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# CHEMISTRY *and* USES
# *of*
# INSECTICIDES

by

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*To my* WIFE
*and our daughter*
GENEVIEVE
*in appreciation of their assistance.*

# Preface

The field of insecticides is not alone that of scientific studies of insect control; it is industrial with a background of legal regulations. Both are incomplete until satisfactory materials are available to all and the public trained in their choice and use. A well informed public will, it is believed, have greater confidence in the production of insecticides by responsible manufacturers once it knows of the strict supervision under which they are produced and of the progress in manufacturing processes.

The book is intended to give a broad picture of the development and use of insecticides. Practices characteristic of western United States are discussed in detail, including mineral oil, sprays, dusting sulfurs derived from gas purification and of citrus orchard fumigation. To the professional worker, this book may serve as a catalog of established insecticides (and other biocides) and of promising new ones that come so rapidly that there is serious danger of forgetting yesterday's progress. The college student will meet the factory problems of supply, labeling, packaging, antidotes and the mechanical problems of grinding, formulation and application.

For the general public there are guides in the index for what may seem a bewildering mass of names. Under the subject headings of "wood preservatives", "weed killers", "cotton boll weevil control" and "industrial fungicides", are grouped the names of chemicals used for such purposes. Old established materials such as sulfur, nicotine, calcium arsenate and copper compounds are seen to be as useful as ever for certain work.

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

I wish to acknowledge my obligation to the manufacturers who have contributed technical information and illustrations, and to the many publications of Federal, State and industrial technicians. I am particularly indebted to Dr. R. C. Roark and his associates, and to Dr. H. L. Haller for constructive criticism. My appreciation is extended to the California State Board of Pharmacy for quotations from their "Official Antidotes", to the Manufacturing Chemists' Association for the use of certain cuts of insecticide labels and to Dr. D. L. Lindgren for illustrations and for criticism of the discussion of citrus fumigation. In the preparation of the "Dictionary of Insecticides", I have utilized "The Condensed Chemical Dictionary" (Third Edition) edited by Francis M. Turner, and the "Concise Chemical and Technical Dictionary" edited by H. Bennett.

*Albany, California*
*September, 1948*

E. R. DEONG

# Contents

# Chapter 1

# Introduction

The use of chemicals to protect man and his crops from the attack of insects and fungus diseases has increased steadily since about 1860. There was occasional mention of chemical control prior to that date, through the eighteenth century, and almost as far back as the history of man extends; but such early uses were sporadic and without attempt at continuous effort. Examples of the early uses of insecticides include arsenical baits for grasshoppers, powdered pyrethrum flowers for "household vermin", varied types of concoctions to prevent "wormy" apples, and the burning of sulfur to check insect infestation of stored products and as a disinfectant.

The control of insects on growing crops by chemical applications, being naturally associated with similar problems in checking mildews and blights, led to the development of specialists in fields distinct from medicine. The new profession separated into two groups: those having a basic knowledge of insects and related forms, known as economic entomologists, and those specializing in the fungi and bacteria which attack plants, known as plant pathologists. The two new professions developed their own terminology of "insecticides and fungicides", just as the medical profession had sponsored the use of "medicines and drugs". New terms were added later, including "herbicides" (weed killers), "rodenticides", "ascaricides", and other specialized forms. All these may well be included in the generic term "insecticides", which is sufficiently comprehensive to cover every field of pest control. The comprehensive term "pesticide" has been suggested as including all the various branches of control chemicals, but it has not come into general use. "Economic poisons" has been suggested as a substitute for "insecticides and fungicides", and is in common use on the Pacific Coast of the United States; but this is criticized as laying undue stress on the word "poison"—generally considered by the public as a danger sign. Such an attitude, however, may easily lead to restricted consumption of materials that are necessary in the constant war to protect growing and stored crops and thus to contribute to our personal welfare. Insecticides and fungicides may and frequently do include dangerous and poisonous chemicals, as stated on the label. Materials containing dangerous concentrations of toxic chemicals are required by law to be labeled "Poison", and are sold under strict Federal and State regulations; they must be used with both care and understanding. The same statement, however, applies to medicines; every medicine closet may contain such dangerous drugs as iodine, phenol (carbolic acid), mercury (calomel), strychnine (heart tonic), and arsenical compounds. These drugs, if in sufficient concentration, are also required to be labeled "Poison" to insure careful use. They are not, however, advertised and sold as poisons, but as remedies for certain diseases.

Insecticides have commonly been divided into three groups: "stomach poisons", "contact sprays" and fumigants. The first term was applied to chemicals used in the control of biting insects, that is, those consuming the tissue of leaves, fruits and twigs. Examples include grasshoppers, caterpillars (larvae of moths and butterflies), beetles and termites. Death results from ingestion by the insect of substances coated with the poison. The earlier forms of stomach poisons were calcium arsenate, Paris Green (copper-aceto-arsenite) and London Purple, all of which are arsenicals. The term "contact spray" was applied to chemicals which killed only by intimate contact with the body of the insect. These compounds were used in the control of "sucking" insects, by which is meant those that feed by withdrawing liquids from the leaves and twigs of the growing plant; this group includes the scale insects, leaf hoppers, thrips and plant lice (aphids). Death of the insect occurs after penetration of the insecticide into the breathing tubes (tracheae), through the segments of the external skeleton, or through the connective tissue. The earlier forms of contact sprays included kerosene emulsion, lime-sulfur solution and tobacco infusion, the forerunner of nicotine sulfate solution. Fumigants are chemicals of sufficient volatility as to give off lethal concentrations of gases, usually at room temperatures; they include carbon disulfide, hydrogen cyanide and sulfur dioxide. Fumigation was probably first attempted with burning sulfur, used both as a disinfectant and as an insecticide. The limited insecticidal value of this substance led to the development (about 1870) of hydrocyanic acid gas as a successful fumigant. Carbon disulfide had been used in a limited way before this, but it was years before it came into active use as a fumigant for grain insects and as a control for rodents.

Studies in the toxicology of insecticides have shown that the terms "stomach poison" and "contact spray" do not form an accurate basis for classification purposes. Arsenicals continue to be the basic control of many biting insects, but certain arsenical compounds are also recognized as active fungicides, and a gaseous form of arsenic, known as "arsine", is used as a fumigant. Sulfur is toxic in the volatilized form as a fumigant and also in a combined form as a contact spray. Elemental sulfur may also act as a stomach poison. Kerosene, particularly the less refined fractions, is an active fumigant. Less volatile fractions, after penetrating the body of the insect or the breathing tubes, may kill by releasing toxic, volatile portions as well as by chemical reactions of the non-volatile fractions. Nicotine, commonly listed as a contact spray, is known to be an active fumigant, and is also a stomach poison in the "fixed" form. Such confusion of terms and functions confirms the value of a general term such as "insecticide" to cover the entire field of pest control in every phase.

Present custom in the classification of insecticides is based largely on the field in which they are used, together with the predominating interests of the manufacturer. Thus we have the terms "agricultural insecticides and fungicides" and "household insecticides" in common use both in technical groups and in the industry. This plan is followed in the large manufacturers' associations; there are the Agricultural Insecticide and Fungicide Association and the National Association of Insecticide and Disinfectant Manufacturers. The former handles all types of sprays and dusts* used in the treatment of growing crops, including grain, fruit and vegetables. The latter includes the manufacturers who prepare and distribute fly sprays, moth, roach and ant remedies and certain disinfectants. Fumigants are handled by both the agricultural and household groups of manufacturers.

The early field of insecticides for the most part included inorganic chemicals, such as arsenic, lead, calcium, barium and mercury, while copper and sulfur were the principal fungicides. Only slight attention was given to the few known organic chemicals obtained from ground pyrethrum flowers, tobacco extract and kerosene emulsion. Only a few insecticides were available, and these were general in their field of usefulness rather than specific. Arsenic was the principal agency for insect control, but the three forms in which it was available—calcium arsenate, Paris Green and lead arsenate—offered little choice in plant tolerance and insect toxicity. The slight differences between the compounds were largely those of solubility, stability, and the physical qualities of the particle.

About 1895 the limitations of arsenic as a general insecticide were for the first time being recognized and evaluated. Arsenic is a protoplasmic poison, active both on plants and animals; but when it is applied either as a spray or dust it may leave a residue that becomes a public health menace, unless it is carefully removed from all fruit and vegetables. It is retained in most soils for a long time and may accumulate to a degree that interferes with normal cropping. In certain fields, notable the boll weevil problem of cotton, the free use of arsenicals is frequently followed by an increase in the number of aphids. The predators and parasites, which tend

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* Many insecticides, including nicotine, sulfur and arsenicals, may be applied in spray form when suspended in water, which acts as the carrier. They may also be mixed with an inert dust base, such as hydrated lime, and applied as a dust to the crop. The choice between the two forms of application usually depends on the type of application machinery available.

to hold the aphids in check, succumb to the arsenical dust applied for the boll weevil, thus permitting the aphids to breed unchecked. The long-continued use of arsenic against the codling moth is thought to have developed strains resistant to arsenic, which results in the application of increasingly heavy doses of arsenic. In addition to the difficulties that the entomologists were experiencing with the limited field of inorganic chemicals, the plant pathologists were encountering problems in the control of fungi that could not be satisfactorily handled with the available copper and sulfur fungicides.

The period of slowly developing arsenicals and other inorganic chemicals also showed progress in respect to the earliest organic materials. Ground pyrethrum flowers were found to be of value in agricultural practices as well as for household insects. Nicotine had been developed as a standardized commercial concentrate that could be shipped economically and used in graduated dosages, as desired, both in sprays and dusts. Kerosene emulsion was evolving into distillate fractions of crude types, but with a wider insecticidal field; these were later to develop into the highly refined, light lubricating oils or "white oils". The organic chemist for the first time came into the field with attempts to synthesize nicotine. Rotenone, a derivative of Derris and other tropical plants, was studied intensively as a substitute for arsenic in codling moth control. This particular venture was not a success, but many other new uses for rotenone were developed. The active principles of the pyrethrum flower were isolated and, like nicotine, were then prepared in standardized commercial forms capable of very accurate dosages. The search for organic compounds that are active insecticides has broadened greatly and continues to expand at a rapid rate.

The new field of organic insecticides has brought many types of problems. The complex form of organic compounds makes them generally less stable and more specific than inorganic compounds. They are more subject to oxidation, to the action of bright sunshine, and to chemical reactions. For example, the extracts from pyrethrum flowers (Pyrethrins 1 and 2) are very unstable in the presence of alkalies, and hence cannot be used with hydrated lime as the carrier. Some of the chlorinated compounds, including DDT, are decidedly valuable for certain types of insects and almost valueless for others. In contrast to the inorganic insecticides, they are decidedly specific in their action; they cover smaller fields, but in these fields they are more effective than those that are more general in their action. In this respect a similarity to the field of medicine will again be noted.

The manufacture of insecticides began with the simplest forms of home preparations, including Bordeaux mixture (copper sulfate and lime), calcium arsenate (from lime and arsenic acid) and lime-sulfur solution, first used as a control of San Jose scale on apple and peach trees. Some of the State Experiment Stations took the lead in the development and publication of formulas and directions for the preparation and use of insecticides. A widely published formula for lime-salt-sulfur solution, together with directions for cooking in an open kettle, was generally adopted in the apple- and peach-growing districts. Such preparations varied greatly in their content of sulfide sulfur, which was finally found to be the active principle. The early supplies of arsenical compounds were also deficient in stability and varied in the amount of water-soluble arsenic. Government-supported laboratories were established to improve and standardize the making of insecticides, which had suddenly grown in popularity. Commercial manufacture of the arsenical compounds, conforming to newly established legal standards, now largely supplanted home preparations. Further studies of lime-sulfur solution established the superiority of the factory type of manufacture. High concentrations of sulfide sulfur were found to be possible only when prepared in closed containers. Since marketable products must conform to definite standards, the surveillance of a control chemist was required. Nicotine concentrates of guaranteed standards were developing. Potassium cyanide had become the standard fumigant for citrus trees. The infant industry had moved from the backyard into the chemical factory. Careful control that could meet rigid Federal and State standards had replaced the old haphazard methods of preparation, whose products of varying concentration necessarily gave uncertain results.

Factory manufacture of insecticides developed in the larger fruit- and vegetable-producing areas, being influenced by the source of supply of raw products, cheap power, low transportation costs and available labor. New York and adjacent areas became the earliest producing district, with additional factory development extending into the larger fruit-growing areas as they expanded. The present location of the principal plants extends from Boston down the Atlantic Coast into Florida. Another line of factories begins on the Gulf Coast of Texas and continues north into Tennessee, Arkansas, Missouri, Ohio, Illinois and Michigan. The remaining plants are located almost entirely on the extreme West Coast. Specialized industries, such as the manufacture of concentrated nicotine, are located chiefly near ample sources of raw materials. Factory locations follow tobacco planting, extending from Virginia to St. Louis and south into Tennessee. Factory location for the manufacture of organic insecticides is influenced by the proximity of chemical plants having supplies of raw products, including benzene, chlorine, tars and alcohols, and also by considerations of markets, labor and cheap power.

The insecticide industry, including both the agricultural and the household branches, had reached approximately the hundred million dollar stage at the opening of World War II. Manufacturing equipment for the industry includes many large plants devoted solely to insecticide manufacture besides the special units found in many of the well equipped chemical factories. This remarkable growth, largely of the past forty to fifty years, is the best proof of the values which chemistry has brought to agriculture, the home and sanitation.

The marketing of household insecticides follows closely the custom of small package handling. The usual outlets are drug, grocery, household supply, and chain variety stores. The field is largely seasonal, resulting in small-quantity buying with a correspondingly high percentage of profit to the dealer.

The application of household insecticides was originally made by the individual householder, but to an increasing extent this operation is now being performed by professionals. The change in practice is due largely to the more frequent use of toxic fumigating gases both as insecticides and as disinfectants. Rodent baits and chemicals used in termite control also require trained applicants. The need of experienced operators for applying household insecticides has led to enactment by a number of states of legislation* requiring the examination and licensing of candidates and attempts at regulating operations, particularly those having a public health hazard.

Household remedies include both fly and mosquito sprays, with increasing attention to repellents, as research develops more lasting forms. Moth and carpet-beetle remedies include both sprays and dusts, together with the mild fumigants, such as paradichlorobenzene and naphthalene. The latter two may also function as repellents. Roach powders are sold mostly in seaboard towns and the larger inland cities. Ant syrups and powders are distributed generally, but most abundantly in districts where the Argentine ant has been introduced. Louse and bedbug remedies are now sold only in limited quantities—proof of the winning battle which sanitation is waging. Flea control, which was once a problem only for the pet owner, is now a matter of general concern, with the recognition of this insect as a carrier of dangerous diseases. Various chemicals now used commonly in the household have contributed greatly to comfort, to the protection of foods and textiles, and to the solution of health problems. Their sale has grown and extended until they are now found in almost every grocery, variety and general store.

Sales of agricultural insecticides are predominantly at wholesale, that is, from a hundred pounds to a carload or more. Smaller volumes are handled as small package sales, at customary margins of profit, in seed, hardware and farm supply stores. Under present conditions 60 per cent of agri-

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* Structural pest control act of California. Division 3, Chapter 14, Sections 8500 to 8677 of the Business and Professions Code of California.

cultural insecticides are handled by commercial fruit- and vegetable-packing houses, cotton gins and farmer's cooperatives at cost, or at least below usual profit margins. The non-profit handling of insecticides by the packing houses is a service to the grower whose crops they handle, as a means of increasing production of marketable produce. The commercial growing of fruit and vegetables is now standardized to such a degree that only the best quality can be profitably packed; any encouragement given the grower to produce higher quality, more marketable fruit, also increases the output of the packing house to just that degree. This system has the added advantage of utilizing the packer's warehouse, usually located in rural rather than urban areas, whose staff is familiar with local credit conditions and agricultural practice. The latter point is of particular importance, as the sales force of a packing house, after training by the insecticide manufacturer, can act as advisor to the grower in the use of specialized products.

The application of chemicals to deciduous orchards, grain fields and truck crops, both by spraying and dusting, is to a very great extent handled by the grower. Increases in size, covering capacity and cost of equipment, and the use of airplane applicators, however, all tend toward the contract type of application for growing crops in both the eastern and western districts. The treatment of citrus groves in the southwestern United States, including spraying, dusting and fumigating, has become so highly specialized that it is handled largely by trained operators. This custom originated in the high initial cost of fumigating tents, power sprayers and duster. The small grove owner found it more economical to pay an acreage charge to experienced operators for pest-control work than to buy equipment and assemble a crew of men who probably would be inexperienced. Commercial applications of insecticides are handled by crews working directly from the packing house or by independent contractors who, in California practice, are licensed by a Government officer and work under a certain amount of supervision.* This custom has been modified in the citrus districts of other countries, where in certain districts only Government officers are permitted to handle dangerous chemicals.

The use of insecticides, in the broad sense of the term, extends into almost every phase of human life and endeavor. Agriculture, including commercial and home production of vegetables, has long been dependent on the chemical control of pests from the time of seed planting, through the growing crop, to the warehouse, and the kitchen shelf. It is not only the orchardist and truck grower who depends on sprays and dusts; the grain grower also treats his seed with disinfectants, dusts the wheat fields for rusts, builds barriers to check migrating chinch bugs, and scatters grasshopper baits over waste and cultivated areas alike.

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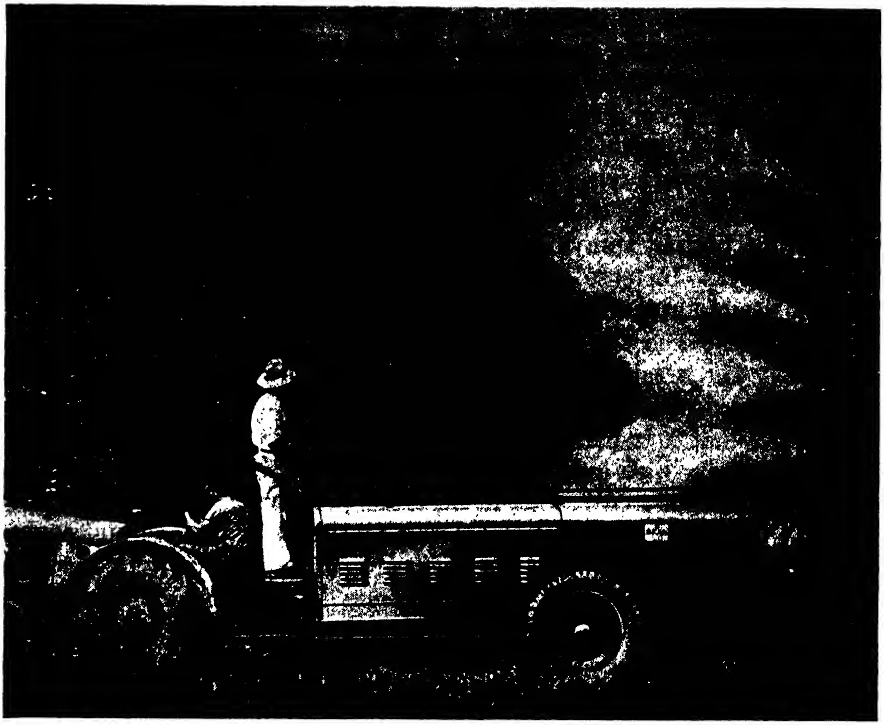
* Division 2, Chapter 1, Section 150 of the Agriculture Code of California.

The livestock breeder must be constantly alert for both external and internal parasites. Lice, mites, ticks and fleas may develop in short notice, while bot flies, stomach worms and liver flukes may, if unchecked, ruin the best herds. The defense against these hordes lies in the newest types of synthetic organics and certain plant derivatives.

Florists and nurserymen are particularly dependent upon detecting and checking insects and parasitic diseases before their depredations ruin the crops and a season's work is lost. Again there is recourse to both the older and the newer forms of sprays, dusts and fumigants.



(Courtesy John Bean Manufacturing Co., Lansing, Mich.)

FIGURE I. Seven gun spraymast designed to do rapid, efficient work with a great saving of labor. Mast can be operated by the tractor driver, thus making it a one man outfit.

Forests, lumber and shade trees are to an increasing extent being protected by specialized chemicals against dry rots, lumber stains, defoliators and borers. Vast sums are spent annually to check outbreaks of serious diseases that sweep through forests like fire. The chemical treatment of lumber, as forests continue to shrink, is a growing industry that promises large dividends by prolonging the life of timbers exposed to the attack of both insects and fungi.

The fight to protect crops does not end with harvest, but must extend through the warehouse, mill and packing house. At every step experienced operators are using fumigating gases, dust and oil coatings, as well as extremes of heat, cold and desiccation in checking molds, bacteria, beetles and moths that attack foods and textiles in every form.

The home, camp, and wherever men assemble in numbers is a meeting place for his annoying and sometimes formidable foes. Out of this struggle has grown the warfare that Public Health officials wage continuously against the carriers of some of mankind's most dreaded enemies. Yellow fever, Bubonic Plague, malaria, typhus fever and spotted fever are some of the better known diseases that are recognized as being transmitted by insects and ticks, but which to an increasing extent are being controlled by the careful use of the chemicals which we know as insecticides.

