described on page 32.

In addition to the above formulations, pesticides are also available as tablets (Phostoxin), balls (Naphthalene), paste (Warfarin), soaps (Fish oil rosin soap), etc.

**ADJUVANTS**

The supplemental ingredients incorporated in the pesticidal formulations are called as adjuvants. They impart desirable properties like wetting, spreading sticking, stabilizing, etc. to the formulations and in some cases even enhance their toxicity. Some of the important adjuvants are described below:

(1) Emulsifiers.—These are used to impart stability to the emulsion. Two types of emulsifiers, viz., water soluble and oil soluble are used. Non-ionic type of emulsifiers like glycerol monoleate, manitan monolaurate, aliphatic esters of sorbitol and their polyoxyalkalene derivatives and polyalkaline ether alcohol are added in most of the emulsifiable concentrates.

(2) Wetting and spreading agents.—These are used in the preparation of wettable powders. Since most of the plants and insect cuticles are provided with lipoid layers which are strongly hydrophobic, the water sprays tend to form droplets due to surface tension. In order to lower the surface tension of the spray material, thereby making it wet and spread well on the treated surfaces, wetting and spreading agents are incorporated in the formulation. Soaps, besides being emulsifiers, also act as wetting and spreading agents. The sulfonated aliphatic esters and amides such as dioctyl-sodium sulfosuccinate and sodium sulfonated petroleum products serve as wetting and spreading agents. They are used as dispersing agents in wettable powders.
(3) **Stickers.**—These are added to spray formulations to help the spray deposits to adhere well to the treated surfaces. Though it is normally the function of wetting and spreading agents, certain supplementary adhesive agents or stickers are usually added to the formulations to improve their sticking properties which is quite essential especially under heavy rainfall conditions. Substances like casein, gelatin, soybean flour, blood albumin, clays, bentonites, petroleum and vegetable oils are used as stickers.

(4) **Stabilising agents.**—These are usually used in the formulations of unstable insecticides so as to prevent their decomposition in storage. For instance, antioxidants such as mixed isopropyl cresols are used to prevent the decomposition of pyrethrins, while acid inhibitors such as epichlorohydrin are added to the formulations of aldrin and toxaphene to avoid dehydrochlorination.

(5) **Deodourants or masking agents.**—Some insecticides such as thiocyanates, pyrethrins, methylated naphalenes, etc. have unpleasant or disagreeable odour. Substances like pine oil, cedar oil and scents of various flowers are incorporated at concentrations of 0.1 to 1.00 per cent. in formulations to mask their unpleasant odours.

(6) **Synergists.**—These are the chemicals which by themselves are non-toxic or only slightly toxic but when mixed with the pesticides increase their toxicity. Some of the commonly used synergists are piperonyl butoxide; sesamin, 2, 6-bis-(3, 4-methylene dioxyphenyl)-3, 7-dioxabicyclo-(3.3.0)octane, sesoxane, 2-(3, 4-methylene dioxyphenoxy)-3, 6, 9-tioxaundicanic; Safroxan, 4-(3’, 4’-methylenedioxy)-5-methylmetadioxan; MGK 264, N-(2-ethylhexyl)-bicyclo-(2.2.1)-5-heptene-2, 3-dicarboxymide, etc. They synergize pyrethroids, nicotine, some organophosphates and carbamate insecticides.

In addition to the adjuvants mentioned above, defloculating agents such as glue gelatin, deposit builders like petroleum sulfonates and correctives or softners like ferrous sulphate with lime sulphur are also used in certain formulations.

**Characteristics of an Ideal Insecticide**

The following are the important points which should be taken into consideration while selecting an insecticide:

(1) It should be highly toxic to pests but should not have adverse effects on beneficial species.

(2) It should not be toxic to higher animals and plants.

(3) It should be compatible with other insecticides, fungicides, herbicides and fertilisers.

(4) It should not cause tainting of edible plant products.
(5) It should be non-inflammable, non-corrosive and stable under ordinary conditions of storage and transport.
(6) It should not have off-flavour.
(7) It should be cheap and readily available in different formulations.