# Chapter 2

# Arsenic and Its Compounds

Crude arsenic, principally arsenious oxide ($As_2O_3$) or "white arsenic" forms the basis for the manufacture of the arsenical insecticides. An estimated 30,666 short tons of white arsenic was consumed in 1941 for this purpose.[4] It is obtained principally as a by-product of smelting operations. The accumulated low-grade flue dusts are further treated, resulting in a crude arsenic of 90 to 98 per cent $As_2O_3$. According to the standards of the Bureau of Mines, "refined arsenic" refers to 99 per cent or more $As_2O_3$. World production of white arsenic for the period 1936 to 1941 is shown in Table 1, except where data were unavailable due to war conditions. Rates of consumption, imports and exports are given in Table 2 for the periods ranging from 1925 to 1929 and 1938 to 1941 inclusive.[1]

**White Arsenic.** ($As_2O_3$). There are three forms of arsenious oxide, the amorphous or vitreous form, the crystalline (octahedral), and the rhombic. The specific gravity of the vitreous form is 3.74, of the octahedral 3.68, and of the rhombic 4.15. It is very slowly soluble in cold water, equilibrium being reached only over a period of many weeks;[2] it dissolves readily in hot alkaline solutions. Various forms of arsenites and arsenates exist, corresponding to the respective acids.

The arsenites, except Paris Green, are products of arsenious oxide and a base. Arsenates are combinations of tribasic or orthoarsenic acid, $H_3AsO_4 \cdot \frac{1}{2}H_2O$, and a metallic oxide. Arsenic acid results from oxidizing arsenious oxide.

White arsenic is seldom used alone, because of its tendency to injure foliage. Limited use has been made of this substance as a soil sterilizer and herbicide, for termite control in the soil, and in grasshopper baits, although for the latter purpose a solution of sodium arsenite is often preferred.

**Paris Green** [$Cu(C_2H_3O_2)_2 \cdot 3\ Cu(AsO_2)_2$]. Paris Green was the first of the commercially prepared arsenicals to come into general use. It was developed originally in the control of the Colorado potato beetle, *Leptinotarsa decemlineata*, as this insect swept eastward in the '60's. Paris Green was generally accepted for combating various defoliators and the codling moth, *Carpocapsa pomonella*. For these purposes[5] it is stated that from 1,500 to 2,000 tons are used annually in the United States. The latter figures has not been exceeded even in the production of 1943.[4]

Variability in composition and large amounts of water-soluble arsenic in the early manufactured Paris Green led to the passage of one of the first insecticide laws, (State of California, 1901) requiring a minimum concentration of 50 per cent of arsenious oxide in Paris Green and a maximum of 4 per cent of uncombined arsenious oxide.[5]

Table 1. World Production of White Arsenic (1936–41) in Various Countries (in metric tons)

| Country[1] | 1936 | 1937 | 1938 | 1939 | 1940 | 1941 |
|---|---|---|---|---|---|---|
| Australia: | | | | | | |
| New South Wales | 124 | — | — | [2] | [2] | [2] |
| Western Australia | 3,526 | 2,087 | 4,063 | 1,439 | 3,385 | [2] |
| Belgium-Luxembourg (exports) | 2,731 | 3,039 | 2,706 | 3,332 | [2] | [2] |
| Brazil | 732 | 717 | 519 | 713 | 1,088 | 1,203 |
| Canada | 619 | 630 | 987 | 790 | 950 | [2] |
| China | [3] | [2] | [2] | [2] | 800 | [2] |
| Chosen (Korea) | 230 | — | [2] | [2] | [2] | [2] |
| France | 9,750 | 6,501 | [2] | [2] | [2] | [2] |
| Germany (exports) | 2,739 | 2,852 | 2,845 | [2] | [2] | [2] |
| Greece | 85 | 234 | 77 | 113 | [2] | [2] |
| Hungary | — | 100 | [2] | [2] | [2] | [2] |
| Italy | — | — | 810 | [2] | [2] | [2] |
| Japan | 2,629 | [2] | [2] | [2] | [2] | [2] |
| Mexico | 8,527 | 10,762 | 8,894 | 7,063 | 9,268 | 12,844 |
| Portugal | 150 | 112 | 1 | [2] | [2] | [2] |
| Rumania | — | 6 | 3 | [2] | [2] | [2] |
| Southern Rhodesia | — | — | 19 | — | [2] | [2] |
| Sweden (sales)[4] | 8,647 | [2] | [2] | [2] | [2] | [2] |
| United Kingdom | 155 | 97 | 66 | [2] | [2] | [2] |
| United States | 13,952 | 15,253 | 15,136 | 20,267 | 22,664 | 29,466 |
| | 55,700 | [2] | [2] | [2] | [2] | [2] |

[1] Arsenic is also believed to be produced in Czechoslovakia, Iran, Peru, Turkey and U. S. S. R. Production figures are not available for these countries.

[2] Data not available.

[3] Data not available. Estimate included in total.

[4] Arsenic content of ores mined is as follows: 1936, 23,312 tons; 1937, 20,954 tons; 1938, 21,480 tons; data not available for later years.

The theoretical composition of Paris Green is arsenious oxide 58.55 per cent, copper oxide 31.39 per cent, and acetic anhydride 10.05 per cent.[8,7] Examination of 25 commercial samples in 1937[57] showed a range of 53.15 to 57.81 per cent $As_2O_3$. Carter and Smith report that samples sold as Paris Green examined in 1939 and 1940[7] showed a range of 35.4 to 68.5 per cent of $As_2O_3$ and 27.4 to 31.5 per cent of copper oxide. The lack of acetic anhydride in three of the samples indicates that they do not contain

Paris Green. The arsenic and copper contents suggest copper metaarsenite monohydrate, $Cu(AsO_2)_2 \cdot H_2O$.

Homologs of Paris Green have been prepared[9] by substituting certain of the higher fatty acids for acetic acid. Dearborn[10], in a study of the homologs, concludes that they are compounds of copper metaarsenite and the particular copper compound corresponding to the acid used. None of these homologs has reached commercial importance.

Table 2. Salient Statistics for Arsenic in the United States, 1925–29 (average) and 1938–41*

| | | 1925–29 (Average) | 1938 | 1940 | 1941 |
|---|---|---|---|---|---|
| WHITE ARSENIC | | | | | |
| Domestic sales:[1] | | | | | |
| Crude | short tons | 2,364 | 9,428 | 16,688 | 28,661 |
| Refined | do | 10,035 | 3,732 | 6,651 | 6,123 |
| Imports for consumption | do | 10,769 | 14,238 | 9,929 | [2]7,578 |
| Apparent consumption[3] | do | (4) | 25,098 | 31,668 | [5]40,442 |
| Ave. value for dom. sales:[1] | | | | | |
| Crude | cents per lb. | 2.69 | 1.40 | 1.10 | 1.47 |
| Refined | do | 3.57 | 1.73 | 1.47 | 2.24 |
| OTHER ARSENICALS | | | | | |
| Imports for consumption: | | | | | |
| Metallic arsenic | lbs. | 208,672 | 16,868 | 13,228 | [2]2,240 |
| Sulfide (Orpiment & realgar | do | 575,506 | 241,602 | 656,498 | [2]11,025 |
| Arsenic acid ($H_3AsO_4$) | do | 14,692 | 55 | — | — |
| Calcium arsenate | do | 1,452 | 400,000 | 432,785 | [2]1,230,960 |
| Lead Arsenate | do | [6]2,133 | — | — | — |
| Sheep dip | do | 135,929 | 168,932 | 341,556 | [2]264,200 |
| Paris Green & London Purple | do | 4,402 | 103,556 | 25,003 | [2]4,000 |
| Sodium arsenate | do | 82,105 | 11,881 | — | — |
| Exports: | | | | | |
| Calcium arsenate | do[7] | 2,159,168 | 5,242,882 | 4,879,391 | [2]2,675,097 |
| Lead arsenate | do[7] | 1,328,828 | 1,021,345 | 2,900,250 | [2]3,749,115 |

[1] Includes sales by domestic producers for export.

[2] Figures cover 9 months only; data for last quarter of year are confidential.

[3] Adjusted for exports by domestic producers.

[4] Complete data not available.

[5] Actual consumption.

[6] 10,467 pounds in 1925 and 200 pounds in 1929; no imports from 1926 to 1928 incl.

[7] Average for 1928–29; exports of calcium arsenate and lead arsenate not separately recorded by the Department of Commerce prior to 1928.

* Figures on imports and exports compiled by M. B. Price, of the Bureau of Mines from records of the Department of Commerce.

The particle size of Paris Green, like that of other insecticides, influences the toxic action. During the process of developing commercial supplies of Paris Green, the particle size has been lowered from that of particles passing a 100-mesh screen[5] to 1 micron[11] or less,[12] the last substance being referred to as micronized Paris Green. Better distribution, suspension and adhesion is possible with the finer particles, but through the increase of surface there is apparently also an increase in water-soluble arsenic. McGovran and co-workers[11] have shown that Paris Green having particles averaging 22 microns in diameter caused a lower mortality and permitted a greater amount of feeding than resulted from the use of particles of 12 microns.

Paris Green is used principally as a dust (combined with sulfur) against cotton insects both in southeastern United States and in the cotton districts of South America. It is recommended on potatoes, in the garden trade, and for the control of the larval stage of the malaria-carrying mosquito.

### Calcium arsenates and arsenites.

The use of calcium as a combining base with arsenic was encouraged during the period of home manufacture of insecticides because of the low cost and ease of suspension in the spray tank in comparison with Paris Green. A common procedure was to boil 1 pound of white arsenic and 2 pounds of lime in 2 gallons of water for 40 minutes and then to dilute with 300 to 400 gallons of water. A small additional amount of lime is recommended. Calcium arsenite produced in this way was safer than the available Paris Green containing 3 to 4 per cent of uncombined arsenious oxide.[5]

The commercial calcium arsenate of a later period did not compete seriously with lead arsenate, as the latter was a more stable compound, with less hazard to foliage and greater adhesion. Public criticism of dangerous spray residues later turned attention to calcium arsenate as a substitute for lead arsenate. The increased hazard of lead over calcium, as the combining base for arsenic, gave impetus to the improvement of the cheaper calcium arsenate for general control purposes. Calcium arsenate has the added advantages of higher arsenic content and lower cost. The instability of calcium arsenate limits its use as a spray material, although it has come into very wide use as a dusting compound for the more resistant plants. Estimated production[4] of calcium arsenate in 1941 was 75 million pounds, in comparison with 63 million pounds of lead arsenate. Total production of calcium arsenate in the United States from 1927 to 1943 is given in Table 3.[14a] Exports from United States for the period from 1937 to 1942 are found in Table 4.[14a]

**Calcium Hydrogen Arsenate** ($CaHAsO_4$) is also known as dicalcium arsenate. This compound, as prepared in the laboratory, gave after dehydration the following analytical results:[13]

| | | |
|---|---|---|
| Calcium as | $CaO$ | 31.20% |
| Arsenic as | $As_2O_5$ | 63.83% |

It had been prepared by combining solutions of calcium chloride and sodium acid arsenate, after acidifying with acetic or hydrochloric acid. Soluble chlorides are removed by washing.

Calcium hydrogen arsenate is too soluble in cold water to be safe for foliage applications. It breaks down in acid and alkaline solutions more quickly than tricalcium arsenate.

**Tricalcium Arsenate** ($Ca_3(AsO_4)_2$. This compound, also known as tertiary or normal calcium arsenate, may be prepared from solutions of calcium choride and sodium acid arsenate. Sodium hydroxide is added to the latter to convert the salt to sodium arsenate. The two solutions, when combined, form a precipitate which after drying at 175°C gives a calcium arsenate with the following analysis:[13]

| | | |
|---|---|---|
| Calcium as | $CaO$ | 42.16% |
| Arsenic as | $As_2O_5$ | 57.73% |

The compound is sufficiently soluble in cold water to be somewhat dangerous to foliage, requiring the addition of small proportions of calcium hydroxide to combine with the soluble arsenic as formed.

Another method of producing calcium arsenate is by direct union of calcium hydroxide and arsenic acid.[14] A smooth paste of calcium hydroxide is combined with a cold arsenic acid solution and stirred until alkaline to phenolphthalein. It is then filtered, dried and ground.

Calcium carbonate also combines with arsenic acid, but produces at room temperature an acid compound with the formula of $CaH(AsO_4)_2$; by heating this may be converted into dicalcium arsenate, $CaHAsO_4$. Calcium carbonate is not, however, sufficiently alkaline to carry the conversion to the tricalcium arsenate stage.[14]

Clifford and Cameron[15] have thrown doubt on the existence of the compound $Ca_3(AsO_4)_2$, and Smith and Murray[16] report that commercial calcium arsenates seldom show the presence of tricalcium arsenate as such.

**Basic Calcium Arsenate.** Pearce and co-workers report[18,19] the formation of dicalcium arsenate, $CaHAsO_4$; pentacalcium arsenate, $Ca_5H_2(AsO_4)_4$; tricalcium arsenate, $Ca_3(AsO_4)_2$; and basic calcium arsenate, $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$, from the combination of calcium hydroxide and arsenic pentoxide at 90°C. Another method of producing a basic calcium arsenate, $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$, devised by Pearce and Avens,[18a] consists in heating a mixture of $Ca(OH)_2$ and dicalcium arsenate in the presence or absence of moisture. The reaction proceeds rapidly at 100°C or higher, but more slowly at 60°C. The proportions used are 155 parts of pulverized dicalcium arsenate and 55 parts of calcium hydroxide. The product obtained is about 90 per cent basic calcium arsenate and 10 per cent uncombined calcium hydroxide. Total arsenic content is about $As_2O_5$, 46 per cent, water-soluble arsenic 0.40 per cent, calcium content as CaO about 44 per cent.

To overcome the hazard of using arsenical compounds on foliage zinc, which is used in the spray tank as a preventive of injury, may be combined in the formula. Seven parts of dicalcium arsenate and 2.75 parts of zinc oxide (ZnO) are mixed and autoclaved for 2 hours under steam pressure. The arsenical content stated as $As_2O_5$ is 42 per cent, zinc as zinc oxide 33 per cent, and calcium as calcium oxide 22 per cent. Copper may also be added to the formula to give fungicidal value.[18a]

Calcium arsenate has been used commercially in large quantities in the apple orchards of northwestern United States as a substitute for lead arsenate, but the instability of the compound both in the spray tank and on the foliage makes it somewhat hazardous. Excess calcium hydroxide in the spray tank may combine with soluble arsenic, as formed, but carbonation of the lime on the sprayed surface may again release arsenic in dangerous amounts. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) has been found to increase the safety of calcium arsenate on apples, using one pound per 100 gallons of spray.[19b]

Table 3. United States Production of Calcium Arsenate

| Year | Thousands of pounds |
|---|---|
| 1927 | 27,282 |
| 1929 | 33,064 |
| 1931 | 26,129 |
| 1935 | 43,295 |
| 1937 | 37,002 |
| 1939 | 39,282 |
| 1940 | 49,966 |
| 1941 | 59,368 |
| 1942 | 77,796 |
| 1943 | 69,863 |

Commercial calcium arsenate, stored in dry powdered form, has been found to absorb carbon dioxide from the atmosphere with a corresponding increase of water-soluble arsenic.[19a] Air-tight containers are recommended for storage, either steel drums or multiwall paper bags with special treated liners that retard air movement.

The stability of calcium arsenate may be affected by the method of manufacture, ratio of calcium to arsenic and the presence of moderate but not excessive amounts of calcium hydroxide. Hard water, containing calcium, magnesium and ferrous bicarbonates, may increase the amount of soluble arsenic.[19c] Calcium arsenite may be present in appreciable amounts as the result of imperfect oxidation of arsenious into arsenic acid, with an increased hazard from the presence of water-soluble arsenious acid resulting from decomposition.

Safer types of calcium arsenates are on the market, which probably contain varying amounts of the more basic form and to that extent retard the formation of soluble arsenic. The present uses are, however, confined more generally to resistant foliage such as cotton. Calcium arsenate is also used, but to a less extent, on tomatoes and potatoes.

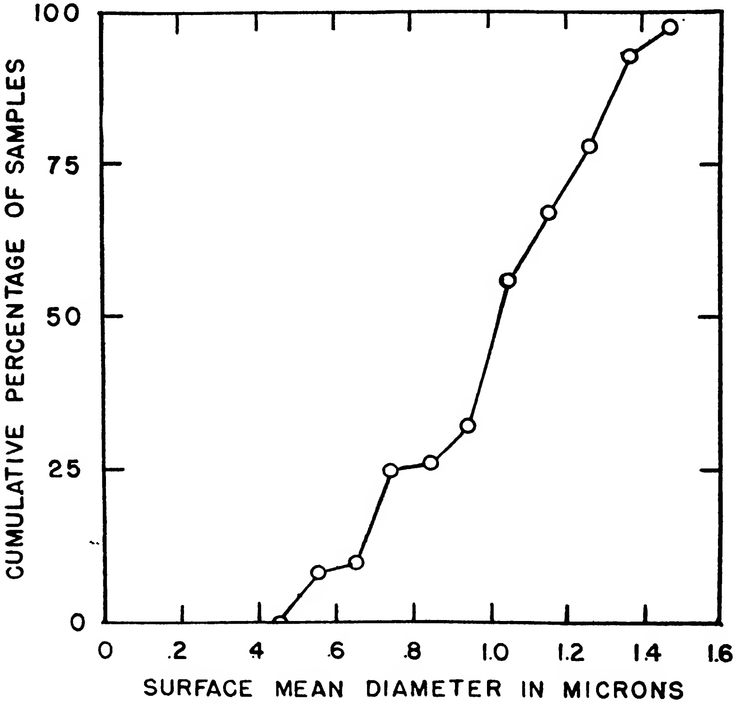


FIGURE 2. Average particle size of commercial calcium arsenates as determined by the permeation method.

Commercial calcium arsenate both for dusting and spraying purposes should be a light, fluffy powder of uniformly fine particle size, occupying at least 90 cubic inches to a pound. It should contain an excess of lime (uncarbonated) to insure stability and to combine with any soluble arsenic that may be released. The molar ratio of calcium oxide and arsenic pentoxide has been found to lie between 3.3 and 3.4.[29a]

A study of samples of commercial calcium arsenate collected in 1941 and 1942 showed a mean particle daimeter of about one micron in practically all samples.[19d] The actual range in size of the particles is shown in Fig. 2. No definite relationship could be determined between particle size and soluble arsenic as determined by the Geneva method. (*Pearce et al.*[20])

Yearly production of calcium arsenate in the United States is shown in Table 3, and the data for exports are given in Table 4.

**Calcium Arsenate as an Insecticide.** Boll weevil, *Anthonomus grandis*, control by calcium arsenate has become a standard practice in cotton-growing districts. The dosage varies from 3 to 10 pounds per acre as applied by hand dusters,[21] power machines and airplanes. The commercial mixtures used generally contain a certain amount of the basic calcium arsenates. Dicalcium arsenate has been reported to be more effective against boll weevil than the basic form, but it would also be more hazardous to the cotton plant. Blends of calcium arsenate and sulfur are being used to an increasing extent. The combination is apparently as effective as the arsenical compound used alone and would also seem to have value in controlling the cotton flea hopper, *Psallus seriatus*. The calcium arsenate-sulfur mixture is also used in the southwestern United States as a control for the western plant bug, *Lygus hesperus*. One of the difficulties in the use of calcium arsenate for the boll weevil and defoliators has been the increase of aphids; this may be avoided by the use of 0.75 per cent of rotenone or 1.0 per cent of nicotine in the arsenical dust. Satisfactory diluents for the calcium arsenate-rotenone mixture are sulfur, diatomaceous earth, clay and pyrophyllite.[20a] For use of calcium arsenate on beans, Hawkins reports the superiority of a high magnesia content (32 per cent magnesium expressed as magnesium oxide) hydrated lime to one containing 72 per cent calcium, expressed as calcium oxide, and 0.5 per cent magnesium.[20b] The alfalfa weevil, *Hypera postica*, is controlled in western United States with 3 pounds of calcium arsenate per acre. Large amounts of calcium arsenate in combination with sulfur are used in California on tomatoes against defoliating caterpillars and the tomato mite, *Phyllocoptes destructor*. A snail or slug bait is recommended using calcium arsenate combined with bran, metaldehyde, and molasses for garden use,[22] but omitting the last two ingredients when used in citrus groves.

**Compatibility of Calcium Arsenate.** This substance should not be combined with the fluorine compounds, including cryolite (sodium fluoaluminate), sodium fluosilicate, and barium fluosilicate. Neither soaps made from fatty acids nor fish oils should be combined with calcium arsenate. Rotenone, pyrethrins and dinitro-*o*-cyclohexylphenol should not be combined with this arsenical, as they react with alkaline substances.

Sulfur, hydrated lime, lime-sulfur solution, nicotine sulfate and petroleum oil emulsions,[24a] except certain types of emulsifiers, may be combined with calcium arsenate.

## Table 4. United States Exports of Calcium Arsenate, 1937–1942

| Country | 1937 Pounds | 1938 Pounds | 1939 Pounds | 1940 Pounds | 1941 Pounds | 1942[2] Pounds |
|---|---|---|---|---|---|---|
| Argentina | 260,023 | 242,470 | 279,894 | 121,115 | — | — |
| Bolivia | — | — | 10,000 | 1,000 | — | — |
| Brazil | — | — | 286,860 | — | — | — |
| Canada | 37,001 | 45,672 | 444,109 | 81,996 | 188,173 | 13,301 |
| Chile | 2,200 | 65,500 | — | — | 871 | — |
| Colombia | 430,000 | 1,040,308 | 40,000 | 130,000 | — | 135,016 |
| Costa Rica | — | 18,100 | — | 200 | 532 | — |
| Cuba | 34,992 | 4,416 | 1,728 | 31,918 | 20,697 | 2,000 |
| Egypt | — | — | 32,000 | 31,968 | 30,000 | — |
| Guatemala | — | 3,984 | — | 2,000 | 600 | — |
| Haiti | — | 200 | 13,084 | 20,016 | — | — |
| Mexico | 2,451,508 | 75,964 | 653,106 | 498,752 | 722,144 | 1,891,998 |
| Mozambique | — | — | — | 4,500 | 11,200 | — |
| Nicaragua | 216,884 | — | 1,000 | 100,050 | 100,000 | — |
| Peru | 1,792,060 | 3,647,700 | 4,867,580 | 3,702,300 | 4,532,825 | 1,751,082 |
| Philippine Islands | 53,000 | 50,000 | 23,000 | 24,000 | 77,000 | — |
| Salvador | 100,552 | 40,572 | 62,936 | 17,904 | 200 | 47,512 |
| Union of South Africa | 1,000 | 240 | 528 | — | 500 | — |
| Venezuela | 300 | 2,310 | 13,034 | 107,000 | 209,356 | 100,500 |
| Other[1] | 3,845 | 5,446 | 2,244 | 4,672 | 3,500 | 313 |
| Total | 5,383,365 | 5,242,882 | 6,731,103 | 4,879,391 | 5,897,598 | |

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[1] Shipments of less than 10,000 pounds during any one year are included in "Other."

[2] Includes only countries in the Western Hemisphere.

**Calcium Arsenite as an Insecticide and Fungicide.** A mixture of 1 part of calcium arsenite and 3 parts of hydrated lime is recommended as a control for the mormon cricket, *Anabrus simplex*, in Colorado.[23]

Monocalcium arsenite, $CaHAsO_3$, is recommended as a dormant application for controlling brown-rot blossom blight, *Sclerotinia laxa*, in apricots. However, it is too dangerous to foliage for use during growth and must then be supplemented by Bordeaux mixture or other copper sprays.

**London Purple.*** This arsenical compound was brought to America to test as an insecticide about the same time that Paris Green was introduced. Originally it was a by-product of the manufacture of aniline dyes.[26] It is now manufactured directly to a limited extent. It has been shown[27] to be a mixture of calcium arsenite, $Ca_3(AsO_3)_2$, calcium arsenate $Ca_3(AsO_4)_2$, and an organic dye. Variable but usually rather large amounts of water-soluble arsenious oxide and arsenic oxide have been reported[2] in analyzed samples of the earlier commercial products. Later types of production are claimed to be safe for use even without the addition of lime.

## Lead Arsenates.

The discovery by Moulton in 1892 of the value of lead arsenate as an insecticide and its recommendation[25] for this use has been the basis for the devolopment of this leading arsenical compound. Yearly production of lead arsenate in the United States from 1927 to 1943 is given in Table 5 and the exports for the same period in Table 6.[30a]

A paste form of lead arsenate containing about 50 per cent moisture was the basis for the earlier commercial shipments. This has been largely displaced by the powdered form, which is light and fluffy; when used with proper dispersing agents it gives good suspensions in the spray tank. The particle size of a number of commercial forms is given in Table 7.[45a] The usual method of shipment is in small multiwall paper bags, packed in cartons. It is sold in one, three, six and ten-pound bags, corresponding to the dosage per 100 gallons and the common sizes of the spray tank.

The stability of lead arsenate, both in the spray tank and on foliage, is greater than many of the other arsenical compounds. The percentage of water-soluble arsenic is small and does not increase readily by atmospheric action. It is usually applied as a spray rather than a dust, and in this form is very adhesive. It carries a lower content of arsenic than Paris Green, calcium arsenate and certain other arsenical compounds, but has a greater health hazard because of the lead base. The two types of commercial lead arsenates—the acid or standard and the basic—offer a range of stability and plant tolerance that make it possible to choose a type and

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* "London Purple" is a trade mark term but is not in active use as such.

dosage satisfactory to a large variety of plants and conditions. None of the arsenicals, however, should be used on citrus trees, as such applications tend to decrease the normal acidity and total solids of the fruit, resulting in a serious impairment of flavor.[29b] The effect of arsenical applications may persist for two years or longer or until all arsenical-coated leaves have fallen.

**Monolead Orthoarsenate** $[PbH_4(AsO_4]_2$. This compound is very unstable, highly soluble in water and too dangerous to foliage to use in spraying.[28] It is stable only at high concentrations of arsenic acid.[29a]

**Lead Metaarsenate** $[Pb(AsO_3)2]$ may be prepared from monoarsenates by ignition. Its specific gravity is 6.42. This arsenate is readily decomposed by water and hence cannot be safely used in spraying.[28]

Table 5. United States Production of Lead Arsenate

| Year | Thousands of pounds |
|---|---|
| 1927 | 21,528 |
| 1929 | 30,682 |
| 1931 | 37,974 |
| 1933[1] | 30,000 |
| 1935 | 52,146 |
| 1937 | 63,291 |
| 1939 | 59,569 |
| 1941 | 74,443 |
| 1942 | 63,577 |
| 1943 | 80,955 |

[1] Incomplete census of production.

**Dilead Orthoarsenate** ($PbHAsO_4$) is also known as "diplumbic", "acid", "standard" and simply as "lead arsenate." This is the most important of all the insecticidal lead arsenates, including about 90 per cent or more of all the arsenates consumed. The specific gravity of the crystal form is given as 6.042 and 6.053; the amorphous form has a specific gravity of 5.93.[28] Robinson and Tartar show the specific gravity as 5.79.[31]

Long-continued exposure to constantly changing water causes decomposition of acid lead arsenate, both lead and arsenic dissolving; but the latter may dissolve at a more rapid rate, leaving the residue more basic than dilead arsenate.[28]

The instability of acid lead arsenate results in decomposition from the salinity and hardness of the diluting water, particularly chlorine.[29a,30,31] The material is stable at a pH range of 3.3 to 8.5[33], but high alkalinity may cause hydrolysis.[32]

A legal requirement for commercial acid lead arsenate states that it shall contain not less than 30 per cent of arsenic pentoxide and not more than 2.14 times as much lead monoxide as arsenic pentoxide.[36a]

**Trilead Orthoarsenate** $[Pb_3(AsO_4)_2]$ is also known as triplumbic arsenate of lead. The treatment of dilead orthoarsenate with dilute ammonia produces first the trilead orthoarsenate, followed by basic arsenates.[28] The stability of the solid phase is stated to lie between pH 5.5 and pH 7.0.[29a]

Table 6. United States Exports of Lead Arsenate (1937–1942)

| Country | 1937 pounds | 1938 pounds | 1939 pounds | 1940 pounds | 1941 pounds | 1942[2] pounds |
|---|---|---|---|---|---|---|
| Argentina | 275,361 | 279,780 | 235,050 | 420,012 | 872,106 | 104,933 |
| Australia | 70,254 | 28,740 | 47,932 | — | — | — |
| Bolivia | — | 24,000 | — | — | — | — |
| Brazil | — | — | 567,845 | 1,538,313 | 7,131,853 | 43,500 |
| Canada | — | 13,915 | 60,442 | 16,956 | 18,192 | — |
| Chile | 110,000 | 122,014 | 200,912 | 154,360 | 121,208 | — |
| Colombia | — | 13,000 | 50,724 | 135,084 | 20,718 | — |
| Cuba | 23,448 | 61,716 | 72,305 | 42,755 | 163,675 | 102,776 |
| Dom. Rep. | 80,564 | — | 10,225 | — | — | — |
| Leeward Is. | — | — | — | — | — | 26,840 |
| Mexico | 44,406 | 42,280 | 47,549 | 51,232 | 126,893 | 203,834 |
| Mozambique | — | — | — | — | 14,480 | — |
| Neth. E. Indies | — | — | — | 23,654 | 677,000 | — |
| New Zeal. | 123,975 | 107,561 | 81,710 | 68,320 | 53,396 | — |
| Paraguay | — | — | — | — | — | 22,018 |
| Peru | 11,200 | 16,500 | — | — | — | — |
| Phil. Is. | — | — | 21,500 | 18,548 | 50,024 | — |
| Portugal | — |  | — | 27,504 | — | — |
| Switzerl. | — | — | 46,725 | — | — | — |
| Union of S. Afr. | 267,869 | 262,530 | 184,352 | 293,602 | 259,536 | — |
| United Kingdom | — | — | 20,000 | — | — | — |
| Uruguay | — | — | — | 39,524 | 50,600 | 35,280 |
| Venezuela | — | 16,300 | — | 39,208 | 16,410 | — |
| Other[1] | 35,803 | 32,919 | 65,312 | 31,178 | 15,852 | 16,668 |
| Total | 1,042,880 | 1,021,345 | 1,712,583 | 2,900,250 | 9,594,483 |  |

[1] Shipments of less than 10,000 pounds during any one year are included in "other."

[2] Includes only countries in the Western Hemisphere

**Lead Hydroxy Arsenates** *4,1,3,1-Lead-Hydroxy Arsenate* $[Pb_4(Pb\ OH)(AsO_4)_3 \cdot H_2O]$. The theoretical composition is: lead oxide 75.0 per cent, arsenic oxide 23.20 per cent, water of constitution and crystallization 1.80 per cent.

*5,2,4-Lead-hydroxy arsenates* $[Pb_5(Pb\ OH)_2(AsO_4]_4$. Analysis shows a range of lead oxide from 76.57 to 76.90 per cent, arsenic oxide 22.38 to 22.63 per cent, water 0.74 to 0.88 per cent.[28]

The above compounds and probably others make up commercial basic arsenate of lead. This compound is decidedly more stable than acid lead arsenate in hard and saline waters[29a,33], particularly in the presence of chlorine. It is reported to be stable in a pH range of 2.0 to 11.2.[33]

A legal requirement of commercial basic arsenate of lead states that it shall contain not less than 22 per cent of arsenic pentoxide, and not less than 31 times as much lead monoxide as arsenic pentoxide. It shall not contain more than 0.50 per cent arsenic (metallic) in ammonia-soluble form.[36a]

**Colloidal Arsenate of Lead.** The chemical combination of lead nitrate and disodium arsenate in the presence of a protective colloid, such as gelatin, forms a colloidal arsenate of lead. Material formed in this way passes through filter paper and remains in suspension for days. It forms a tenacious thin film over the leaf surface. The formula used is:

| | |
|---|---|
| Lead nitrate | 331.4 gm. |
| Disodium arsenate | 311.96 “. |
| Gelatin | 17.35 “. |

The type of precipitate formed in combining the solutions depends upon the concentration. The 0.1 *M* solution was the only one producing the colloidal form of lead arsenate.[35]

**Use of Acid Lead Arsenate.** This is the most widely used of any arsenical in the spraying and dusting of orchards, ornamentals and soil treatments. A certain degree of hazard to the plant from water-soluble arsenic accompanies its use in practically all cases. For this reason the use of correctives or "safeners" to minimize the danger of arsenical injury has become a common practice. Such usage is particularly necessary in the frequently used combination of lead arsenate and lime-sulfur solution. The correctives in common use include hydrated lime,[41,42] casein and powdered milk, and a number of metallic salts, such as ferrous sulfate, zinc sulfate and manganese sulfate. It should be noted, however, that the use of large amounts of correctives or dust bases and diluents, particularly salts of a basic nature, may lead to a lowering of its toxicity as an insecticide.[31]

To increase the efficiency of sprays by improved wetting and coverage, frequent use has been made of auxiliary substances called "spreaders." The value of lead arsenate applications however, is more dependent upon the type of deposit and adhesion than upon the degree of wetting. Spreaders give a more or less uniform type of coverage in contrast with the splotch or spot cover resulting from the use of arsenicals alone.

Auxiliary substances are frequently used to give better dispersion, and thus facilitate uniform coverage and give a tenacious or retentive type of coverage. The term "spreaders" has been applied to these substances also, but preferably they are known as "deposit builders and stickers." Martin has mentioned two of their effects on retention: their viscosity influences the amount of spray fluid retained on a leaf surface, and they also improve or increase spray deposit.[37] Materials used as "adhesives" include casein, soybean powder, flour paste, dextrin and oils, including fish oils and refined petroleum fractions. The use of adhesives does not necessarily give an increased deposit at the first application, but may result in higher deposits or "build up" following further applications.[38,39,40] (See "Inverted spray mixtures page 134.) Residual deposit may also be present in larger amounts at the end of the spraying season.

Certain auxiliary materials, including mineral oil, Bordeaux mixture and lime, produce significant changes in the ratio of lead to arsenious oxide after prolonged weathering. The first two materials reduce and the third increases the rate of decomposition.[43]

Table 7. The Particle-size Distribution, Density, and Loose Bulking Value of Samples of Commercial Lead Arsenate

Percentage Between Indicated Diameters

| Sample No. | Above 40 mic. | 40–20 mic. | 20–10 mic. | 10–6 mic. | 6–4 mic. | 4–2 mic. | 2–1 mic. | Below 1 mic. | Density (g. per cc.) | Bulking Value (cu. in. per lb.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 0.9 | 3.4 | 7.2 | 9.0 | 27.0 | 26.5 | 26.0 | 5.89 | 72.2 |
| 2 | 0.0 | 1.0 | 2.1 | 2.1 | 1.5 | 18.3 | 38.7 | 36.3 | 5.86 | 85.0 |
| 3 | 0.3 | 0.6 | 4.5 | 3.6 | 8.9 | 37.0 | 34.6 | 10.5 | 5.85 | 86.3 |
| 5 | 0.3 | 0.6 | 4.0 | 1.8 | 8.7 | 28.0 | 35.2 | 21.4 | 5.88 | 81.2 |
| 7 | 0.0 | 0.6 | 1.8 | 1.8 | 6.3 | 16.8 | 40.2 | 32.5 | 5.99 | 80.8 |
| 8 | 0.3 | 0.6 | 4.7 | 1.0 | 4.7 | 17.1 | 24.8 | 46.8 | 5.90 | 85.8 |
| 9 | 0.0 | 0.3 | 3.1 | 5.0 | 8.4 | 27.3 | 42.5 | 13.4 | 5.92 | 68.4 |
| 11 | 0.0 | 0.6 | 1.2 | 3.0 | 6.6 | 24.6 | 28.8 | 35.2 | 5.74 | 92.5 |
| 12 | 2.0 | 0.3 | 3.3 | 5.0 | 2.0 | 18.9 | 39.5 | 29.0 | 5.90 | 64.5 |
| 14 | 0.0 | 0.0 | 4.7 | 7.1 | 10.5 | 24.5 | 15.0 | 38.2 | 5.85 | 57.0 |
| 15 | 0.6 | 0.3 | 2.7 | 5.7 | 7.0 | 16.5 | 30.6 | 36.6 | 5.95 | 79.5 |
| 16 | 1.5 | 0.6 | 0.6 | 3.8 | 3.6 | 6.2 | 23.4 | 60.3 | 5.90 | 130.0 |

Spreaders, in the more exact sense of materials which promote wetting, are well illustrated by the use of soaps. These materials, however, break down readily in hard water, and certain forms tend to increase the amount of soluble arsenic. Lime-casein, sulfite liquor or the dehydrated form—a by-product of the paper industry—and certain of the sulfonic acid groups are active spreaders and are largely independent of hard waters.[37]

In combination with lead arsenate sprays spreaders must be used with care or excessive run-off will seriously reduce the deposit. Graham and Richardson studied the action of sodium oleyl sulfate-resin compound, soybean flour, and lime-casein as lead arsenate spreaders and found no increase in efficiency from their use.[44] Isley and Horsfall showed that all spreaders added as powders decreased the deposit of lead arsenate.[39] Smith found that codling moth control was similar whether using the coarse, over-spray or film coverages at dosages of 4 pounds of lead arsenate to 100 gallons of spray. At dosages above 4 pounds to 100 gallons the film coverage gave the best protection.[45]

## Spray Materials Combined with Lead Arsenate

**Lead Arsenate-Lime Sulfur combinations.** The lack of fungicidal value in the arsenicals frequently requires a supplementary material such as lime-sulfur solution. The combination of acid lead arsenate and lime-sulfur solution, however, results in a number of chemical reactions and the formation of a heavy sludge, varying in color from brown to a deep black.[2,46,47,48,49] The lead arsenate is largely converted into lead sulfide, the range reported by Thatcher and Streeter[47] being from 55 to 59.7 per cent. Robinson[46] shows a 5 per cent content of soluble arsenic in the mixture and a reduction of 35 per cent of the polysulfide sulfur. Ruth[50] found 22.5 per cent of free sulfur in the sludge. Bradley and Tartar[51] found the sludge to contain lead sulfide, free sulfur, lead arsenate and calcium arsenate. Goodwin and Martin[48,49] and also Ginsburg and Perlgut[49] report finding hydrogen sulfide as a decomposition product. This compound is an active solvent for lead arsenate, thus increasing soluble arsenic.

A number of materials act as preventives of the decomposition of acid lead arsenate and lime-sulfur solution. Robinson[46] recommended adding 10 pounds of hydrated lime to the diluted lime-sulfur solution before lead arsenate is added. The value of calcium hydroxide as a preventive of the decomposition of acid lead arsenate was later confirmed by Ginsburg and Perlgut.[49] Thatcher and Streeter[47] show the value of casein and skim milk as a stabilizing factor. Hodgkiss, Frear and Worthley[52] found that milk and casein caused an increase in soluble arsenic, but stabilized the polysulfide content. Ferrous sulfate was recommended by Goodwin and Martin as a stabilizer for the lead arsenate-lime sulfur solution spray, and this has been confirmed by Kearns, Marsh and Martin.[53] Manganese sulfate, zinc sulfate and ferric oxide have all been recommended as correctives for combinations of sulfur and lead arsenate. The latter material has been found quite useful in reducing injury from arsenical burn and also as an adhesive.[54]

Basic arsenates of lead combined with lime-sulfur solution are changed only slightly either in appearance or chemically. The residue is gray and flocculent in nature.[46,47]

**Lead Arsenate and Soaps.** One of the most commonly used spreaders for both acid and basic lead arsenates is soap, even though the combination is recognized as dangerous. Fish-oil soap, one of the most commonly used in combination with arsenicals, has been found to release very large amounts of water-soluble arsenic, as shown in Table 8.[2] Pinckney[55] has shown that sodium oleate dissolved two to seven times as much soluble arsenic from a monoplumbic lead arsenate as from a triplumbic ortho lead arsenate. It was also noted that both sodium stearate and sodium oleate dissolved soluble arsenic from basic lead arsenate, the stearic soap being the more active. Ginsburg has shown a relationship between strong and weak soap bases as compared with the amount of soluble arsenic released. Ammonium oleate produced less soluble arsenic than did either potassium or sodium oleates, while the smallest amount of arsenic released was by the weak base triethanolamine.[5]

**Sulfur.** Elemental sulfur, in contrast with the combined sulfur of lime-sulfur solution, is reported as neutral or with only slight chemical reaction when combined in the spray tank with acid lead arsenate.[67] A mixture of acid lead arsenate 1 pound, and sulfur 8 pounds, after standing for one year, showed an increase in the amount of soluble sulfur.[42] Since no lead or hydrogen sulfide could be detected, there is the possibility of a reaction between oxidation products of the sulfur and the lead arsenate. Combinations of spreaders and lead arsenate plus sulfur may cause injury owing to the type of spreader used.

Table 8. Arsenic Rendered Soluble on Combining Lead or Calcium Arsenate with Fish-oil Soap

| Material analyzed | Arsenic (As) present in sample taken (gram) | Arsenic (As) rendered soluble after standing for 1 day (gram) | Per cent |
|---|---|---|---|
| Calcium arsenate[1] | 0.1753 | 0.0003 | 0.17 |
| Acid lead arsenate[2] | .1717 | .0032 | 1.86 |
| Calcium arsenate plus fish-oil soap (1 pound to 50 gallons) | .1753 | .0503 | 28.69 |
| Acid lead arsenate plus fish-oil soap (1 pound to 50 gallons) | .1717 | .1475 | 85.90 |
| Calcium arsenate plus fish-oil soap (2 pounds to 50 gallons) | .1753 | .0667 | 38.05 |
| Acid lead arsenate plus fish-oil soap (2 pounds to 50 gallons) | .1717 | .1703 | 99.18 |

[1] Calcium arsenate at the rate of 0.93 pound per 50 gallons.

[2] Lead Arsenate at the rate of 1.11 pounds per 50 gallons.

**Nicotine Solutions.** Combinations of nicotine sulfate and lead arsenate are considered compatible, as no increase of soluble arsenic has been shown. Dusting compounds of lead arsenate and nicotine sulfate are also in common use. Free nicotine (nicotine alkaloid) is combined with lead arsenate in both sprays and dusting compounds.

**Bordeaux** (Lime and copper sulfate solution). Lead arsenates are commonly combined with Bordeaux mixtures without increase of soluble copper or arsenic acid. A decrease of soluble arsenic over that found with the arsenate alone indicates that the excess lime in the Bordeaux mixture combines with the water-soluble arsenic to form an insoluble calcium arsenate.

**Oil Emulsions.** Refined petroleum oil emulsions are commonly combined with lead arsenates[53] in codling moth sprays. The oil itself will not react with the lead arsenate, but the emulsifier and spreader, if used, must be chosen to avoid undesirable chemical reactions. Combinations of lime, $Ca(OH)_2$, and casein or other proteins are commonly used as spreaders, usually with beneficial results. Spreaders or emulsifiers made with ammonia and casein must be used with caution, as a slight excess of ammonia will react with acid lead arsenate. The organic type of emulsifier, including sulfated and sulfonated alcohols, oils and fatty acids, clays and blood albumen, are less likely to decompose acid lead arsenate than is the mineral type, including sodium, potassium and ammonia.