VII. INSTRUCTIONS FOR THE SAFE HANDLING OF PESTICIDES

Most of the pesticides used in plant protection are toxic to human beings and domestic animals if not carefully handled.

They are usually safe if properly stored, handled, transported and used with necessary precautions.

A. Precautions while storing

1. Keep pesticides in labelled containers only.
2. Store pesticides in a cool, dry and safe place preferably under lock and key, out of the reach of children and pets.
3. Never store pesticides near food stuffs or medicines.

B. Precautions while Handling

2. In the handling of dangerous pesticides, necessary protective clothing and other devices must be used.
3. Do not tear open the pesticide bags but cut them with a knife.
3. The preparation of spray mixtures from concentrated dangerous pesticides should be done in deep mixing vessels with long-handled mixers to protect the operator from splashing and to permit stirring from a standing position. Dusts and granules should be removed from the containers by a scoop with a long wooden handle.

C. Precautions at the time of Application

1. Wash hands thoroughly with soap and water (i) every time the sprayer/duster is filled with pesticides, (ii) before eating, drinking or smoking and (iii) at the end of the day’s work.
2. Never eat any thing or chew tobacco or smoke while spraying or dusting or sowing treated seeds.
3. Do not blow, suck or apply mouth to any sprinkler, nozzle or other spraying equipment.
4. Never carry out spraying or dusting operations against the wind.
5. While spraying tall trees, care should be taken to avoid the drifts directly falling on body of operator.
6. Separate clothes should be used while working. They should be washed and changed as frequently as possible.
D. Precautions after application

1. Do not allow the cattle to graze in the sprayed or dusted area at least for two to three weeks.

2. Do not use treated commodities for consumption. Allow a period of at least a fortnight to elapse after application of pesticides. It would be desirable to wash them thoroughly with water before consumption.

E. General precautions

1. Read the label carefully and follow the manufacturer’s instructions.

2. Do not use the empty containers of pesticides for any other purpose but destroy them.

3. Contaminated effluents from washing of the equipment and mixing vessels must be disposed off by scattering over barren land or burying in the ground. Never wash vessels, sprayers, etc. in the tanks, streams, rivers, etc.

4. Operators should not work for more than 4-8 hours a day. Operators engaged in handling dangerous pesticides should be checked by a physician periodically.

First Aid Precautions

In case of poisoning due to pesticides, CALL A PHYSICIAN IMMEDIATELY. Awaiting the Physician’s arrival, apply FIRST AID:

1. Swallowed poisons.—Remove poison from the patient’s stomach immediately by inducing vomiting. Give common salt 1/2 oz. in a glass of warm water and repeat until the vomit fluid is clear. Gently stroking or touching the throat with the finger or placing the blunt end of a spoon will aid in inducing vomiting when the stomach is full of fluid.

   If the patient is already vomiting, do not give emetic or vomiting substance (common salt 1/2 oz. in a glass of warm water) but give large amounts of warm water and then follow the specific directions suggested.

   Do not induce vomiting if the patient is in coma, unconscious, in convulsion and when the patient has swallowed petroleum products, kerosene, gasoline, etc. and corrosive acids or caustic alkalies, (symptoms: severe pain, burning sensation in mouth and throat and vomiting).

2. Inhaled poisons.—(a) Carry the patient (do not let him walk) to fresh air immediately.

   (b) Open all doors and windows.

   (c) Loosen all tight clothing.

   (d) Apply artificial respiration if breathing has stopped or is irregular. Avoid vigorous application of pressure to the chest.

   (e) Prevent chilling.
Wrap the patient in a blanket.
Keep the patient as quiet as possible.
If the patient is convulsing, keep him in bed in some dark room. Avoid jarring noises.
Do not give alcohol in any form.

3. Skin contamination.—(a) Drench the skin with water (showers, hose, or pump).
(b) Apply a stream of water on the skin while removing clothing.
(c) Cleanse the skin thoroughly with water.
(d) Rapid washing is most important for reducing the extent of injury.