**Zinc Arsenate** [$Zn_3(AsO_4)_2$]. Analyses of commercial samples have shown a range of 23 to 24 per cent of metallic arsenic.[57,59] Water-soluble arsenic is 0.2 to 0.5 per cent. This compound has had but limited use[2] because of instability and foliage injury by the earlier supplies. Later developments in commercial production and the demand for lead substitutes as a combining base again attracted attention to this arsenical. It was reported as superior to many other compounds, but was listed with manganese and barium arsenate as somewhat inferior to lead arsenate in the control of codling moth on apple in the northwest.[24a] Limited use is reported in midwestern areas.

Cotton boll worm control is said to be improved by the use of calcium-zinc arsenate compared with calcium arsenate alone.[59]

**Zinc Arsenite.** The commercial product is supposed to contain $Zn_3(AsO_3)_2$ with surplus zinc oxide.[62] Metallic arsenic in this compound ranges, according to analyses, from 29.0 to 31.1 per cent.[24a,57,60] It has had limited use because of the amount of water-soluble arsenic present. On resistant foliage such as potato it has been successful as a control for the potato beetle, *Leptinotarsa decemlineata.*[61] Zinc arsenite has had some use in the western states in codling moth control on apples by combining it with one pound of iron sulfate to the 100 gallons of spray. Ferric oxide has also been used for this purpose.[24a] Hill reports serious increases in the aphid population on potatoes treated with zinc arsenite and suggests substituting barium fluosilicate as a control for the flea beetle, *Epitrix cucumeris.*[60]

Zinc meta-arsenite has been used to an increasing extent as a wood preservative since 1937.[63]

**Basic Copper Arsenate** [$Cu(CuOHAsO_4)$]. This compound, developed about 1939, has the advantage of eliminating residual lead; moreover, a fungicidal advantage is claimed from the copper base.[C4] Analyses of commercial samples[36] show a range of 36.6 to 38.7 per cent of arsenic pentoxide ($As_2O_5$), see Table 9. The ratio of CuO to $As_2O_5$ corresponds to the formula given above. The material is quite stable and has a low content of water-soluble arsenic. Successful control of the Mexican bean beetle and the Colorado potato beetle is reported with concentrations of 3 pounds per 100 gallons of spray.[C6] It also acts as a repellent of the potato leaf hopper. Rosenstiel has found a combination of basic copper arsenate and sucrose useful in controlling the cherry fruit fly, *Ragoletis cingulata.*[8]

Table 9. Analyses of Copper-arsenic Compounds Used as Insecticides

| Material | Samples Number | | CuO Per Ct. | $As_2O_3$ Per Ct. | Molecular Ratio $CuO/As_2O_3$ | Water-Soluble $As_2O_3$ Per Ct. | Mean Particle Diameter[1] Microns |
|---|---|---|---|---|---|---|---|
| Paris Green | 9 | Min. | 30.0 | 56.1 | 1.33 | 0.47 | 15 |
| | | Max. | 31.1 | 57.3 | 1.35 | 2.12 | 31 |
| | | Av. | 30.55 | 56.8 | 1.34 | 1.21 | — |
| Copper arsenite | 5 | Min. | 47.0 | 38.1 | 3.03 | 1.1 | 0.3 |
| | | Max. | 48.2 | 38.9 | 3.13 | 2.6 | 1.0 |
| | | Av. | 47.88 | 38.46 | 3.08 | 2.95 | 0.5 |
| Copper metaarsenite | 3 | Min. | 27.4 | 66.3 | 0.99 | 0.5 | 3 |
| | | Max. | 28.8 | 69.4 | 1.08 | 1.5 | — |
| | | Av. | 28.13 | 67.85 | 1.02 | 0.82 | — |
| | | | | $As_2O_5$ | $CuO/As_2O_5$ | $As_2O_5$ | |
| Basic copper arsenate | 18 | Min. | 53.2 | 36.6 | 4.01 | 0.01 | 0.5 |
| | | Max. | 55.8 | 38.7 | 4.28 | 0.29 | 1.6 |
| | | Av. | 54.46 | 38.2 | 4.10 | 0.10 | 0.9 |
| Basic copper arsenate + sulfur 1:1 | 15 | Min. | 26.1 | 18.4 | 4.05 | 0.07 | 3 |
| | | Max. | 27.8 | 19.8 | 4.16 | 0.28 | 4 |
| | | Av. | 26.95 | 18.94 | 4.11 | 0.19 | 3.5 |
| Basic copper arsenate + sulfur 1:2 | 2 | Min. | 18.6 | 13.0 | 4.13 | 0.07 | 5 |
| | | Max. | 18.8 | 13.1 | 4.15 | 0.14 | 5 |
| | | Av. | 18.7 | 13.05 | 4.14 | 0.10 | 5 |
| Copper hydroarsenate + sulfur 1:1 | 5 | Min. | 25.0 | 16.5 | 3.93 | 0.10 | 0.5 |
| | | Max. | 26.1 | 18.1 | 4.57 | 0.30 | 0.5 |
| | | Av. | 25.3 | 17.4 | 4.19 | 0.21 | 0.5 |

[1] The results for Paris Green refer to that particle diameter, determined by sedimentation, which divides the sample into two equal parts by weight. All other figures refer to surface mean diameter as determined by the air-permeation method.

The compound is compatible with hydrated lime and elemental sulfur in dust mixtures.[C7]

**Copper hydroarsenate.** This compound is said to be a basic tricupric arsenate, $Cu_3(AsO_4)_2 \cdot Cu(OH)_2$.[69] The content of basic arsenate ranges from 41 to 46 per cent. The molecular ratio of CuO to $As_2O_5$ is reported to be 4.19:1.[8] Copper hydroarsenate was found more toxic than calcium arsenate to the imported cabbage worm, *Pieris rapae*, while the reverse was the case with the Colorado potato beetle larva and corn earworm, *Heliothis armigera*. The material was safer on foliage than calcium arsenate and Paris Green.[70]

**Copper hydro-arsenate-arsenite.**[70] This compound is said to contain approximately 32 per cent of basic cupric arsenate and 8 per cent of basic cupric arsenite. The insecticidal value is similar to that of calcium arsenate and copper hydroarsenate. The copper compounds show greater repelling value than calcium arsenate.

**Magensium arsenate** is a compound used largely in the control of the Mexican bean beetle but now largely displaced by Derris and rotenone preparations.[2,71,72] The commercial product is stated to be a mixture of the dimagnesium salt, $MgHAsO_4$, and two basic salts, principally one of the composition $Mg_3(AsO_4)_2 \cdot MgO \cdot H_2O$.[62] Analyses of commercial brands have shown a range of arsenic pentoxide ($As_2O_5$) of 31.38 to 32.69 per cent.[57]

In a review of the literature on magnesium arsenate Dearborn lists seven types: (1) monomagnesium orthoarsenate, $MgH_4(AsO_4)_2$; (2) dimagnesium orthoarsenates, $MgHAsO_4 \cdot xH_2O$; (3) magnesium pyroarsenate, $Mg_2As_2O_7$; (4) trimagnesium orthoarsenates, $Mg_3(AsO_4)_2 \cdot xH_2O$; (5) basic magnesium orthoarsenates (a) $Mg_3(AsO_4)_2 \cdot MgO xH_2O$, (b) $Mg_3(AsO_4)_2 \cdot 2MgO \cdot xH_2O$; (6) magnesium ammonium orthoarsenate, $MgNH_4AsO_4 \cdot 6H_2O$; (7) double salts of magnesium arsenate.[72a]

**Manganese arsenate.** The commercial product has approximately the composition $[Mn_3(AsO_4)_4]$. By analysis it is shown to contain 41 per cent or slightly more of arsenic pentoxide, $As_2O_5$.[57] Young reports that it may be combined with dry lime-sulfur spray without the formation of the black sludge that is characteristic of combinations of acid lead arsenate and lime-sulfur solution. Soluble arsenic was reduced to a negligible amount when lime was added.[74] Control of codling moth on apples in the northwest was reported to be similar to that of lead arsenate when combined with small amounts of petroleum oil or fish oil.[24a]

**Iron arsenate.** Importations of arsenic from Sweden and Japan being closed on account of war conditions, interest turned to increased production by the smelters of United States, Mexico and South America. Investigation also began of the use of iron arsenate, both of the manufactured ferrous arsenate, $Fe_3(AsO_4)_2 \cdot 6H_2O$, and the natural formation known as scorodite, a ferric arsenate of iron, $FeAsO_4 \cdot 2H_2O$. Samples of the latter have shown an arsenic pentoxide content ranging from 28 to 40 per cent. Water-soluble arsenic is reported to be only a trace. Insecticidal values are yet to be determined. There is no commercial production at this time.[75]

## Arsenical Deposit and Residue Removal.

Satisfactory deposits of sprays and dusts must not only be efficient as control agents but must include good coverage, resistance to weathering, safety to fruit and foliage, and ease of removal at harvest. The factors influencing deposit and its retention include the type of arsenical, spreaders and adhesives, climatic conditions, type of foliage and fruit; particularly important are waxiness and the diluting water or dust base.

The residues of spray and dust toxicants remaining on fruit when harvested must be made to conform to legal standards established in the interests of public health. The Federal Food and Drug administration has established the following tolerances: arsenic 0.025 grain per pound of fruit (3.57 milligrams per kilogram of fruit); lead 0.05 grain per pound (7.14 milligrams per kilogram). The removal of excess lead and arsenic is influenced by the degree of their solubility in the chemicals used in the wash water, the amount and character of wax naturally present on the fruit, and the tenacity of the adhesive used in the spray, such as casein, petroleum and fish oils.

Studies on the amounts of residual spray materials remaining on fruit and vegetables when harvested were begun in 1915 by the U. S. Dept. of Agriculture. A report issued in 1922[76] stated that but little spray material was present on fruit when harvested provided that it had been sprayed in accordance with recommendations issued by the Bureau of Entomology and Plant Industry. In 1925 the British Ministry of Agriculture reported instances of residual arsenic on apples imported from Canada and the United States that exceeded the British legal tolerance of 1/100 grain of arsenic trioxide per pound of food. State regulations on arsenical residues issued in 1926 were followed in 1927 by a ruling of the Federal Food and Drug Administration establishing the legal tolerance for arsenic at 0.025 grain of arsenious trioxide per pound of fruit. This was later lowered to conform to the British standard, but in 1940 it was placed at 0.025 grain for arsenic and 0.05 grain for lead. In the attempt to reduce excessive residues to legal tolerances, various devices of wiping and brushing were tried and were found lacking; attention then turned to chemical washes. The difficulty of applying mechanical and chemical treatments to the "soft" fruits, peaches, apricots and cherries, has restricted such measures largely to apples and pears. No insecticide containing metallic lead in excess of 0.25 per cent is registered for sale or recommended for application in California on berries, grapes (following bloom), or on leafy vegetables or any vegetable within 30 days of harvest time.[78] Elsewhere emphasis is placed on the use of calcium and magnesium arsenate and the fluorine compound cryolite instead of lead arsenate. Preference is given to Derris, the extractive rotenone, and organic compounds such as DDT in treating vegetables, particularly those of a leafy nature such as cabbage and lettuce.

**Chemical Washes.** Studies made by Robinson[79] of solvents for lead arsenate residues included (1) a mixture of sodium carbonate, sodium hydroxide, and borax and (2) a dilute solution of hydrochloric acid. Exposure in the washing machine ranges from 38 seconds to 2 minutes. The use of basic mixtures dissolves the natural wax coating of the fruit and injures the keeping value. Of all the formulas tested none was found superior to a 1.0 per cent hydrochloric acid solution, about 3 gallons to 100 gallons of water. The concentration may be lowered to 0.5 per cent on fruit with lower residues. A later paper by Robinson and Hatch[80] suggests the addition of 1 gallon of a very light petroleum oil (40 to 55 seconds Saybolt or kerosene) to 1.0 per cent hydrochloric acid solution for the removal of very adhesive residues, probably resulting from late applications of petroleum or fish-oil adhesives.

Sodium silicate was also found helpful in removing heavy residues; from 60 to 76 pounds of a sodium silicate solution testing 58 to 60° Bé was used per 100 gallons of spray. This material is used only in washes heated to at least 90°F. These results have not been corroborated under eastern conditions, where a 1.5 per cent hydrochloric acid solution has been found more effective, presumably from the more general use of lime in lead arsenate sprays.[84] McLean and Weber[81] reviewed the value of certain wetting agents as used in the wash tank at room and moderate temperatures. Penzer[82] found it necessary to use as high as 1.5 per cent of hydrochloric acid, which with proper wetting agents cleaned the oil-lead arsenate-sprayed apples. Prompt rinsing of fruit after acid treatment is suggested to remove soluble arsenic and reduce the danger of contamination by mold spores. Arsenical injury to apples from the use of varying formulas, concentrations and temperature exposures has been shown by Overley and Overholser.[83] The importance of using washing methods that will remove both lead and arsenic in approximately the same ratio as that of acid lead arsenate, namely 2.09, is stressed by Haller and associates.[85]

**Arsenical Residues on Forage Plants.** The practice of dusting or spraying alfalfa as a control for the alfalfa weevil has become very common in some western states; this raises the question of livestock poisoning either from feeding on the treated alfalfa or hay made from it.

Feeding tests were made with sheep, horses and cattle fed only on alfalfa hay which had been dusted with calcium arsenate, using 3 pounds of calcium arsenate per acre on one alfalfa field, and 6 pounds per acre on the other. Both dosages are excessive, since the accepted practice is to use only 2 pounds per acre. Ten days after treatment the alfalfa was cut and stacked; it stood until December, and was then fed to a variety of cattle, sheep and horses of varying ages. The treated hay was the only feed given the animals for a period of 40 days. The animals receiving the hay treated with 3 pounds of calcium arsenate to the acre showed no injurious effects. Alfalfa hay dusted with 6 pounds of calcium arsenate to the acre and fed to the same livestock caused no bad effects, although some of the cattle did not gain in weight. The horses gained weight throughout the experiment and were sleek and glossy. The sheep also gained throughout the experiment.[86]

Feeding experiments with calves grazing continously on grass beneath trees sprayed with the customary dosage of lead arsenate (3 pounds per 100 gallons) showed little if any effect on the test animals. Dosages of 6 to 10 pounds per 100 gallons may result in serious to dangerous reactions if the grass is eaten continuously. The length of feeding time varied from 31 days for the lightest dosage to something over 4 days for the heaviest. The approximate amount of arsenic consumed per day by a test animal ranged from 1.06 grams in the 3-pound dosage per acre, 2.1 grams in the 6-pound dosage and 3.2 grams in the 10-pound dosage. The exact amounts consumed cannot be given, since a certain amount of the arsenical deposit on the grass is removed by tramping. Sheep substituted for the calves showed similar results, those feeding under trees sprayed with dosages of 3 pounds per 100 gallons showed no acute poisoning; only slight poisoning was noted with a dosage of 6 pounds per 100 gallons. With the heaviest dosage of 10 pounds per 100, all the sheep survived but showed definite symptoms of poison.[87]

The application to wheat and barley of a mixture of calcium arsenate and Paris Green, at the rate of 20 to 30 pounds per acre, resulted in what was diagnosed as arsenical poisoning to cattle grazing near a treated wheat field. Analyses of the straw after the grain was harvested showed a range of 3.7 to 47.6 ppm. of $As_2O_3$.[85]

Applications of 110 to 120 gallons per acre of a 0.6 per cent sodium arsenite solution was reported to be dangerous to grazing livestock until after heavy rains have fallen.[89]

**Effect on Honeybees of Arsenic from Sprayed Trees.** The necessity of spraying many types of fruit trees with arsenicals, for controlling codling moth and curculio during or following the blooming season, has frequently led to charges of poisoning bees present in the orchard. Such claims of losses have been general by a number of writers; the minimum amount of arsenic to cause death has been set at 0.0004 to 0.0005[90,91] milligram of arsenic trioxide ($As_2O_3$). The arsenic has been found both in the nectar and pollen from sprayed blossoms, and consequently the final effects of the arsenic may be greatly postponed beyond the time of working sprayed bloom. The proper timing of sprays to avoid the heaviest bloom will do much to avoid such danger, especially if through the coöperation of the bee-keeper, the hives are closed for a day or two of the most dangerous period.

**Effect of Arsenicals on Plants.** Foliage burn and even twig and trunk injury has been noted in varying degrees from the use of practically all forms of arsenicals. Complete lack of injury has been found only with the most stable forms, especially the very basic ones, and then accompanied by a lowered toxicity to insects. This implies a very narrow margin of safety between plant tolerance and the ability to give satisfactory control of insect pests. Standardization of arsenicals, in relation to plant injury, has been attempted largely through the required statement of the percentage of water-soluble arsenic present. In addition to the percentage of arsenic oxide, those of the basic oxide (lead, calcium, etc.) are usually required. These regulations form the basis for our first Federal and State Insecticide Laws. Later writers[29a,31,32,33] have stressed the stability of the arsenical compound, that is, the rate at which additional soluble arsenic may be formed, as much more important in judging the quality than the original amount of soluble arsenic present.

Varietal differences in susceptibility to arsenical injury have been somewhat definitely defined. Peach foliage is generally recognized as susceptible to the toxic action of arsenic.[32,33] The minimum concentration of arsenic acid toxic to peach foliage is stated to be the equivalent of 0.0012 per cent of arsenic pentoxide.[32] It should be noted that arsenical injury to foliage is cumulative, and repeated releases of minute amounts of soluble arsenic may finally cause injury. Since difficulty has been experienced in the use of all forms of arsenicals on tender foliage such as bean and peach, attention has been given to the use of "correctives" (p. 22) as a means of minimizing such damage. Injury to citrus fruits from the use of arsenicals is described on p. 20.

In addition to injuring foliage, under certain conditions arsenical compounds cause damage to the tree trunk and limbs by absorption through wounds, lenticels and latent buds; both roots and branches are susceptible to this type of injury. It may result from surface applications, such as the runoff from spray applications. The smooth, unbroken bark of the apple tree is said to be practically impervious to arsenical solutions.[92]

**Effect of Arsenicals through the Soil.** Continued heavy applications of arsenicals over a period of years, such as used in codling moth spray programs, results in the accumulation of toxic amounts of arsenical compounds in the soil. Several thousand acres of former orchard sites in the state of Washington are reported to show such a degree of toxicity as to be useful only for such resistant crops as asparagus, potatoes, tomato, carrot, tobacco, dewberry, grape, and red raspberry.[93] A direct correlation was shown between the amount of arsenic absorbed in peach leaves from toxic soil and foliate injury and defoliation. Injury was noted with concentrations of 2 ppm of arsenic in the dried leaf. The soil under sprayed trees showed a heavy accumulation of arsenic in the top foot.[94] Sudan grass and bush beans grown in sodium arsenite solutions showed a suppression of growth at 12 and 1.2 ppm, respectively, for the former and the latter.[95] Studies with oats grown in water cultures containing arsenic have shown a tendency to decrease the rate of moisture transpiration. This resulted in the development of pale narrow leaf blades.[96a]

**Arsenicals as Soil Insecticides.** Dosages of 2,000 pounds per acre of acid arsenate of lead gave good control of the larval stage of the Japanese beetle, *Popillia japonica*, but were injurious to certain plants. Nasturtium and snapdragon were unaffected, but Calendula and strawberry made a poor growth. Acid lead arsenate becomes more basic or insoluble in the soil, with a corresponding loss of toxicity to insects.[96]

Basic arsenate of lead was of no value as a soil insecticide. Paris Green, copper oleoarsenite and certain other homologs were of equal value to acid lead arsenate. The arsenates of calcium, magnesium, and manganese, when first applied, seemed more effective than acid lead arsenate. Barium, magnesium and sodium fluosilicates were effective agains the beetle larva, when freshly applied, but soon decomposed in the soil and became harmless.[97]

**Arsenical Herbicides.** Compounds of arsenic, including arsenic acid ($H_3AsO_3$), sodium arsenite and sodium arsenate, are in common use as herbicides. The treatment of soil with such arsenical compounds is usually spoken of as "soil sterilization," in contrast to the effect of certain types of petroleum fractions and organic compounds whose activity is largely exhausted in one year. However, the action of soluble arsenical herbicides does not usually continue more than from 2 to 4 years, depending on rainfall and the type of soil. Longer periods of sterilization are possible with excessive dosages, especially in semi-arid soils. Sodium arsenite is recommended for quick results and deep penetration on sandy soils containing little clay. Heavier sedimentary soils reduce the toxicity of the compound, and light annual applications (2 to 4 pounds per square rod) of sodium arsenite are suggested or the less soluble arsenious trioxide.[98] Combinations of arsenic and sodium chlorate in any proportions are reported more satisfactory for soil sterilization than arsenic used alone. This mixture makes possible the use of dry mixtures of arsenious trioxide and the chlorate; the latter is immediately active, but leaches out readily, while the slowly dissolving arsenic is effective over a longer period.[99] Applications of standard lead arsenate (see page 32) show but slight activity as herbicides and are reported to leach quite slowly from the soil.[97]

White arsenic ($As_2O_3$) dissolves slowly in water—a difficulty which has lead to the general use of some form of the more soluble sodium salts for making solutions.[100] Commercial arsenical herbicides may contain varying amounts of different sodium arsenites, sodium arsenate or small proportions of sodium hydroxide ($NaOH$) and arsenious acid.