4. Eye contamination.—(a) Hold eyelids open.
(b) Wash the eyes gently with a stream of running water immediately. Delay of even a few seconds greatly increases the extent of injury.
(c) Continue washing until physician arrives. Cleanse the skin thoroughly with soap and water. Soap is specially useful in case of skin contamination with organophosphorous pesticides as it quickly hydrolyses them.
(d) Do not use chemicals. They may increase the extent of injury.

(b) Do not use a hot water bottle.
(c) Raise foot on bed.
(d) Apply plastic bands to arms and legs.
(e) Give strong tea or coffee.
(f) Hypodermic injection of stimulants, such as caffeine and epinephrine.
(g) Fluid administration of dextrose 5% intravenously.
(h) Blood or plasma transfusion.
(i) Do not exhaust the patient by too much or too vigorous treatment.

GENERAL SUGGESTIONS FOR TREATMENTS

In many cases of poisoning, the nature of the toxic agent is not known. The treatment is therefore, symptomatic and may include—

(1) Emesis and gastric lavage if poison has been taken internally.
(2) Evacuation of the gut (avoiding oily laxatives where it is possible that an organic solvent or a halogenated insecticide is involved).
(3) Thorough washing of the eyes or body. If there has been external contact with the poison, wear rubber gloves while aiding the patient.
(4) Supportive therapy—
(a) Sedatives.—Sodium pentobarbital is preferred for acute poisoning because of its rapidity of action. Phenobarbital is useful in maintaining a prolonged level of sedation to combat persisting hyperexcitability or recurrent convulsions.
(b) **Stimulants.**—In treating vascular collapse, substances such as adrenalin should be useful only after careful consideration, as they are contraindicated in poisoning by the halogenated hydrocarbon insecticides, even though the patient may be in severe depression or coma.

(c) **Transfusions.**—Patients in shock, for whatever reason may be helped by transfusion unless pulmonary oedema or some other contraindication is present. If blood is not readily available or if simple dehydration is present, 5 per cent. glucose or normal saline infusions are indicated. Intravenous fluids should not be continued long with a careful laboratory evaluation of the acid-base balance.

(d) **Artificial Respiration.**—It is more important to provide artificial respiration to an anoxic patient than to move him to a doctor or hospital if the latter is out of reach in short time. Frequently the physician is on telephone. Contact with the patient's family or associates quite early. The physician should inquire about the victim's breathing and colour. If anoxia seems to be present or imminent, a warning should be given against moving the patient and someone, trained and equipped for giving emergency mechanical artificial respiration (usually from the fire department) should be called.

(e) **Oxygen therapy.**—Conventional oxygen-carbon dioxide mixtures should be administered to patients showing cyanosis or severe respiratory difficulty. Patients with pulmonary edema require oxygen under positive pressure as well as postural drainage and dehydration therapy until the exudate is checked.

In case the poison is taken internally, remove it by inducing vomiting. Give the universal antidote which consists of half an ounce of a mixture of activated charcoal two parts, magnesium oxide one part and tannic acid one part in half a glass of warm water. It absorbs or neutralises poisons. It is useful in poisoning by acids, liquid glycosides and heavy metals. Except in case of poisoning by corrosive substances, it should be followed by gastric lavage.

**SYMPTOMS, SIGNS AND TREATMENT**

**Administer antidotes immediately and properly.**

**Chlorinated hydrocarbons.**

In general the signs and symptoms include headache, malaise, dizziness, loss of equilibrium, clonicotonic convulsions, hyper-irritability and hyperexcitability.

**Treatment**

1. Removal of poison taken internally by gastric lavage and saline laxatives. Oil laxatives should be avoided as they promote the absorption of these insecticides and of many organic solvents.

2. If necessary give sedatives.
3. Removal of poison from the skin by soap and water.

Barbiturates like phenobarbital (0.7 gram per day in epilepsy) and pentobarbital (0.25 to 0.5 gms.) are known to control convulsions of central origin.

Organophosphorous compounds.—The symptoms include headache, giddiness, blurred vision, weakness, nausea, cramps, diarrhoea, discomfort in the chest and nervousness while signs include sweating, miosis, tearing, salivation, pulmonary oedema, cyanosis, papilledema, uncontrollable muscle twitches, convulsions, coma and loss of reflexes and sphincter control.

Treatment

1. Artificial respiration preferably by mechanical means.
2. Atropine, 2 mg. intravenously as soon as cyanosis is overcome. Repeat at 5 to 10 minutes intervals until signs of atropinization appear (dry flushed skin and tachycardia as high as 140 per minute).
3. Decontaminate the skin or empty the stomach.
4. Treat symptomatically.
5. Never give morphine.

Carbamates (Sevin).—Symptoms include sweating, headache, dizziness, blurring of vision and nausea followed by vomiting, profound weakness, salivation, pain in the chest, abdominal cramping and diarrhoea.

Treatment.—Induce vomiting. Artificial respiration. Give two tablets of 1/100 grain atropine by mouth as an emergency.

Insecticides of plant origin

1. Pyrethrum product.—Contact dermatitis is most common. The usual picture is a mild erythematous vesicular dermatitis with papules in moist areas and intense pruritus. Some individuals may manifest sneezing, serous nasal discharge and stuffiness.

Treatment.—It is symptomatic. Antihistamines are of value. In case of nervous manifestations pentobarbitals should be used while in diarrhoea atropine may be administered.

2. Nicotine preparations.—Symptoms include headache, giddiness, nausea and vomiting, disturbed vision and hearing, mental confusion, asthemia, rapid respiration, faintness, prostration, convulsions and death by respiratory failure.

Treatment.—Parpanit (intravenously at 20 to 30 mg./kg.) suppresses toxic action of nicotine while diparicol (intravenously at 15-30 gm./kg.) protects against lethal doses of nicotine.
(5) Rodenticides—(1) Zinc Phosphide.—If the patient has taken the poison within 24 hours proceed as follows:—(1) Stir one tea spoonful of mustard powder into a glass of warm water and make the patient drink it; (2) After vomiting from treatment has stopped (i) give the patient 5 gms. of Potassium permangnate dissolved in a glass of warm water, (ii) ten minutes after the above treatment let the patient drink a solution made of ½ tea spoonful of copper sulphate in a glass of water; and (iii) fifteen minutes after treatment give the patient a solution made by dissolving one table spoonful of magnesium sulphate (Epsom salt) in glass of water. If the poison has been taken earlier than 24 hours, omit treatment (1) above and give the others in order.

(2) Warfarin—Initial symptoms:—Back and abdominal pains followed by vomiting and gum and nose bleeding.

Treatment.—Give Vitamin ‘K’ 65 mg. thrice on 1st day and continue in small doses till the prothrombin time has reached normal. In serious cases, small transfusion of carefully matched whole blood should be given and continued until the patient has returned to normal.

(6) Cyanides.—Cyanides (Calcium cyanide, Sodium Cyanide etc. including Hydrogen cyanide): Carry the patient to fresh air immediately. Break an amyl nitrite ampoule in a clean cloth and hold it to the nose of the patient for five seconds at intervals of 15 seconds. Inject intravenously 10 c.c. of 3% sodium nitrite solution at 2·5 c.c. per minute followed by 50 c.c. of 25% sodium thiosulphate solution. If breathing has stopped, administer artificial respiration.

7. Fungicides—(1) Mercury compound.—(Inorganic salts except calome and metallic mercury): Give milk or white of egg beaten with water, then a tablespoonful of salt in a glass of warm water and repeat till the vomit fluid is clear. Repeat milk or white of egg beaten with water. Organic mercury compounds vary so widely in their properties that only a physician should consider them individually.

2. Copper Compound.—Gastric lavage with large quantities of water containing one ounce of milk of magnesia. When the vomit fluid is clear, give milk as demulcent. Give potassium ferrocyanide 0·5 gm. in water.
ANNEXURE I

Some Antidotes and other Substances to be stocked for use in Emergency Treatments:

Activated charcoal.

Alcohol, Ethyl.

Amyl nitrite.

Atropine tablets.

Caffeine sodium benzoate.

Calcium gluconate.

Common salt (Sodium chloride).

Copper sulphate.

Dextrose.

Distilled water.

Epinephrine.

Gelatin.

Magnesium oxide.

Magnesium sulphate (Epsom salts).

Menadione.