Several forms of arsenites have been identified, which apparently result from combining varying proportions of arsenious trioxide ($As_2O_3$), sodium hydroxide, and sodium carbonate. The following proportions of arsenic and sodium compounds are said to give the compound indicated:

Sodium meta-arsenite ($NaAsO_2$) with a ratio of 1 pt. $NaOH$ to 2.48 pt. $As_2O_3$
Sodium acid arsenite ($(ONaH(AsO_3)_2$ with a ratio of 1 pt. $NaOH$ to 4.96 pt. $As_2O_3$
Sodium tri-basic ortho arsenite, $Na_3AsO_3$ with a ratio of 1 pt. $NaOH$ to 0.825 pt. $As_2O_3$
Sodium di-basic ortho arsenite, $Na_2HAsO_3$ with a ratio of 1 pt. $NaOH$ to 1.235 pt. $As_2O_3$
Sodium mono-basic ortho arsenite, $NaH_2AsO_3$ with a ratio of 1 pt. $NaOH$ to 2.48 pt. $As_2O_3$

Commercial preparations of arsenical herbicides are usually mixtures of the different sodium arsenites with perhaps a small proportion of sodium arsenate. A common formula used for concentrated herbicides contains 1.4 pounds of sodium hydroxide and 4.0 pounds of arsenious trioxide, which with water gives a total weight of 12 to 13 pounds per gallon.[100]

Comparisons of the toxicity of arsenious trioxide and the sodium arsenites to the common barberry have shown the former to be more toxic and trisodium arsenite the least active. Two gallons of a commercial sodium arsenite, containing 8 pounds of arsenious trioxide to the gallon and diluted with 40 parts of water, when poured about the roots, were sufficient to kill a single barberry bush. All parts of the dead plant were found to have absorbed arsenic in amounts ranging from 0.007 to 0.188 per cent. This same concentration of arsenic killed numerous other plants. Spraying the parts of the plant above ground with the solution killed only the treated portions. The content of arsenic in the soil beneath the dead barberry bushes decreased from 0.676 per cent at the time of treatment to 0.04 per cent after 14 months with a rainfall of 30 inches.[102] Plants seeded in the soil containing 0.04 per cent of arsenic germinated, but growth was abnormal. By contrast with the results reported from a solution of sodium arsenite, it was found that neither germination of seeds nor growth of plants was affected by dosages of lead arsenate applied to the surface soil at the rate of 10 to 100 pounds per 1000 square feet.[103]

Arsenical herbicides are commonly used as a control for the deep-rooted wild morning glory,[101] *Convolvulus arvensis*, especially in the fog belt lying along the Pacific Coast. Careful timing, according to the state of growth, of such applications is necessary to insure killing the entire root system. Such arsenical solutions are of less value in the hot interior valley of this district, where rapid evaporation gives less opportunity for the plant to absorb the arsenic.

A combination of arsenical solution and sulfuric acid is recommended as favoring the absorption of the arsenic into the leaves to be transmitted throughout the root system. The stock arsenical solution used contains 4 parts by weight of arsenious trioxide, 1 part of sodium hydroxide and 3 parts of water. These proportions should generate sufficient heat to dissolve the arsenic. To make 100 gallons of herbicide solution, add one-half gallon of the stock arsenic solution to 96 gallons of water and then, while agitating thoroughly, pour in slowly 2½ gallons of concentrated sulfuric acid. Use at the rate of 500 gallons per acre of solid infestation of morning glory.

Care must be used in all arsenical applications to vegetation to avoid the danger of stock poisoning, as cattle feed readily on sprayed foliage. If vegetation killed by arsenic is burned, avoid inhaling the smoke, as it will carry dangerous amounts of arsenic.[100]

Sodium arsenite solutions as a control for the disease of grape vines, known as "Black Measles" has been used both in European and California vineyards. The solution is applied by spraying or swabbing the pruning wounds with a brush. The application is made soon after pruning. The recommended formula is 3 pounds of sodium arsenite to 50 gallons of water.[105]

**Arsenical Baits.** The use of baits, containing comparatively much higher concentrations of arsenic than are customary in spraying trees, is the usual control for grasshoppers, crickets, snails, cutworms and certain beetles. The more active forms of arsenicals are commonly used in such baits as Paris Green, sodium arsenite, crude white arsenic, calcium arsenate and zinc arsenite.[112] No effort is made to avoid using compounds dangerous to foliage, since the bait is usually scattered very lightly over grain fields, range or waste land. Baits are usually taken more freely when in a moist condition; for this reason, as well as to increase adhesiveness, crude molasses has been recommended, but present custom favors the use of water only for mixing, or the addition of a refined lubricating oil of 20 to 30 SAE viscosity.[113] Attractant materials such as amyl acetate and sliced lemons have been used commonly, but are now largely discarded. A typical formula is:[111]

| | |
|---|---|
| Bran | 100 pounds |
| Sodium arsenite (50 per cent $As_2O_3$) | 2 quarts |
| Water | 10 to 11 gallons |

This bait is used at the rate of 100 pounds dry weight per 10 to 15 acres.

Bran is commonly used as the base for grasshopper and cricket baits, although sawdust may be substituted in part. Equal porportions of bran and sawdust are used; one part of a mill-run bran and three parts of sawdust has also proved quite satisfactory. Ground cottonseed hulls and ground corn cobs have been found to be a good substitute for sawdust.[111]

Little danger of stock poisoning occurs, even when grazing on poisoned ranges, when the bait is properly distributed. Danger to poultry and wild birds, from feeding upon well scattered poisoned bait or poisoned grasshoppers, has been found to be extremely remote or practically unknown. There is also considered to be no danger to human beings from eating chickens that have had opportunity to feed on scattered bait or poisoned insects.[115]

Snail bait, generally used in the citrus groves of California, consists of 16 pounds of bran to one pound of calcium arsenate.[116] Metaldehyde is now commonly used in the formula, both alone and combined with the calcium arsenate, at a concentration of 2.5 to 3 per cent by weight. Bait made with metaldehyde should not be scattered, but left in small piles. Sawdust may be substituted in part for the bran.[117]

**Arsenical Cattle Dips.** The usual procedure for treating cattle in the control of ticks is to drive them through a vat of arsenical solution sufficiently deep to permit the entire animal to be submerged. Two formulas are in common use, the "high strength" dip used for treating cattle being transported to a tick-free region, only two dippings 5 to 10 days apart being the custom. "Low strength" dips are used for regular eradication work on the range, all cattle being dipped every two weeks for months.

Formula for low strength bath: "Boiled Dip"

| | |
|---|---|
| Sal soda (or monohydrated sodium carbonate 11 lbs.) | 24 lbs. |
| White arsenic ($As_2O_3$) 99 per cent pure (powdered) | 8 lbs. |
| Pine tar | 1 gal. |

Heat 25 gallons of water to boiling and add the sal soda; when dissolved, add the white arsenic and boil for 15 minutes or until the arsenic dissolves. Cool to 60°C (140°F) by adding cold water and pour in pine tar slowly while stirring vigorously. Add to water in dipping vat and make up to 500 gallons.

Formula for high-strength bath: "Boiled Dip"

Use 10 pounds of white arsenic and 25 pounds of sal soda (or 11 pounds of monohydrated sodium carbonate ($Na_2CO_3 \cdot H_2O$). Prepare in the same way as for the low strength bath, raising the total volume to 500 gallons.[106]

The "self-boiled" dip contains the same proportions of white arsenic, but a more active form of alkali is substituted for a portion of the sal soda.

Formula for the "self-boiled" high strength dip is:

| | |
|---|---|
| Caustic soda, NaOH, 85 per cent pure, dry granulated | 4 lbs. |
| White arsenic, 99 per cent pure, fine powder | 10 lbs. |
| Sal soda, crystals, ($Na_2CO_3 \cdot 10\ H_2O$) | 10 lbs. |

Dissolve the caustic soda in 1 gallon of cold water and as soon as dissolved begin adding the arsenic, as fast as it will dissolve without boiling. When the arsenic is dissolved, stir in the sal soda after diluting to about 4 gallons. The tar may be dissolved separately by dissolving ¾ of a pound of caustic soda in 1 quart of water and adding tar while stirring vigorously. An imperfect mixture will probably require more soda.[106]

The amount of arsenic in the solution should never fall below a definite point. For the "high strength" the theoretical percentage of $As_2O_3$ is 0.24 per cent for the 10 to 25 formula and 0.19 per cent $As_2O_3$ in the "low strength" or the 8 to 24 formula. Methods of making field determinations of the amount of arsenious trioxide present and corrections for variations have been prepared for keeping the arsenical content to the desired concentration.[107]

In dipping solutions which have been used once and then stored for varying lengths of time the arsenic has been found to change from sodium arsenite to sodium arsenate, a less active form. This change is an oxidizing process, largely due to the growth of microorganisms. Analyses should be made as outlined to detect changes in the dipping strength.[108]

The conversion of the arsenite to the less active arsenate may be retarded, according to Turner's work,[110] by the addition of 6 pounds of lactose to a dipping tank with a capacity of 2,250 gallons.

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# Chapter 3

# Copper and Its Compounds

The importance of copper as a fungicide was first realized under war conditions, when it became necessary to protect all growing food supplies against loss by plant diseases and when commercial supplies of copper sulfate were suddenly found inadequate to meet expanding needs. The sudden increase in consumption of both doměstic and export supplies of copper sulfate, as well as the tremendous demands for metallic copper in the war program, were all met by heavier production of new copper, larger recoveries of secondary copper (scrap and alloys) and imports of refined copper, particularly from Chile.

The United States has the history of heavy production of domestic copper. The domestic smelter output from 1925 to 1929 was 51 per cent of the world's output. During the last 10 years, the per cent of world production has varied from 17 to 25, as shown in Table 10. Copper production by states is given in Table 11, ranging from 1845 to 1941.[1] Domestic production of copper from smelter and mine returns for 1941 approached two billion pounds, with imports for the first nine months amounting to 746,736 short tons. The latter were principally from Chile, Canada, Belgian Congo, Cuba, Mexico, Newfoundland, Bolivia and Peru. In addition to supplies of new copper, both domestic and imported, United States production of secondary copper from alloys and other scrap increased from 532,100 short tons in 1937 to 726,396 tons in 1941, the equivalent of 76 per cent of the domestic mine output. The increased production from scrap copper was a large factor in supplying the demand for copper sulfate, which by 1942 had more than trebled since 1934.

## Copper Sulfate

This chemical, known also as bluestone and blue vitriol, is the most important agriculturally of the copper compounds, not only for its use in this form but as a basis for the preparation of other compounds, such as copper carbonate. About 90 per cent of the copper sulfate produced in the United States is used for agricultural purposes, including timber treating. Other large uses of this compound are for water purification and for flotation purposes in mining districts.

The production of copper sulfate has increased steadily since 1932, as

Table 10. Salient Statistics of the Copper Industry in the United States, 1925 to 1929 (average) and 1938 to 1941, in short tons[1]

| | Average (1925–29) | 1938 | 1939 | 1940 | 1941 |
|---|---|---|---|---|---|
| New copper produced— | | | | | |
| From domestic ores, as reported by— | | | | | |
| Mines | 885,826 | 557,763 | 728,320 | 878,086 | 958,149 |
| Ore produced: | | | | | |
| Copper ore | 59,505,871 | [1][2]37,794,938 | [1]55,239,098 | [1]69,278,476 | [3] |
| Average yield of copper (%) | 1.44 | 1.34 | 1.25 | 1.20 | [3] |
| Smelters | 892,730 | 562,328 | 712,675 | 909,084 | 966,072 |
| Per cent of world total | 51 | 25 | 30 | [3] | [3] |
| Refineries | 890,767 | 552,574 | 704,873 | 927,239 | 975,408 |
| From foreign ores, matte, etc., refinery reports | 317,287 | 239,842 | 304,642 | 386,317 | 419,901 |
| Total new refined, domestic and foreign | 1,208,054 | 792,416 | 1,009,515 | 1,313,556 | 1,395,309 |
| Secondary copper recovered from old scrap only | 347,512 | 267,300 | 286,900 | 333,890 | 412,699 |
| Copper content of copper sulfate produced by refiners | 4,601 | 4,978 | 4,868 | 5,643 | 6,984 |
| Total production, new and old and domestic and foreign | 1,560,167 | 1,064,694 | 1,301,283 | 1,653,089 | 1,814,992 |
| Imports (unmanufactured)[4] | 391,212 | 252,164 | 336,297 | 491,342 | [5]524,974 |
| Refined[4] | 59,236 | 1,802 | 16,264 | 68,337 | [5]220,762 |
| Exports of metallic copper[6] | 522,616 | 421,012 | 427,517 | 427,650 | [5]107,793 |
| Refined (ingots, bars, rods, etc.) | 482,868 | 385,223 | 396,406 | 377,108 | [5]77,824 |
| Stocks at end of year | 307,200 | 414,000 | 355,500 | 334,500 | 317,500 |
| Refined copper | 86,100 | 181,000 | 95,500 | 91,500 | 77,500 |
| Blister and materials in solution | 221,100 | 233,000 | 260,000 | 243,000 | 240,000 |
| Withdrawals from total supply on domestic account: | | | | | |
| Total new copper | 778,123 | 406,994 | 714,873 | 1,008,785 | [7] |
| Total new and old copper | 1,288,700 | 767,000 | 1,215,000 | 1,541,000 | [7] |
| Price, average . . . cents per pound | 14.7 | 9.8 | 10.4 | 11.3 | 11.8 |
| World smelter production, new copper | 1,761,000 | 2,254,000 | [8]2,405,000 | [3] | [3] |

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[1] Includes old tailings.

[2] Exclusive of Alaska, figures for which Bureau of Mines not at liberty to publish.

[3] Figures not yet available.

[4] Data include copper imported for immediate consumption plus material entering country under bond.

[5] Figures cover 9 months only; data for last quarter of year confidential.

[6] Total exports of copper, exclusive of ore, concentrates, composition metal, and unrefined copper. Exclusive also of "Other manufactures of copper," for which figures of quantity not recorded.

[7] Bureau of Mines not at liberty to publish calculated totals owing to confidential nature of foreign trade data for last quarter of year.

Approximate.

shown in Table 12. Prior to the rapid development in 1940 large quantities were imported through 1931 and 1932, principally from Belgium and Germany. All imports in recent years have dropped to negligible amounts. Both Chile and Venzuela are now producing copper sulfate in quantity.

Table 11. Copper Produced in the United States, According to Smelter and Mine Returns, by States, 1940 to 1941 and 1845 to 1941, in short tons[1]

| State | 1940 | | 1941 | | | 1845-1941, smelter output | |
|---|---|---|---|---|---|---|---|
| | | | Smelter returns | | | | |
| | Smelter returns | Mine returns | Per cent of total | Quantity | Mine returns | Total quantity | Per cent of total |
| Alaska | 64 | 55 | 0.01 | 95 | 72 | 676,783 | 2.38 |
| Arizona | 287,266 | 281,169 | 34.01 | 328,550 | 326,317 | 9,414,487 | 33.07 |
| California | 6,549 | 6,438 | .42 | 4,015 | 3,943 | 574,471 | 2.02 |
| Colorado | 13,186 | 12,152 | .67 | 6,483 | 6,748 | 271,515 | .95 |
| Georgia | 13 | 13 | ........ | ........ | ........ | [1] | [1] |
| Idaho | 3,689 | 3,349 | .37 | 3,551 | 3,621 | 91,490 | .32 |
| Michigan | 45,743 | 45,198 | 4.84 | 46,752 | 46,440 | 4,637,385 | 16.29 |
| Missouri | 819 | 685 | .08 | 773 | 1,400 | [1] | [1] |
| Montana | 129,070 | 126,391 | 13.32 | 128,712 | 128,036 | 6,082,756 | 21.37 |
| Nevada | 78,621 | 78,454 | 8.33 | 80,518 | 78,911 | 1,453,477 | 5.11 |
| New Mexico | 70,484 | 69,848 | 7.64 | 73,848 | 73,478 | 1,010,303 | 3.55 |
| North Carolina | [2] | [2] | [2] | [2] | [2] | [1] | [1] |
| Oregon | 101 | 88 | .01 | 84 | 83 | 11,535 | .04 |
| Pennsylvania | [2] | [2] | [2] | [2] | [2] | [1] | [1] |
| South Carolina | ........ | [3] | ........ | ........ | [3] | [1] | [1] |
| South Dakota | 6 | 6 | ........ | ........ | ........ | [1] | [1] |
| Tennessee | [2] | [2] | [2] | [2] | [2] | [4]259,508 | [4].91 |
| Texas | 33 | 30 | [5] | 7 | 6 | [1] | [1] |
| Utah | 248,732 | 231,864 | 28.02 | 270,647 | 266,838 | 3,667,738 | 12.89 |
| Virginia | ........ | ........ | ........ | ........ | ........ | [1] | [1] |
| Washington | 10,511 | 9,612 | .90 | 8,667 | 8,686 | 48,276 | .17 |
| Wyoming | 2 | 2 | [5] | 4 | 4 | 15,869 | .06 |
| Undistributed | 14,195 | 12,732 | 1.38 | 13,366 | 13,566 | [6]248,957 | .87 |
| | 909,084 | 878,086 | 100.00 | 966,072 | 958,149 | 28,464,550 | 100.00 |

[1] Included under "Undistributed"; figures not separately recorded.

[2] Included under "Undistributed"; Bureau of Mines not at liberty to publish figures.

[3] Less than 1 ton.

[4] Approximate production through 1928. Figures for 1929 to 1941 confidential and included under "Undistributed."

[5] Less than 0.01 per cent.

[6] Includes Tennessee for 1929 to 1941.

Exports of copper sulfate are principally to the Latin-American countries, this trade having grown very rapidly because of the development of the banana disease (Sigatoka) and the restriction of European shipping. In 1935, according to the Bureau of Census, the total exports of copper sulfate from the United States were 4,508,161 pounds. Shipments were principally to Mexico, Canada, Argentina and Bolivia. In 1937, exports amounted to 23.5 million pounds, the largest amounts going to Honduras, Guatemala, Mexico, Turkey, Canada and Argentina. By 1942, the total exports had reached 70 million pounds, the increase going almost entirely to the banana groves of Central America, with smaller amounts to other South American countries and also to Algeria.

Copper sulfate is produced in this country principally (1) by the chemical industry from various forms of scrap, or (2) as a by-product in the electrolytic refining of copper. In European countries, copper sulfate is also derived from copper-bearing pyrites used in the manufacture of sulfuric acid and as a by-product of nickel refining. The greater part of the copper sulfate produced in the United States is from copper scrap.

Electrolytic refining of copper is carried on in the United States on a vast scale. Copper sulfate obtained in this way, as a by-product, accounts for the greater part of its production from other sources than from scrap. The compound is also produced in small quantities as a by-product in the parings of gold and silver and in the smelting of lead, where copper-bearing ore is used. The capacity for producing copper sulfate has normally been in excess of the demand.

A typical method of production is as follows; the copper scrap as received is cleaned and freed of all foreign matter. It is then pressed into bricks which are melted in furnaces. The melted copper is drawn off into a cold vat of water where it is crystallized into clinkers which are called "shot". This shot is loaded into large lead-lined wooden tanks which are then filled with dilute sulfuric acid. The contents of the tank are then heated with steam and agitated with air. After the copper has been dissolved the liquor is allowed to cool; as it cools, crystallization takes place. The liquor which remains is drawn off and used again and again for utmost recovery. The crystals are loaded into train buckets and transferred to washing towers, where any remaining impurities are removed. The crystals are then centrifuged to remove the water, after which they are crushed to a more or less uniform size, graded and packaged. The purity of the product is approximately 99 per cent. Commercial grades include large and small crystals, rice, snow and powdered forms. Copper sulfate is also produced from unrefined copper concentrate residue, which is also sometimes referred to as scrap. In this and in the electrolytic process profitable separation is considerably enhanced by the recovery of other valuable metals, including lead, zinc, silver and tin.

The production of copper sulfate in the United States occurs principally in the central Atlantic coast, northern Illinois, Tennessee, El Paso, Texas, and California. Containers for shipping are principally 250, 350 and 450-lb. barrels (net) and also 100-lb. kegs and 100-lb. bags (either cotton or multi-wall paper bags).

**Monohydrated Copper Sulfate** ($CuSO_4 \cdot H_2O$) is produced by heating sulfate crystals to a temperature of about 105°C. In commercial practice dehydration may not be carried to the point of complete removal of four molecules of water. The content of metallic copper is approximately 35 per cent, in contrast with 24 per cent in copper sulfate.

The dehydrated powder absorbs moisture readily and hence must be packed in tight steel drums; the usual drum capacity is 450 pounds. For shipping distances of 1000 miles or more the material is packed in light-weight "one trip" steel drums that are sold with the contents.

Table 12. Copper Sulfate Production in the United States*
(pounds)

| Year | Total Production |
|---|---|
| 1932 | 50,714,299 |
| 1933 | 49,024,703 |
| 1934 | 52,739,349 |
| 1935 | 62,394,791 |
| 1936 | 70,407,497 |
| 1937 | 94,506,733 |
| 1938 | 88,900,782 |
| 1939 | 86,531,847 |
| 1940 | 134,031,827 |

* U. S. Dept. of Interior, Bureau of Mines.

Monohydrated copper sulfate is generally applied as a dust with hydrated lime as a diluent, the usual proportions being 80 to 20; if desired, calcium arsenate may be added to the mixture. Following application, the copper sulfate absorbs moisture and tends to form Bordeaux mixture on the leaf. The chief advantages over the use of the pentavalent form are a saving of freight, ease and speed of application, and reduction in weight compared with a water spray. Copper-lime dusts are well adapted to power applications and compare favorably with standard Bordeaux mixture in effectiveness.