Milk of magnesia.

Mustard powder.

Normal saline solution.

Petrolatum (Liquid paraffin).

Phenobarbital.

Potassium ferrocyanide.

Sodium benzoate.

Sodium bicarbonate.

Sodium nitrite.

Sodium thiosulphate.

Tannic acid.

Tincture of iodine.

Vitamin K and K2.
APPENDIX

Tolerance Limits

Since most of the pesticides used in pest control work have long residual property, they leave toxic residues on treated products which produce deleterious effects on human beings and animals consuming them. Some of them, especially the chlorinated hydrocarbons, are stored in body fat and even are excreted through milk. The contamination of food stuff with pesticidal residues, therefore poses an important problem in human welfare. In advanced countries like U.S.A. legal provisions are made to fix tolerance limits for different pesticides on various products so as to avoid toxicity hazards. These values are given below which will be useful in knowing the extent to which the pesticidal residues are admissible in food stuffs.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Name of the insecticide</th>
<th>Tolerance limits (Parts of pesticidal residues per million parts of food stuff).</th>
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List of Indian Standards Published on Pesticides.

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<td>43</td>
<td>Zinc phosphide</td>
<td>Technical</td>
<td>1251—1958</td>
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List of some important Firms Dealing in Pesticides

5. Messrs. Cyanamid India Ltd., Annie Besant Road, P. O. Box 65-67, Bombay-18.
7. Messrs. Gerdau India Corporation, 1-C, Sindhu House, Nanabhai Lane, P. O. Box No. 1979, Bombay-1.
8. Messrs. Hoechst Pharmaceuticals Ltd., Dugal House, Backbay Reclamation, P. O. Box No. 273, Bombay-1.
14. Messrs. Union Carbide India Ltd., Kasturi Building, Jamshedji Tata Road, P. B. No. 610, Bombay-1.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Name of pesticide and its formulation</th>
<th>Trade names</th>
<th>Names of the firm(s)</th>
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<td>Aldrox 5% dust</td>
<td>Messrs. National Organic Chemical Industries Ltd. (NOCIL).</td>
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<td>Messrs. Bharat Pulverising Mills.</td>
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<tr>
<td>38</td>
<td>Heptachlor 6%</td>
<td>Mico 6% heptachlor, Heptaf 6%</td>
<td>Messrs. Mysore Insecticides Co., Messrs. Rallis India Ltd.</td>
</tr>
<tr>
<td>39</td>
<td>Heptachlor 20% E.C.</td>
<td>Mico 20% heptachlor</td>
<td>Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>40</td>
<td>Heptachlor 25% E.C.</td>
<td>Mico 25% heptachlor</td>
<td>Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>41</td>
<td>Isobenzan 1% dust</td>
<td>Telodrin 1% dust</td>
<td>Messrs. NOCIL.</td>
</tr>
<tr>
<td>42</td>
<td>Isobenzan 15% E.C.</td>
<td>Telodrin 15% E.C.</td>
<td>Messrs. NOCIL.</td>
</tr>
<tr>
<td>43</td>
<td>Lindane 0.65% dust</td>
<td>Geigy vegetable dust, Hexamar lindane, Micodane D-065</td>
<td>Messrs. Rallis India Ltd., Messrs. Bharat Pulverising Mills, Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>44</td>
<td>Lindane 6.5% WP WP</td>
<td>Hexamar lindane 6.5% W.D.P., Micodane W-065</td>
<td>Messrs. Bharat Pulverising Mills, Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>Serial No.</td>
<td>Name of pesticide and its formulation.</td>
<td>Trade names.</td>
<td>Names of the firm(s)</td>
</tr>
<tr>
<td>-----------</td>
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<td>---------------------</td>
</tr>
<tr>
<td>46</td>
<td>Lindane 1.3% dust</td>
<td>Hexamar lindano 1.3%</td>
<td>Messrs. Bharat Pulverising Mills, Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>47</td>
<td>Malathion 50% E.C.</td>
<td>Malamar 50% E.C.</td>
<td>Messrs. Bharat Pulverising Mills, Messrs. Cynamid India Ltd, Messrs. Mysore Insecticides Co.</td>
</tr>
<tr>
<td>48</td>
<td>Malathion dust</td>
<td>Malamar 5% dust</td>
<td>Messrs. Bharat Pulverising Mills, Messrs. Cyanamid India Ltd.</td>
</tr>
<tr>
<td>50</td>
<td>Menazon 70% WP</td>
<td>Sayfos</td>
<td>Messrs. I.C.I. Pvt. Ltd.</td>
</tr>
<tr>
<td>51</td>
<td>Methyl demeton 25% E.C.</td>
<td>Metasystox</td>
<td>Messrs. Bayer India Ltd.</td>
</tr>
<tr>
<td>52</td>
<td>Methyl parathion</td>
<td></td>
<td>Messrs. Bayer India Ltd.</td>
</tr>
<tr>
<td>53</td>
<td>Movinphos</td>
<td>Phosdrin</td>
<td>Messrs. NOCIL.</td>
</tr>
<tr>
<td>54</td>
<td>Dibromochloropane</td>
<td>Nenagon</td>
<td>Messrs. NOCIL.</td>
</tr>
<tr>
<td>55</td>
<td>Nicotine sulphate</td>
<td>Black leaf 40</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>Parathion 50% E.C.</td>
<td>Foliod E 605</td>
<td>Messrs. Bayer India Ltd, Messrs. Bharat Pulverising Mills, Messrs. Sandoz India Ltd.</td>
</tr>
<tr>
<td>57</td>
<td>Parathion 2% dust</td>
<td>Foliod 2% dust</td>
<td>Messrs. Bayer India Ltd, Messrs. Bharat Pulverising Mills, Messrs. Sandoz India Ltd.</td>
</tr>
<tr>
<td>58</td>
<td>Parathion 1% dust</td>
<td>Ekatox 2% dust</td>
<td>Messrs. Sandoz India Ltd.</td>
</tr>
<tr>
<td>59</td>
<td>Phorate 10% G.</td>
<td>Thimet</td>
<td>Messrs. Cyanamid India Ltd.</td>
</tr>
<tr>
<td>60</td>
<td>Phosphamidon WP &amp; E.C.</td>
<td>Dimecron 100% 50%, 20%, E.C. 50% WP</td>
<td>Messrs. Ciba India Ltd.</td>
</tr>
<tr>
<td>Serial No.</td>
<td>Name of pesticide and its formulation</td>
<td>Trade names</td>
<td>Names of the firm(s)</td>
</tr>
<tr>
<td>-----------</td>
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</tr>
<tr>
<td>62</td>
<td>Sulphur WP</td>
<td>Thiovit 80%</td>
<td>Messrs. Sandoz India Ltd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulta£</td>
<td>Messrs. Rallis India Ltd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solbar</td>
<td>Messrs. Bayer India Ltd.</td>
</tr>
<tr>
<td>63</td>
<td>Thiometon 25% E.C.</td>
<td>Ekatin 25%</td>
<td>Messrs. Sandoz India Ltd.</td>
</tr>
<tr>
<td>64</td>
<td>Morphothion 3% dust</td>
<td>Ekatin M. dust</td>
<td>Messrs. Sandoz India Ltd.,</td>
</tr>
<tr>
<td>65</td>
<td>Thuricide dust or WP</td>
<td></td>
<td>Messrs. Mysore Insecticide Co.</td>
</tr>
<tr>
<td>66</td>
<td>Toxaphene 10% dust</td>
<td></td>
<td>Messrs. Bharat Pulverising Mills.</td>
</tr>
<tr>
<td>67</td>
<td>Toxaphene 5% dust</td>
<td></td>
<td>Messrs. Bharat Pulverising Mills.</td>
</tr>
<tr>
<td>68</td>
<td>Trichlorphon 80%</td>
<td>Dipterex</td>
<td>Messrs. Bayer India Ltd.,</td>
</tr>
<tr>
<td>69</td>
<td>Zinc phosphide powder</td>
<td></td>
<td>Messrs Bharat Pulverising Mill.</td>
</tr>
</tbody>
</table>

* WP = Wettable powder.
† E.C. = Emulsifiable concentrate.