**Copper Sulfate as a Fungicide and Insecticide.** Copper sulfate is readily soluble in cold water and in this form is an active fungicide, even at low concentrations, for many forms of fungi. It is too dangerous in this form, however, to be used on foliage; in fact it has had much use in European practice as a herbicide at 3 to 10 per cent concentrations. Treatment of fence posts (green or unseasoned) is recommended with solutions containing two pounds of copper sulfate in one gallon of water. From 1 to 3.5 pints of this solution are used for posts 3 to 6 inches in diameter. Treatment time varies from 30 to 50 hours.[2] This treatment gives protection against wood decay, fungi, and termites. The protective period is shortened by exposure in wet soils, as this chemical is readily leached out. Copper sulfate is also used for internal treatment of sheep in removing certain of the *ascarids* commonly spoken of as stomach worms. It is indirectly a preventive of liver flukes in sheep and cattle when used as a control for certain species of snails, which act as the secondary host of the fluke. Snails and slugs are also repelled by a barrier of copper sulfate solution on cloth or cord. Another use of copper sulfate solutions is for treating the paper wraps used in packing fresh pears and apples.

Solutions of copper sulfate are slightly acid and because of their danger to fruit and foliage are restricted in their use as a fungicide. The discovery in 1885 of the value of adding lime to the solution, as a means of reducing plant injury, is attributed to Millardet[3] in the treating of grape vines for mildew in France. Later this formula became known as Bordeaux mixture. The amounts of copper sulfate, lime and water vary, according to the purpose for which it is intended, a common formula being 4–4–50; the first number refers to the amount of copper sulfate, the second to the amount of lime and the third to number of gallons of water. The formula is changed with the season and the crop upon which it is to be used, from ½–½–50 for tender foliage to as high as 8–8–50 for dormant applications. Whatever the formula used, the proportion of copper sulfate to lime usually remains constant, which gives a slight excess of lime over the chemical equivalent.

The earliest formulas for Bordeaux mixture called for burned limestone ($CaO$) and the lump form of copper sulfate, both of which are objectionable because of the labor required in handling. The available limestone was frequently of poor quality with varying amounts of grit and magnesium. Both burning and slaking of the limestone might yield inferior products, with much waste and sediment in the finished mixture, which causes excessive wear both to the spray pump and nozzle. These difficulties have been met by the general use of hydrated lime. A high-grade "spraying lime" is now generally available at a slight premium over the usual grade of builder's lime. Copper sulfate in lump form, although listed as readily soluble in cold water, actually requires hours to dissolve. This delay has been met by the use of powdered or of "snow" copper sulfate, which dissolves readily within a few minutes.

Lime, when added to a copper sulfate solution, neutralizes the acid and forms calcium sulfate, while by hydrolysis calcium sulfate and water continue to form until the copper sulfate is decomposed. Complete neutrality occurs when 0.75 per cent equivalent of calcium hydroxide combines with one equivalent of copper sulfate. The combining of equal amounts of lime and copper sulfate gives an excess of lime, which results in an alkaline mixture. The type of basic copper sulfate which precipitates in the lime-copper sulfate mixtures varies with the proportions of the two chemicals.

Pickering's work[4] in the chemistry of the Bordeaux mixture corroborates that of previous workers and shows that the initial product of the interaction of copper and lime is the least basic sulfate. Other compounds of a less basic nature result from the use of smaller amounts of lime. Martin[5] shows that the very basic copper compound, $10\ CuO \cdot 3CaO$, is formed when equal amounts of lime and copper are used.

*Preparing Bordeaux Mixture.* Stock solutions of copper sulfate and lime may be prepared in advance of spraying and combined in the spray tank immediately before application. Dissolve the copper sulfate in cold water using a wooden or earthenware, but not a metal container. Mix the lime and water in a separate wooden container. The two solutions may be further diluted with water, using all or much of the total amount required. Pour the two dilute solutions together, stirring constantly meanwhile. Add water as needed to bring the total amount required in the formula. Concentrated solutions should not be combined, as the precipitate from dilute solutions is more tenacious and consequently weathers better than that resulting from the preparation of Bordeaux mixture from concentrated solutions.[8] Measurements by Wilson[6] of the rate of weathering of Bordeaux mixture on peach and apricot twigs with a rainfall of 3 to 4 inches showed losses of 18, 34 and 38 per cent of the copper from the use of dilute solution of copper sulfate and lime, compared with losses of 65, 70 and 58 per cent when the mixture was prepared from concentrated solutions.

A tank mix may be prepared by using powdered or "snow" copper sulfate and hydrated lime. To make a 4–4–50 mixture, fill the spray tank with 50 gallons of water, start the agitator and add powdered copper sulfate. Then sift in the hydrated lime and if desired 0.01 per cent of powdered casein. The mixture is then ready to apply. The precipitate in Bordeaux mixture is of a colloidal nature and is made up of numerous membranes, blue in color, floating in a solution of calcium hydroxide and calcium sulfate. These membranes enclose lime water and particles of lime. Properly made Bordeaux mixture remains suspended for hours, the rate of settling being prolonged by agitation; after being deposited on the leaf surface it dries and adheres very closely. If the mixture is allowed to stand from 24 to 48 hours, crystals of calcium sulfate and rounded copper crystals will form and the membranes almost entirely disappear. This change in the physical characteristics of Bordeaux mixture is apparently the chief difference between a freshly prepared mixture and that of a dry powdered form. The physical condition of a freshly made Bordeaux mixture can be conserved by the use of sugar. This principle has been recognized for a number of years and practical application was made of it in the commercial preparation of Bordeaux. As much as 4 pounds of cane sugar to 50 gallons of Bordeaux mixture has been recommended, but this amount "is unnecessarily large, at least for the 5–5–50 mixture so frequently used in America. Not only is sugar expensive, but also it seems to act as a reducing agent if the mixture is kept for any length of time. Glucose also serves as a preservative, but in a yet more pronounced way reduces copper."[8]

The Pickering type of Bordeaux mixture[9] substitutes saturated lime water for either slaked calcium oxide or hydrated lime as used in the standard type of Bordeaux mixture. A stock solution of copper sulfate is made up containing 1 pound copper sulfate per gallon of water. Saturated lime water is prepared by adding 2 pounds of unslaked lime (CaO) or 4 pounds of lime paste to 50 gallons of water. Agitate the mixture for 5 or 10 minutes and allow to settle. The clear lime water may then be drawn from the top of the barrel or drawn off through a spigot placed a few inches from the bottom of the barrel. Add 5 gallons and 3 quarts of the above copper sulfate stock solution (1 pound copper sulfate to 1 gallon water) to 94 gallons and 1 quart of clear, saturated lime water and stir for 1 minute. If an arsenical is desired in the spray mixture, either lead arsenate or calcium arsenate may be added.

This type of Bordeaux mixture is neutral or acid in its reaction and is generally reported as being quicker in its fungicidal activity because of greater solubility. This quality is in itself a weakness since this form of Bordeaux mixture is too dangerous for certain types of foliage and less lasting than the excess-lime Bordeaux mixture. Studies by Lutman[8] and Butler[7] of the Pickering sprays have shown that the film membranes are more permanent than those of excess-lime Bordeaux mixture, and that the sphere-like crystals of copper do not form in the sprays made according to the Pickering formulas.

*Effect of Bordeaux Mixture on Plants.* It is generally recognized that spraying with Bordeaux mixture deepens the green foliage, which change may be due to an increase in the total amount of chlorophyll produced or to slow removal of the products of assimilation.[7]

Copper may be absorbed by the leaf from a copper sulfate solution, such as would occur with imperfectly neutralized Bordeaux mixture, but there probably would be no effect on foliage treated with Bordeaux mixture which contains no free copper sulfate. Bordeaux mixture on potato foliage was found by De Long[11] to kill leaf hoppers transferred to the treated leaves 4 to 5 days following the application.

Increases in the transpiration rate of foliage sprayed with Bordeaux mixture has been noted by Wilson and Runnels in a series of papers beginning in 1933.[12] Their findings have been corroborated by Horsfall,[10] who points out that the conflicting statement of Lutman[8] is explainable in that his work was with field-grown plants, with thickened cuticle, while later experiments, showing increases in the transpiration rate, were made on greenhouse plants, which have a thinner cuticle.

The shading effect of Bordeaux mixture with excess lime is noted by Butler[7], who states that the physiological response produced by Bordeaux mixture depends on the degree of opaqueness. When shading is objectionable a formula of 1:½ should be used; when it is desired, a 1:1 Bordeaux mixture should be used.

*Modified Bordeaux Mixture.* The fungicidal action of Bordeaux mixture is protective rather than eradicative. This is due to the insolubility of the basic compounds formed by the interaction of the copper and lime and the slow release of active fungicidal material from the spray deposit. A number of disadvantages result from the nature of the mixture, both in regard to its toxicity and the physical difficulties and inconveniences of preparation, application and wear on spray machinery. These difficulties have led to various attempts at modification which would permit greater ease in application without sacrificing efficiency. The customary method of applying Bordeaux mixture in England[13] is with nozzles, using a No. 0 disc adjusted to give a fine, mist-like spray. The aperture in the disc is 0.5 millimeter in diameter, which is the smallest size practicable. This method permits the application of sufficient amounts of spray to produce a slight drip and gives the maximum fungicidal value with the least danger to the host plant. Such applications, however, result in excessive wear on spray machinery; moreover, the spray has little driving force, a slow application rate, and is not adapted to including eradicant types of fungicides or insecticides for sucking insects. By contrast with the mist-like particles of Bordeaux mixture spraying, there is the coarse, driving application known as "washing". This is made with nozzles having a No. 2 disc with an aperture size of 2 to 3 millimeters, which gives coarse drops that adhere well. This gives greater speed in application and results in a decided saving of time. Modified Bordeaux mixtures combined with other spray materials have been developed; these can be applied as a wash with all the added advantages of this type of spraying. Martin[13] has studied the use of sulfite lye from the sulfite process of paper manufacture. The lye mixture is made by combining a Bordeaux mixture of 10 pounds of copper sulfate, 15 pounds hydrated lime and 100 gallons water with a 0.75 per cent of concentrated sulfite lye (60° Tw.), to which is added 0.02 per cent of nicotine. The lye mixture was found less efficient than the use of glyceride oils of concentrations of 0.5 to 1 per cent. Such use of vegetable oils has been shown by Martin and Salmon[14] to be distinctly fungicidal.* The formula used in the "oil-Bordeaux" spray is 1 gallon of oil, 10 pounds of copper sulfate and 15 pounds of hydrated lime in 100 gallons of spray. An edible, cottonseed oil of a low acid content and crude oil of mustard were used in these experiments. The method of mixing is to add the oil and stock copper sulfate solution (1 pound dissolved in a gallon of water) to 99 gallons of water containing the hydrated lime, and agitate until emulsified. In this combination the Bordeaux mixture is the emulsifier, and differs from the combination of Bordeaux mixture-petroleum oil emulsion used in the citrus region of Florida. The addition of glyceride oil to the Bordeaux mixture improves the retention of copper on the foliage; and this coupled with the fungicidal value of the oil itself permits the reduction of copper in the formula to one-half the usual amount. This modified Bordeaux mixture was found to apply with greater ease and rapidity than the standard formula and also to be a better carrier for insecticides.

Many attempts have been made to increase the safety of Bordeaux mixture by modifying the formula as to the copper-lime ratio. Such variations are limited, as an excess of lime is not usually helpful; it may cause lime injury to the plant and certainly increases the shading effect. Sleesman and Wilson reported[15] on the results of a large series of modifications of the Bordeaux mixture formula in potato spraying. They found no significant difference in the leafhopper population, in disease control, or in yield from such variations from the customary ratio.

*Calculating the Amount of Copper Sulfate in Commercial Bordeaux Mixture.* Labels on commercial packages of Bordeaux are required by the Federal Insecticide Act of 1947 to state the active ingedient, for example copper in per cent by weight. This is usually stated as per cent metallic copper which amount, when multiplied by the factor 3.93, gives the percentage of crystallized copper sulfate present in the concentrated commercial mixture. If the copper is given as copper oxide (CuO), multiply this amount by 3.14 to convert to crystallized copper sulfate. To convert the number of pounds of crystallized copper sulfate in the commercial mixture into the amount present in the dilute spray (such as 4–4–50), multiply the number of pounds of the concentrated Bordeaux mixture to be added to 50 gallons of water by the percentage of copper sulfate. If the commercial paste contains 6 per cent of metallic copper, multiply 6 by 3.93 which gives 23.58, the percentage of crystallized copper sulfate. The paste contains the metallic copper equivalent of 23.58 per cent of copper sulfate. The label states that 8.5 pounds of the paste are to be used to 50 gallons of water. Multiplying 8.5 pounds by 23.58 per cent

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* The author has found that glyceride oils at this concentration are effective controls of a number of species of aphids.

equals 2.004 pounds of copper sulfate. The use of 8.5 pounds of the Bordeaux paste to 50 gallons of water is the practical equivalent of a 2–2–50 formula.[13]

*Burgundy Mixture* is a compound of copper sulfate and sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) which gives a completely water-soluble precipitate. The dried residue from this mixture varies from blue to greenish, but since it is not opaque does not shade the leaf as does the Bordeaux mixture. This compound was developed in France to avoid the mechanical difficulties of applying Bordeaux mixture which contains undissolved lime. The ratio of copper sulfate to sodium carbonate ranges from 1:05:50 to 1:2:50. A suggested formula is:[17]

| | |
|---|---|
| Water | 100 parts |
| Copper sulfate | 4 parts |
| Sodium carbonate (crystals) | 6 parts |

A basic copper carbonate is formed at the higher concentrations suggested which changes to malachite ($2CuO \cdot CO_2$). Using small quantities of sodium carbonate (ratios of 1:0.6 to 1:1) gives an acid mixture with free copper sulfate thus increasing fungicidal activity. The least amount of soluble copper is found with the ratio 1:1:84.

Burgundy mixtures vary in their stability according to the ratios of copper sulfate and sodium carbonate, but the formation of malachite may be retarded by the use of tartaric and citric acids at concentrations varying from 0.04 to 0.067 per cent.

Plants vary in their sensitivity to Burgundy mixtures, the apple being very intolerant of copper sprays. The presence of dew and rain, especially before drying, greatly increases the possibility of injury. Dried Burgundy mixtures differ but little in their effect on plants, whether they are acid, alkaline or neutral. The rates of 1 part copper sulfate to 1 part of sodium carbonate is satisfactory for all requirements.

Calcium arsenate may be safely combined with Burgundy mixtures and tends to neutralize any soluble copper which may be present. There is some doubt of the safety of combining lead arsenate with this mixture.

After the discovery of Bordeaux mixture, other copper compounds were tested, particularly those giving a less conspicuous deposit on foliage. Audoynaud[18] proposed the combination of ammonium hydroxide with copper sulfate solutions as having some advantages over the lime-copper sulfate mixture. One advantage of the copper-ammonia combinations is that these are true solutions, whereas the other copper sprays are suspensions. Copper-ammonium compounds are unstable and require an excess of ammonia to prevent precipitation of cupric hydrate, which is also formed on the foliage as the spray solution dries. Cupric ammonium carbonate is one of the more stable forms, but cupric ammonium sulfate has been found very unstable. A solution of basic copper carbonate in ammonium hydroxide has also been used as an eradicant form of fungicide. The copper ammonium compounds are generally considered more dangerous to foliage than Bordeaux mixture, and are necessarily limited in their use, but are of value when only small amounts of soluble copper are required for protection.

A more stable form of copper-ammonium compounds has been developed by Sessions,[19] using the silicate combination of copper sulfate and ammonium hydroxide as a stabilizing factor.

**Basic or Fixed Copper Compounds.** A number of basic copper compounds have been developed, principally by manufacturers, that are comparable to Bordeaux mixture in fungicidal value and plant tolerance. The group includes basic copper sulfates, acetates, chloride [$(CuCl_2 \cdot 3Cu(OH)_2$], also known as oxychloride, and a few other forms. Oxychloride is analogous to the precipitate of neutral Bordeaux mixture ($4CuO \cdot SO_3$) and is readily formed by the action of air on cupric chloride solutions or scrap copper. It is the active constituent of "Kupperpaster Bosna" and "Caffaro" at one time popular on the European continent.[20] A series of papers reporting results with certain fixed coppers as vegetable sprays has been issued by Wilson and his co-workers.[12, 15, 21, 22] Copper phosphate, $Cu_3(PO_4)_2$, was found by Goldsworthy and Green[21] to be improved in its adhesion by the incorporation of bentonite and lime.

Basic copper compounds are used both as dusts and sprays for treating truck crops and orchards. The usual dosage for truck crop sprays is 1.5 pounds of metallic copper per 100 gallons of spray, which with a 50 per cent copper content would require 3 pounds of the basic copper compound.[15, 27] Oil and invert emulsions are used as adherents.[56] (See p. 134)

Basic copper sulfate has been studied by Holland and his co-workers as a substitute for Bordeaux mixture, principally for application as a spray, with limited studies in its use as a dust application.[26] The chief advantages of this product are that it comes to the grower in a uniform finished state, ready for the spray tank and without the necessity of the usual equipment and labor required in preparing Bordeaux mixture.

Carbonates are preferred to hydroxides in preparing basic copper sulfate. Precipitated calcium carbonate, $CaCO_3$, precipitated basic magnesium carbonate, $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and sodium carbonate, $Na_2CO_3$, are used for the purpose. Complete precipitation of the copper was obtained by combining 1 mole of copper sulfate with 0.8 mole of the carbonate.

Copper acetate has received but little attention as a fungicide in the United States. Butler and Smith[28] first called attention to European practice in controlling fungi with two copper acetates: normal or neutral acetate of copper, $Cu(C_2H_3O_2)2H_2O$, containing 31.8 per cent of metallic copper, and basic acetate of copper, $(C_2H_3O_2)CuO \cdot 6H_2O$, containing 34.4 per cent of metallic copper. It is stated that basic acetates of copper form even less conspicuous deposits on the fruit than do the cuprammoniums, and for the equivalent in copper are many times less injurious to the plant. The acetates are rated very near to Bordeaux mixture in safety to host plants and in fungicidal properties.

"Neutral copper acetate dissolves readily in cold water forming a clear bluish green solution with faint acetic odor." The salt decomposes very quickly after being applied as a spray. "Basic copper acetate is more adhesive than the neutral copper acetate but decomposes more rapidly on exposure to air."[28] The neutral acetate is considered less toxic than the basic form. Gelatin at the rate of 0.05 per cent is recommended as an adhesive for the neutral form.

*Formulas suggested:* The weaker concentration is used in place of cuprammonium, the stronger one instead of Bordeaux mixture. Prepare a stock solution of the acetate by dissolving in water at the rate of one pound of either basic or neutral acetate to a gallon of water. For the weak concentration use one gallon of the stock solution to 49 gallons of water. Use 4 gallons of the stock solution to 46 gallons of water. The neutral acetate is used at the same concentration.

Cuprous oxide, $Cu_2O$, is recommended as a control for the "damping off" of spinach. Favorable results have been secured principally in combating the fungus *Pythium ultimum* and to a lesser extent *Rhizoctonia solani.* Black oxide of copper, $CuO$, is of little value for treatment. Cuprous oxide is a bright red color and should be free from the black oxide. A light dusty form, free from oil, is preferred. The product is suggested for use on seeds of spinach, beet, chard, tomato, eggplant, pepper, pea, cucumber, squash, lima bean, and melon. Dosage: 1 pound of cuprous oxide to 65 to 70 pounds of spinach seed.[29]

"Dosage for most seeds should be 2½ per cent by weight or 1 level teaspoonful per pound. The dosage for big seeds like peas or cucumbers should be ¼ to ½ per cent, or $\frac{1}{10}$ teaspoonful per pound. Six per cent is the optium for beets, but this dosage should be halved for sowing in dry soil. A low organic matter content in the soil, such as would occur in sand; drought; or presoaking of the seed before treatment may result in injury."[29] Following the successful use of cuprous oxide for seed treatment the compound came into general use as a spray for both orchards and truck crops.[15, 27, 41] On carrots it was found somewhat injurious at dosages of 2 pounds per 100 gallons of spray.

Horsfall and co-workers have shown that the fungicidal value of both cupric and cuprous oxide depends upon manufacturing methods and particle size.[30]

Table 13. Toxicity of Copper Ammonium Zeolite of Three Degrees of Fineness to Spores of *Sclerotinia fructicola*

| Particle size (microns) | Spray time (seconds) | Copper deposit (micrograms per sq. cm.) | % of spore germination inhibited |
|---|---|---|---|
| | | | Average of 2 tests |
| 1.6 | 3 | 0.7 | 27 ±2 |
| 10.0 | | | 25 ±1 |
| 13.3 | | | 2 ±0 |
| Commercial Z-0 | | | 2 ±1 |
| 1.6 | 8 | 1.8 | 42 ±1 |
| 10.0 | | | 39 ±2 |
| 13.3 | | | 10 ±2 |
| Commercial Z-0 | | | 12 ±2 |
| 1.6 | 13 | 2.9 | 60 ±2 |
| 10.0 | | | 54 ±2 |
| 13.3 | | | 33 ±2 |
| Commercial Z-0 | | | 28 ±1 |
| 1.6 | 20 | 4.4 | 81 ±1 |
| 10.0 | | | 73 ±2 |
| 13.3 | | | 57 ±2 |
| Commercial Z-0 | | | 52 ±2 |
| Control | 0 | 0.0 | 2 ±1 |

(*Courtesy Buffalo Turbine Agricultural Equipment Co., Inc. Gowanda, N. Y.*)

FIGURE 3. Treating a potato field with a spray-duster.

Table 14. Specifications of Some of the Materials Commonly Used in Preparing Dust Mixtures

| Material | Weight per cubic foot (pounds) | Weight per cubic inch (grams) | Per cent through a 325-mesh screen, per cent | | Particle size as determined with a microscope,* (microns) | | | Rate of flow through duster (pounds per minute) | | Reaction pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Dry | Wet | Large | Small | Average | Peerless | Messinger | |
| Talcs: | | | | | | | | | | |
| 1 | 45.56 | 8.59 | 97.8 | 98.70 | 153 | 3.1 | 25.2 | 1.87 | 12.24 | 9.02 |
| 2 | 42.56 | 7.84 | 85.1 | 83.32 | 104 | 1.8 | 27.6 | 1.73 | 7.17 | 9.08 |
| 3 | 38.63 | 6.81 | 95.6 | 96.60 | 119 | 3.0 | 27.2 | 1.60 | 9.15 | 8.97 |
| 4 | 37.56 | 6.69 | 98.3 | 98.90 | 73 | 2.4 | 16.9 | 1.61 | 9.63 | 9.15 |
| 5 | 25.69 | 4.20 | 99.0 | 99.32 | 13 | 1.5 | 6.3 | 1.50 | 4.06 | 9.17 |
| 6 | 42.25 | 7.71 | 86.1 | 88.05 | 128 | 3.0 | 31.5 | 1.81 | 6.62 | 6.40 |
| 7 | 41.00 | 7.37 | 89.6 | 93.96 | 139 | 2.9 | 27.7 | 1.82 | 7.57 | 6.25 |
| 8 | 36.69 | 6.35 | 96.6 | 97.62 | 76 | 2.3 | 27.5 | 1.54 | 8.25 | 6.50 |
| 9 | 33.56 | 6.03 | 96.1 | 97.65 | 77 | 1.0 | 12.6 | 1.44 | ....... | 7.06 |
| 10 | 40.50 | 5.92 | 92.7 | 97.68 | 148 | 2.2 | 11.9 | .70 | 3.35 | 9.30 |
| 11 | 36.37 | 5.43 | 90.3 | 98.20 | 135 | 2.7 | 14.9 | .66 | 4.70 | 9.28 |
| 12 | 33.87 | 5.13 | 90.6 | 97.60 | 108 | 3.9 | 18.4 | .55 | 4.73 | 9.22 |
| 13 | 32.37 | 4.96 | 89.4 | 97.17 | 136 | 2.1 | 24.1 | .66 | 4.45 | 9.32 |
| 14 | 33.06 | 4.92 | 97.4 | 99.10 | 35 | 2.6 | 10.2 | 1.18 | 4.45 | 9.70 |
| 15 | 30.50 | 4.38 | 98.9 | 99.28 | 36 | 2.5 | 8.7 | 1.25 | . .... | 9.72 |
| 16 | 41.25 | 7.33 | 92.8 | 92.50 | 81 | 2.9 | 28.8 | 1.75 | 7.45 | 9.38 |
| 17 | 47.44 | 8.75 | 95.3 | 96.05 | 54 | 2.5 | 17.5 | 1.71 | 6.84 | 9.40 |
| 18 | 38.81 | 6.77 | 99.3 | 99.67 | 45 | 3.0 | 19.8 | 1.29 | 10.11 | 7.98 |
| 19 | 52.31 | 10.17 | 67.1 | 70.67 | 72 | 4.5 | 26.1 | 2.19 | 8.31 | 7.98 |
| Miscellaneous: | | | | | | | | | | |
| Gypsum | 51.13 | 8.93 | 94.8 | 99.32 | 97 | 3.2 | 29.8 | 1.39 | 7.56 | 7.46 |
| Gypsum | 56.87 | 10.83 | 89.8 | 97.76 | 54 | 2.5 | 23.0 | 2.47 | 7.35 | 7.35 |
| Gypsum | 49.06 | 6.81 | 96.1 | 99.21 | 30 | 2.2 | 9.4 | 1.43 | 9.89 | 8.35 |
| 325-mesh whiting | 67.06 | 12.12 | 97.8 | 99.40 | 36 | 2.8 | 12.6 | 1.73 | 9.80 | 8.75 |
| Whiting | 45.75 | 6.72 | 98.7 | 99.95 | 9 | 2.2 | 5.8 | .86 | 5.40 | 8.90 |
| Cherokee clay | 34.87 | 4.90 | 99.0 | 99.72 | 11 | 2.0 | 5.6 | 1.59 | 9.24 | 6.15 |
| Perry clay | 30.06 | 4.71 | 99.5 | 98.90 | 7 | 1.5 | 2.7 | 1.26 | 4.73 | 4.64 |
| Bentonite 300 | 43.63 | 8.13 | 90.2 | ...... | 8 | 1.0 | 3.6 | 1.79 | 14.96 | 9.28 |
| Bentonite 325 | 38.50 | 7.80 | 99.8 | .. | 6 | 1.0 | 2.0 | 1.90 | 14.88 | 9.30 |
| Soya flour | 37.13 | 6.47 | 79.0 | .. | 72 | 5.0 | 14.9 | 2.20 | 7.19 | 6.42 |
| Wheat flour | 31.63 | 4.86 | 74.0 | ..... . | 30 | 2.9 | 18.0 | .90 | 3.63 | 5.82 |
| Diatomaceous earth | 10.81 | 1.51 | . . | 94.04 | 144 | 2.7 | 25.7 | .35 | 1.81 | 7.07 |
| Diatomaceous earth | 9.00 | 1.32 | . | 99.90 | 36 | 2.0 | 4.3 | .23 | .85 | 8.15 |
| Hydrated lime | 27.75 | 3.81 | 98.4 | .... . | ...... | . . | . .... | 1.80 | ...... | 12.25 |
| Hydrated lime | 32.50 | 4.50 | ...... | ...... | ...... | . .. | ...... | . ... | ...... | 12.28 |
| Phosphate rock | 64.14 | 10.95 | 70.4 | 89.60 | ...... | ...... | ...... | ...... | ...... | 5.76 |
| Cryolite | 41.50 | 6.57 | .. . | . ... | 9 | 2.0 | 3.8 | 1.46 | 10.34 | 7.72 |
| Cryolite | 45.06 | 6.75 | .. | . . | 15 | 2.0 | 5.6 | .48 | 4.79 | 7.18 |
| Cryolite | 35.75 | 5.37 | . .... | . ... | ... .. | . .. | ...... | .98 | 4.99 | 6.87 |
| Calcium arsenate | 27.94 | 4.44 | 92.9 | 97.20 | 4 | 1.5 | 1.7 | 1.11 | 7.08 | 11.82 |

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* These measurements are at best only approximate Certain particles of talc, which contained particles 135 microns long but only 15 wide, were measured only in their longest dimension. The average given here represents the particle size which occurred most frequently in the small sample used.

Table 14.—*Concluded*

| Material | Weight per cubic foot (pounds) | Weight per cubic inch (grams) | Per cent through a 325-mesh screen, per cent | | Partical size as determined with a microscope*, (microns) | | | Rate of flow through duster (pounds per minute) | | Re-action pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Dry | Wet | Large | Small | Aver-age | Peer-less | Mes-singer | |
| Derris root | | | | | | | | | | |
| Fixed Coppers: | 20.62 | 3.62 | 89.0 | . .... | 90 | 2.3 | 16.4 | 1.10 | 6.81 | 8.33 |
| 1 | 55.50 | 8.21 | 98.7 | 99.40 | 42 | 1.0 | 8.8 | 1.98 | 15.86 | 6.30 |
| 2 | 50.50 | 8.74 | 99.8 | 99.50 | 4 | 1.0 | 1.8 | 2.18 | . . | 5.84 |
| 3 | 46.88 | 8.27 | 99.3 | 99.42 | 9 | 1.0 | 2.9 | 2.05 | 31.23 | 6.28 |
| 4 | 30.56 | 4.93 | 96.7 | 97.20 | 6 | 1.0 | 3.2 | 1.95 | 22.40 | 8.03 |
| 5 | 26.12 | 4.41 | 99.4 | 99.10 | 7 | 1.0 | 2.5 | 1.43 | 10.92 | 8.23 |
| 6 | 96.06 | 17.45 | 97.2 | 96.00 | 8 | 1.0 | 2.7 | 2.04 | | 5.66 |
| Monohydrated copper sulfate | 47.75 | 8.50 | | . | ... | | . . | 2.10 | .. | .. .. |

Hamilton and co-workers have shown the relation between the particle size and the fungicidal efficiency of copper ammonium zeolite. Ground copper zeolite, of average particle sizes of 1.6, 10 and 13.3 microns, and the original commercial product were compared as to fungicidal values. The results, as shown in Table 13[39] are closely correlated with particle size. The two smaller sizes were found to be decidedly more toxic to spores than were the larger particles.[39]

The use of basic or fixed coppers as dusts has led to the need of satisfactory dust bases and diluents by which the desired amount of copper may be distributed. The usual dosage per acre is 20 to 25 pounds of the diluted material, but with copper compounds carrying from 50 to 53 per cent of metallic copper a high rate of dilution is required. Hydrated lime is usually combined with monohydrated copper sulfate, but this is to render the copper compound safer for use on plants. The high alkalinity of hydrated lime (pH 11.25 to 12.54) and its dehydrating action make it undesirable as a diluent for the fixed coppers. A number of dust bases have been developed for this purpose; and since their adhesive qualities, rate of flow in dusting machines, weight per cubic foot, particle size and chemical activity as related to the pH value all affect their usefulness as carriers, it is desirable to know something of their comparative value. A number of samples of talcs (magnesium silicate), clays (bentonite), flours, and other miscellaneous materials, together with certain of the basic coppers and other insecticides, are listed according to their physical characteristics in Table 14.[23] Particle size is on averages of 10 particles of each material.

## Miscellaneous Copper Compounds

Copper carbonate, a product of hot copper sulfate solution combined with a carbonate such as soda ash, was one of the first copper compounds used commonly as a seed disinfectant. It is recommended as a control of bunt on seed wheat at the rate of two ounces or more to a bushel of seed. Wheat treated with copper carbonate dust is not injured by the chemical even when held in storage for an indefinite period.[31]

The recommended standards for copper carbonate dusts are:[31]

| | |
|---|---|
| Copper carbonate | 52–54 per cent |
| Copper as copper hydrate | 39–43 per cent |
| Impurities permitted | 6– 7 per cent |

Fineness: 99 per cent in aqueous suspension should pass a 200-mesh sieve.
Density: (shaken down dry) not over 32 pounds per cubic foot.
Color: light green, never blue.

Care should be used in treating seed grain not to inhale the dust, as it is quite irritating. Aspirators or dust masks worn over the nose and mouth are recommended for operators of dusting apparatus.

Copper arsenate $Cu(CuOHAsO_4)$, has been found of value both as an insecticide and fungicide. [20, 32] Increasing amounts are being used in the treatment of truck crops.

Cuprous cyanide, $Cu(CN)$, has been reported as a satisfactory substitute for arsenic[33], but in later work it was reported as dangerous to apple foliage. Marsh and co-workers have shown fungicidal value for this compound.[34]

Copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, prepared by dissolving copper in nitric acid and crystallizing, has an action similar to copper sulfate. It is too active on plants to be used alone as a fungicide but has been used as a weed killer. Compounded with other materials to form relatively insoluble compounds, it may be used on plants as a fungicide.

**Organic Copper Salts.** Copper combined with organic acids has a limited use as a fungicide. Copper stearate has compared favorably with Bordeaux mixture as a control for scab on both pears and apples, and without injury to foliage in the experiments reported. Copper oleate, naphthenate, laurates and resinate have all been used alone and in combination with petroleum oil, which is commonly deficient in fungicidal value. The following comparison is made of the chemical and physical properties of copper sulfate and copper resinate:

"Copper sulfate has the formula: $CuSO_4 \cdot 6H_2O$; it contains 25 4 per cent metallic copper and 36 per cent moisture. Copper resinate has the formula: $Cu(C_2H_{29}O_2)_2$. It contains 9.5 per cent metallic copper and no moisture. The lower content of metallic copper in the resinate salt is an advantage from the standpoint of metallic residues on both fruit and vegetables, which overcomes the criticism sometimes made in the past of too free use of Bordeaux. Copper resinate is very light and fluffy and somewhat sticky in nature from the high content of resin present. The physical nature of the salt makes it difficult to mix with oil, so it is handled as a paste containing 70 per cent copper resinate and 30 per cent pine tar oil. This is comparable to lead ground in oil and obviates the mechanical difficulty of mixing and also the danger to the operator of working with a light copper dust that might be inhaled in excessive quantities."[42]

The organic forms of copper salts, when used in oil emulsions, are decidedly superior both in penetration and wetting ability to inorganic forms, such as copper sulfate, whether in Bordeaux or Burgundy mixtures. The organic copper salts usually form a true solution, especially in pine tar oils, and hence are carried directly into the leaf and stem tissues wherever the oil penetrates.

Copper oleate and resinate are recommended[43] for protecting fish nets against the destroying effect of bacteria which harbor in the slime gathered while the nets are in the water.

Vegetables grown in paper containers that had been treated with copper resinate showed a stronger growth than those grown in untreated paper pots. The increased growth was apparently due to the suppression in activity of harmful microörganisms. No evidence of injury to the vegetables from any amount of copper resinate used was noted.[44]

Copper resinate may be prepared by dissolving 5 parts of rosin soap or "size" (30 per cent free rosin and 40 per cent of water) in 100 parts of water. Add the solution of rosin size to one part of copper sulfate dissolved in 25 parts of water. The copper resinate precipitates on top of the solution as a light green mass, which is dried and powdered.

**Comparative Toxicity of Copper Fungicides.** Studies made of the comparative toxic action of copper compounds have shown the following values for copper sulfate, neutral copper acetate, Burgundy mixture, cuprammonium sulfate and Johnson's mixture (copper sulfate and undecomposed ammonium carbonate used in the ratio of 1:2) (Table 15).[35] The value of sugar in these mixtures was also studied in the formula of 4 pounds of sugar in 50 gallons of 4–2–50 Bordeaux mixture. The latter mixture was found more effective against the conidia form of spores of the fungus *Ventura inaequalis* (apple scab).

Spore germination and the toxicity of certain dilutions of fungicides were both affected by temperature. When the temperature was near the minimum or maximum at which germination of spores occurred, some dilutions of fungicides were toxic that were tolerated at the more favorable temperatures. The conclusion is reached that "it is probable that no disease of plants dependent upon urediniospores for its dissemination can be successfully combated by the use of copper fungicides, since sufficient copper to check the fungus would also injure the host plant."[35]

The toxicity of Bordeaux mixture, 1:0.5:50, to the conidia form of the spores of apple scab ( *V. inaequalis*) is increased four times by the addition of sugar. The fungus *Botrytis cinerea* was found to be more susceptible to copper than the fungi *Gronastium ribicola*, as little as 0.0079 per cent of copper preventing the germination of *B. cinerea.*

Table 15. Susceptibility of *Aeciospores* and *Urediniospore* to Copper

| | | Lethal concentration | |
|---|---|---|---|
| Fungus | Fungicide | *Aeciospores* % copper | *Urediniospores* % copper |
| *G. clavipes* | Copper sulfate | 0.0317 | — |
| *G. interstitialis* | Copper sulfate | 0.0635 | — |
| *U. caryophyllinus* | Copper sulfate | — | 0.2540 |
| *C. ribicola* | Copper sulfate | 0.1270 | 0.2540 |
| *U. caryophyllinus* | Copper carbonate | — | 1.1480 |
| *P. antirrhini* | Copper acetate | — | 0.1592 |
| *U. caryophyllinus* | Copper acetate | — | 0.1592 |
| *G. interstitialis* | Burgundy mixture | 0.0570 | — |
| *C. ribicola* | Burgundy mixture | 0.1140 | 0.4580 |
| *P. antirrhini* | Burgundy mixture | — | 0.4580 |
| *P. antirrhini* | Johnson's mixture | — | 0.2540 |
| *C. ribicola* | Johnson's mixture | 0.0635 | 0.1270 |
| *U. caryophyllinus* | Johnson's mixture | — | 0.2540 |
| *C. ribicola* | Cuprammonium sulfate | 0.1270 | — |
| *U. caryophyllinus* | Cuprammonium sulfate | — | 0.5000 |

"The results of laboratory toxicity determinations both before and after exposure to laboratory 'rain' with the spores of *Sclerotinia fructicola*, *Botrytis paeoniae*, *Glomerella cingulata*, *Alternaria solani*, *Uromyces caryophyllinus*, and *Gymmoconia peckiana* demonstrate the marked superiority of Bordeaux mixture to all other compounds. Copper phosphate and basic copper sulfate are very inferior in toxicity. An intermediate class contains copper oxychloride, copper oxalate, and copper zeolite." "Adherence tests based on chemical analyses and toxicity before and after laboratory 'rain' show Bordeaux mixture . . . and copper oxychloride to be the most adherent and copper oxalate and basic copper sulfate the least."[38]

Certain water-soluble salts, including calcium chloride, magnesium sulfate and potassium chloride, are found to counteract or antidote the inhibitory effect of copper sulfate on the germination of the conidia form of spores of the fungus *Sclerotinia fructicola*[40]; hence water of a high degree of purity should be used in making laboratory tests of comparative toxicity.

"Limited phytocidal tests in the greenhouse on lettuce, buckwheat, corn, and bush bean, and out-of-doors on peach and apple indicate that in general those compounds most toxic to fungus spores are also most toxic to the leaves of green plants. The difference in phytocidal properties is not, however, as great as that of fungicidal properties and all compounds out-of-doors injure to some extent. Compounds equal to or exceeding Bordeaux mixture in the degree of injury are . . . copper oxychloride and basic copper sulfate, while compounds producing less injury than Bordeaux are copper zeolite, . . . copper phosphate, and copper oxalate. No copper compound appears to have been developed which combines high fungicidal value with low phytocidal properties. Bordeaux mixture has at least as great a range in this respect as any other compound. In special cases such as lime-sensitive plants, certain of these compounds may be more desirable than Bordeaux. These results indicate that fifty years of experimentation with copper compounds have given us none equal to Bordeaux mixture."[36]

**Copper as a Soil Treatment.** A copper deficiency of tung trees, indicated by a chlorotic condition accompanied by tips and marginal burning of the leaves, was corrected both by spray applications of copper sulfate solutions and by soil applications of the same material.[37]

A diseased condition of citrus foliage known as exanthema, in which a chlorotic or pale mottled appearance occurs, has been found to be associated with copper deficiency; the disease, when pronounced, results in defoliation and gumming of twigs and branches. Analysis of fruit samples from normal trees showed a copper content of 2.8 to 4.9 parts per million of copper on the dry basis. Fruit from trees affected with exenthema had a copper content of dry matter of 1.6 to 3.7 ppm. Applications as high as 5 pounds of copper sulfate per tree square may be used on certain types of soil, although this amount may cause injury in other soils. Larger dosages are used on sandy soil, but vary both with the soil and climatic conditions.[38]

Experiments in Florida[45] in the treatment of peat soils with copper have shown a satisfactory response from many crops, including corn, red top grasses, cabbage, and turnips, but only a slight effect on potatoes. Leguminous plants responded slowly, but stimulation was maintained throughout the year. Besides the response through the current year there was also a residual effect the year following, especially on grasses.

Dosages recommended for peat soil are 30 to 50 pounds of copper sulfate per acre. It is applied in a finely divided condition, either alone or mixed with a small amount of dry peat.

A study has been made by Cook[43] of the absorption of copper by potato plants where the copper spray or solution is applied to the soil in which the plants are growing. The copper was applied in the form of Bordeaux mixture, Pickering's limewater Bordeaux, and in a solution of copper sulfate of equal content. The copper of the two Bordeauxs was in an insoluble form and that of the copper sulfate solution in soluble form. One pint of the spray or solution was applied directly to the soil within 6 inches of the plant, five applications being made in all.

"The leaves, stems, and roots of the plants from the soil receiving the Pickering spray showed an increased copper content with each successive analysis. The largest percentage of the copper was held by the leaves. The roots held in appreciable part of the copper, the amount increasing from 0 in the first sample to 0.0160 per cent in the sample taken on September 3. The tubers contained only minute amounts of copper.

"The plants from the Bordeaux-treated soil showed irregularities, particularly with respect to the copper content of the roots and stems. The leaves and stems contained more copper than those of the plants from the Pickering treated soil, while the roots contained less copper than the roots of the plants from the Pickering treated soil. The amounts of copper found in the tubers were small.

"The vines grown in the soil treated with a solution of copper sulfate showed a marked progressive increase in copper content of the roots with each succeeding analysis. The leaves contained somewhat larger amounts of copper than the stems, but not as much as the roots. The leaves contained less copper than the leaves of the plants grown on the Bordeaux or Pickering treated soils. The tubers from the plot treated with copper sulfate solution were as low in copper as those from the other plots. The analyses of the various portions of the control plants showed the presence of copper, but in smaller amounts than in the plants grown on soil treated with the copper sprays." The experiments show that "copper in an insoluble form may be present in the soil in marked amounts without exerting any apparent toxic action on the growth of potato plants. But little copper was found in the soil as a result of spraying with copper sprays according to commercial practice."[16]

Copper-carrying pyrites [chalcopyrite ($CuFeS_2$) and chalcocite ($Cu_2S$) carrying 1.26 to 1.62 per cent copper] used at dosages of 2.5 to 7 tons per acre, for their sulfur content in treating alkaline soils, caused no injury on calcareous soils. Acid soils were more subject to injury under this type of treatment.[17] Forbes[18] found that copper added to the soil in the form of chalcocite, to the amount of 0.08 per cent, caused no injury to corn, but that only 0.023 per cent of the more soluble copper carbonate was tolerated, which is a much higher dosage of chalcocite than used in the above treatments.

**Effect of Copper on Plants.** The action[9] of copper on foliage varies with the availability or solubility of the copper. Copper sulfate solution itself is too dangerous to use alone on plants, and for this reason it is combined with an alkali such as lime or soda (Burgundy mixture) to form comparatively insoluble copper compounds. Copper in the form of Pickering sprays (using lime water instead of the lime itself in combining copper sulfate) causes severe burning of grape leaves and was found too dangerous to use on apples. "Barium-water sprays of the Pickering type, made with barium hydrate instead of lime and containing 0.7 per cent of copper sulfate, proved very successful as a fungicide for potatoes. Such a spray containing 0.6 per cent of copper sulfate did not injure the foliage or fruit of the apple tree"[9] in the experiments reported.

Apple foliage showed no absorption of copper through the normal cuticle of a healthy leaf. Autumnal changes in the foliage, however, led to a partial change in the nature of the leaf surface, followed by a varying amount of action of Bordeaux mixture, resulting in injury and absorption of copper. Potato foliage showed a different reaction to Bordeaux mixture. The cuticle appears to be more permeable than that of normal apple leaves. Part or all of the cells are capable of exerting a slight solvent action upon the copper compounds, resulting in a limited absorption, but not sufficient to cause injury. Copper absorbed in this way appears to be rapidly translocated and dispersed without harm to the living cells through which it passes.[49] It has been found also that copper may be absorbed through the roots of potatoes and translocated to the aerial parts without injury to cells during transmission. Some local injury to the roots had in this instance been noted. Similar results have been found with the broad bean where copper, absorbed by the roots, was translocated to the leaves without apparently injuring the plant.

The results of copper absorption by plants from Bordeaux mixtures may be summarized as follows: Cells with readily permeable walls (such as germ tubes of fungus spore, root hairs, the interior tissues of leaves, etc.) exert a considerable solvent action on the particles of the copper compounds with which they may come into contact. There is rapid absorption of the dissolved copper followed by death of the cells. In the case of injured foliage such action results in scorching.[22, 49]

The amount of interaction, if any, between other types of cells and the copper compounds is determined by the nature of the cell wall. Direct absorption of copper by leaves of certain types takes place with or without local injury, depending on the nature of the leaf surface. Translocation of the absorbed copper to other parts of the plant may follow.[49]

**Effect of Copper on Animals.** Continued ingestion of small amounts of copper, usually copper sulfate, $CuSO_4 \cdot 5H_2O$, has caused copper poisoning of sheep and other domestic animals. Frequent illustrations of this form of injury have been noticed in Texas[50], where medicated copper mixtures are fed continuously throughout the year to sheep for the removal of intestinal worms. These salt mixtures are made with 5 to 15 per cent of copper sulfate, tobacco dust and sodium chloride making up the remainder of the mixture. An enlarged liver, containing excessive amounts of copper, together with extreme red cell destruction is usually noted as a result of the treatment. Similar symptoms of copper poisoning were noted in sheep which had grazed for several months in an orchard sprayed with Bordeaux mixture.

Feeding experiments with domestic mallard ducks showed that they could tolerate a daily intake of copper carbonate of 0.029 gram per kilogram of live body weight. No symptoms of copper poisoning in the mallard duck were noted after eating food containing 1 to 4000 parts of copper sulfate. Seed wheat treated with dry copper carbonate at the rate of 2 ounces per bushel was definitely unpalatable to fowls.[57]

**Supplements for Copper Fungicides.** In the attempt to improve Bordeaux mixtures, Burgundy spray, acetates, and other copper-carrying sprays, a number of organic substances have been used in combination. Such additional materials may either increase the soluble copper present in the spray or improve the physical qualities by better suspension, lowered surface tension with increased spreading, reducing crystallization and increased visibility of the deposit.[54] Three groups of materials are used for the various purposes:

"(a) Sugars: sucrose, dextrose, lactose, dextrin, and glycerol. These materials produce soluble copper, but used in excess may precipitate cuprous oxide, which is not an active fungicide. Amounts recommended are 5 per cent as much sugar or 10 per cent as much molasses as of copper sulfate, which with 2–2–50 and 4–4–50 Bordeaux yields 0.01 per cent and 0.02 per cent soluble copper.

(b) Certain organic acids, including citric, glyceric, lactic, salicylic, and tannic acids, in the presence of alkalies, form soluble cupric compounds with basic salts. The use of these compounds is less liable to result in the formation of cuprous oxide.

(c) Albuminous substances, including casein, glue, gelatin, and albumen may also produce soluble copper in the presence of alkalies. These substances are more often used to increase wetting, spreading, and adhesiveness, and to improve compatibility with other spray materials. These organic copper compounds are considered less dangerous to foliage than soluble inorganic compounds. Wheat flour, glue, soap, and tannic acid are promising in that they seem to increase the efficiency of the spray in more than one aspect.[54]

**Bordeaux Mixture as an Emulsifier and Stabilizer.** The first petroleum-oil emulsions used as orchard sprays were emulsified with sodium and potassium base soaps. The use of hard water (containing appreciable amounts of lime or magnesium) for diluting such emulsions resulted in a reaction between the sodium or potassium base and the calcium or magnesium soaps. The results of the change from a soluble sodium to an insoluble calcium soap may cause the emulsion to break, giving free oil, which in many instances causes severe injury to the trees where applied. To stabilize the oil-water emulsion and avoid such type of injury, and also to give fungicidal value, a weak Bordeaux mixture (copper sulfate ½ pound, lime ½ pound to 50 gallons of water) is added. The film structure of the Bordeaux mixture, being of a colloidal nature, thus contributed with the soap solution to the formation of the emulsion.[51]

The copper and lime of the Bordeaux mixture may react to a certain extent with the soap emulsifier, but when aided by good agitation in the spray tank, no appreciable separation of oil occurs. However, a certain amount of oil is adsorbed by the lime[52] in the Bordeaux mixture, which in weak emulsions may appreciably retard the kill. To compensate for such loss of oil, a small additional amount of oil emulsion should be used. For example, where emulsions containing 2 per cent of oil have been in successful use, the amount of oil should be raised to 2½ or even 3 per cent when Bordeaux mixture is added. For more concentrated emulsions (containing 4 to 6 per cent oil) the increase in oil, following the addition of the Bordeaux mixture, should not be as great in proportion as in the weeker concentration.

**Copper as a Control for Fruit Rots.** The rotting of pears and apples in storage is due in part to the gray mold caused by the fungus *Botrytis*. The injury caused by this fungus is especially noticeable in boxed pears, the growing strands (mycelium) of the fungus passing through the paper from fruit to fruit. Control of this rot is possible by the use of copper-impregnated wrapping paper.[53] If desired, oiled paper wrappers may also be used for the copper treatment. A 2.5 per cent solution of copper sulfate is used for impregnating paper, the dry wrapper carrying about 1.4 per cent of its dry weight in metallic copper as copper sulfate.

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# Chapter 4

# Sulfur and Its Compounds

Sulfur production in the United States is principally in the elemental form, although increasing amounts of pyrite ore are being mined. Substantial increases in production of both elemental sulfur (crude sulfur) and pyrites are shown in Table 16, for the year 1941, over that of the average production for the 1925–29 period.[1] Sulfur, under normal shipping conditions, is imported in larger amounts as pyrites than as sulfur rock containing 40 to 80 per cent of elemental sulfur. Of the domestic sulfur output for the United States, approximately 83 per cent was produced in Texas, 17 per cent in Louisiana, and 1 per cent in California.

Besides elemental sulfur and that derived from pyrites, large amounts of sulfur in the form of sulfur dioxide gas are derived from smelting copper and zinc concentrates. This is commonly converted into sulfuric acid. There is also sulfur recovery from natural and manufactured gas, oil refineries and coke-oven gas. Elemental sulfur is recovered from manufactured gas (fuel and illuminating gas) by different processes owing to the type of catalyst used. The "Thylox" process uses arsenic as the catalyst, whereas nickel salts are used in a similar process. These methods are commonly used to produce "flotation sulfur" for horticultural purposes. This form of sulfur is marketed both as a paste and as a dehydrated, ground powder.

The consumption of sulfur for agricultural purposes, especially insecticides and fungicides, is shown in Table 17 to be from 20 to 25 per cent of the total consumption in the United States.[1] This varies with the locality; on the Atlantic Coast agricultural sulfur is but a small fraction of the total amount refined, while on the Pacific Coast the reverse is true.

The early insecticidal uses of sulfur are largely that of the element itself, in varying degrees of purity, as a control for certain mites and fungi. This use was based on the subliming or vaporizing properties of sulfur beginning near 20°C (68°F) and increasing rapidly at higher temperatures.[2] The first uses of combined sulfur were that of sulfur dioxide and the sulfides of alkaline earths including calcium, sodium and barium.

Fumigation with sulfur is accomplished by painting sulfur paste on the hot water pipes of greenhouses; by blowing air over sulfur heated from 170 to 230°C (338 to 446°F); by burning sulfur in a closed space and by the use of special types of burners. A combination of sulfur and naphthalene melted together and then powdered has also been used in fumigation practice. The use of sulfur compounds as fumigants, including sulfur dioxide, carbon disulfide and certain organics, is discussed in Chapter 7.

The use of sulfur as an insecticide and fungicide, in agricultural practice, requires uniform distribution through the foliage and sufficient adhesive properties to prevent weathering off or mechanical shattering. Such distribution may be attained by applying the sulfur as a spray, especially with an adhesive substance, or as a dusting sulfur with particles sufficiently fine to aid adhesion. Ground sulfur is not wetted with water; hence the two substances do not mix readily, but by the use of colloidal solutions of soap, glue, sulfite liquor, or casein they may be combined as a paste or "wettable" sulfur.[3]

Table 16. Salient Statistics of the Sulfur Industry in the United States, 1925–29 (Average) and 1938–41

| | 1925–29 (Average) | 1938 | 1939 | 1940 | 1941 |
|---|---|---|---|---|---|
| Sulfur production (long tons) | 1,951,034 | 2,393,408 | 2,090,979 | 2,732,088 | 3,139,253 |
| Shipments of crude sulfur: | | | | | |
| Domestic consumption (do) | 1,397,411 | 1,049,740 | 1,605,998 | 1,812,274 | [1] |
| For export | 707,175 | 579,107 | 627,819 | 746,468 | 474,551 |
| Total shipments | 2,104,586 | 1,628,847 | 2,233,817 | 2,558,817 | 3,401,410 |
| Imports: | | | | | |
| Ore (do) | 1,896 | 51 | 35 | [3] | — |
| Other (do) | 295 | 2,552 | 13,941 | 27,845 | 20,954[2] |
| Exports of treated sulfur (do) | 11,956 | 12,707 | 25,005 | 19,745 | 24,683[2] |
| Pyrites: | | | | | |
| Production (long tons) | 273,936 | 555,629 | [4]519,497 | 626,640 | 659,498 |
| Imports | 372,958 | 334,234 | 482,336 | 407,004 | 224,264[2] |

[1] Bureau of Mines not at liberty to publish figures.

[2] Figures cover January to September, inclusive.

[3] Less than 1 ton.

[4] Revised figures.

Sulfur in the elemental form acts as a toxic material through the vaporized or sublimed sulfur given off by the individual particle. The vaporized sulfur, coming in contact with a spore or other fungus tissue, prevents or inhibits growth. Such action, if over a very short distance, ranging from a small fraction to one or two millimeters, necessitates a very uniform distribution. By thorough distribution and adhesion it becomes possible to attain a fumigating action of the sulfur vapor. A similar effect occurs in the use of elemental sulfur in the control of mites and certain of the sucking insects, including the larval stage of certain thrips and scale insects.

Table 17. Sulfur Consumed in the United States, 1937–41, by Uses, in Long Tons

| Use | 1937 | 1938 | 1939 | 1940 | 1941 |
|---|---|---|---|---|---|
| Chemicals | 777,000 | 484,000 | 695,000 | 800,000 | 1,060,000 |
| Fertilizer and insecticides | 415,000 | 220,000 | 370,000 | 410,000 | 450,000 |
| Pulp and paper | 302,000 | 174,000 | 240,000 | 320,000 | 360,000 |
| Explosives | 68,000 | 50,000 | 64,000 | 74,000 | 83,000 |
| Dyes and coal-tar products | 49,000 | 40,000 | 46,000 | 51,000 | 65,000 |
| Rubber | 37,000 | 29,000 | 43,000 | 47,000 | 55,000 |
| Paint and varnish | 64,000 | 50,000 | 49,000 | 54,000 | 65,000 |
| Food products | 6,000 | 5,500 | 6,000 | 6,000 | 6,000 |
| Miscellaneous | 82,000 | 47,500 | 82,000 | 86,000 | 95,000 |

## Particle Size of Sulfur

The earliest form of finely divided sulfur for agricultural purposes was produced in the purification of manufactured, illuminating gas, the so-called "flotation sulfur". The first commercial use of this product was made in 1926–27[8a, 8b] from sulfur recovered in the plants of the Pacific Gas and Electric Company. Commercial precipitated sulfurs were available prior to this date, but were too expensive for agricultural usage. Mechanical comminution of sulfur by the use of hammer mills and the Raymond mill was developing rapidly at this time. Streeter and Rankin[3a] in 1927 drew the conclusions from their studies that particles larger than those which would not pass a 325-mesh screen (44 microns) were valueless for control purposes because of their lack of adhesion and tendency to weather off from foliage.[5a] Finer division of the sulfur particle was required in order to give a greater coverage per unit of sulfur and a corresponding increase of particle surface, by which a larger amount of sulfur vapor would be released. Smaller particles lodge more securely on pubescent surfaces, thus increasing adhesion and reducing the loss from weathering. To indicate the continued trend toward finer particles, Groves in 1942 stated[12a] that "sulfur particles larger than 27 microns probably do not adhere to foliage sufficiently well to be considered of value." Commercial development of finely divided sulfurs was rapid during this period, as Gooden shows in a survey of "Commercial Insecticidal Sulfurs"; the samples examined are grouped as shown in Figure 4[13] with a range of 5 to 25 microns. A later paper (1943)[13b] shows particle sizes as small as 2 microns in the commercial samples examined. The size of the particle is correlated directly with the toxicity as a fungicide, as shown in Table 18.[13b]

The subdivision of sulfur particles has apparently reached the limit of practical value. Colloidal sulfur[11, 12] as marketed has been found unstable, and the deposit of residual sulfur after weathering is too small to give effective control. Flotation sulfur, as produced in the utilization of commercial supplies of hydrogen sulfide and sulfur dioxide, is marketed in sizes ranging from a fraction of a micron to 10 or 15 microns. Sulfur milling by the micronizer process and in the Raymond mill may produce particles too fine to measure in standard screens. Such finely divided sulfurs, in paste form, may be applied satisfactorily by spraying; but in

Table 18. The Size of Sulfur Particles in Relation to Control of Apple Scab

| Series, year, variety and treatment | Average particle size of sulfur (microns) | Total fruit | Percentage of scabbed fruits | | | |
|---|---|---|---|---|---|---|
| | | | Slight | Medium | Bad | Total |
| *Series 1b*—1937* | | | | | | |
| Delicious | | | | | | |
| Special sulfur 4–100 | 3.7 | 1277 | 3.8 | 3.7 | 2.8 | 10.3 |
| | 6.6 | 486 | 8.2 | 7.8 | 4.3 | 20.3 |
| | 10.3 | 1461 | 18.0 | 17.7 | 14.6 | 50.3 |
| Cortland | | | | | | |
| Special sulfur 4–100 | 3.7 | 3510 | 10.3 | 5.1 | 3.9 | 19.3 |
| | 6.6 | 3453 | 12.5 | 11.6 | 6.4 | 30.5 |
| | 10.3 | 2014 | 14.4 | 20.1 | 29.8 | 64.3 |
| McIntosh | | | | | | |
| Special sulfur 4–100 | 3.7 | 523 | 6.1 | 1.9 | 2.3 | 10.3 |
| | 6.6 | 268 | 18.2 | 9.3 | 26.5 | 54.1 |
| | 10.3 | 365 | 29.6 | 16.8 | 19.5 | 65.9 |
| *Series 3—1938* | | | | | | |
| McIntosh | | | | | | |
| Non-treated | | 3031 | 5.7 | 10.5 | 83.6 | 99.8 |
| Special sulfur 3–100 | 3.7 | 2609 | 4.3 | 3.5 | 3.6 | 11.4 |
| | 6.6 | 4318 | 5.4 | 9.6 | 9.2 | 24.2 |
| Special sulfur 5–100 | 3.7 | 6818 | 1.7 | 1.0 | 1.2 | 3.9 |
| | 6.6 | 4222 | 2.2 | 2.2 | 1.3 | 5.7 |
| | 10.3 | 5786 | 5.6 | 4.4 | 2.8 | 12.8 |
| *Series 5—1939* | | | | | | |
| McIntosh | | | | | | |
| Non-treated | | 7045 | 12.3 | 13.7 | 66.0 | 92.0 |
| Special sulfur 4–100 | 3.7 | 2449 | 0.4 | 0.1 | 0.0 | 0.5 |
| | 6.6 | 9851 | 2.3 | 1.0 | 0.7 | 4.0 |
| | 10.3 | 8355 | 15.0 | 13.6 | 6.8 | 35.4 |
| Special sulfur 8–100 | 10.3 | 5415 | 11.8 | 6.5 | 3.7 | 22.0 |

*Non-treated trees in series 1 were heavily scabbed in June, and all fruits dropped at that time.

dusters, particularly of the power type and the airplane, they drift badly even in a light breeze and by carriage in convection currents from the heated surface of the earth.

The manufacturer of finely divided sulfurs has met and solved a number of problems in the course of development. Dust explosions and serious fires were a constant menace until met largely through the use of "flue gases" and carbon dioxide as inert media in which grinding could be carried on safely. Another difficulty has been the tendency for very finely ground sulfurs to agglomerate or pack loosely on standing. This has been overcome by the addition of small amounts of "conditioners" to the ground sulfur; these are inert powders such as magnesium carbonate, talc, tricalcium phosphate and lime. The incorporation of small proportions of conditioning agents tends to produce a free-running, dust-like powder that may be used either in hand or power dusters.

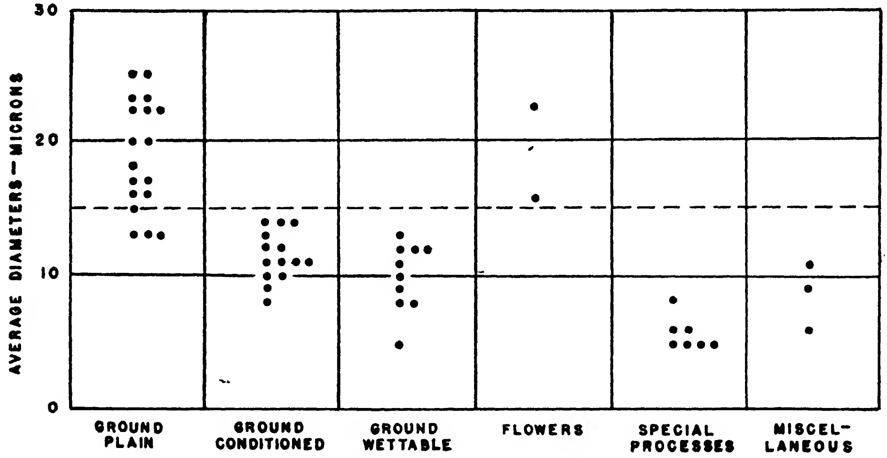

FIGURE 4. Distribution of average diameters among classes of insecticidal sulfurs.

Conditioning agents may also prevent the formation or dissipate the electric charge on the sulfur particles resulting from friction. The electrostatic charge may increase the adhesion of the sulfur particle, but since the charge varies with the mechanical features of the duster and is lost by the inclusion of certain insecticides, it is of secondary value.

Measurement of the sulfur particle may be made by (a) graduated standard sieves, supplemented by the microscope; (b) air-permeation apparatus; (c) sedimentation; (d) air separation. Sulfurs of moderate degree of fineness are graded on sieves ranging from 200 to 325 mesh* or even 400 mesh. Sulfurs of 325 mesh should show 90 to 95 per cent by

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* See page 308 for a discussion of sieve sizes.

weight, or even more passing this screen. Such tests do not, however, show the many very fine particles present in all ground sulfurs. Microscopic analysis, with proper interpretation, is valuable, but it is subject to error. A method of measuring particle size by air permeation has been devised by Gooden and Smith.[13a] Measurements are based on the resistance to the passage of air through a packed[13c] bed of solid particles. The grouping of commercial sulfurs, as shown in Figure 4, is based on this method of analysis. Air-separation analysis is based on the upward carriage of particles of varying size in a moving stream of air.

### Commercial Types of Sulfur

**Sublimed Sulfur** consists of irregular particles of pure sulfur resulting from the rapid cooling of sulfur fumes generated by heating crude sulfur. The particles are bulky, the range usually being from 10 to about 200 microns in diameter. The irregularity of the particle greatly increases the surface area compared with that of a corresponding ground crystal of sulfur. The size of the particle may of course be reduced by grinding. Sublimed sulfur is commonly used for burning in the bleaching of fruits, as the large, irregular particles permit the free movement of air through the mass, thus promoting oxidation.

**Ground Sulfur** is prepared from crude sulfur by grinding in a hammer mill or the Raymond mill. The particle size usually ranges from 5 to 25 microns. The choice of the fineness of grinding is influenced by the type of applicator and the purpose for which it is prepared. Ground sulfurs are commonly used in the pure form, except for small amounts of "conditioners" to improve the physical qualities. To avoid the danger of sulfur burn, which may occur on certain types of plants at maximum temperatures of 100°F and above, sulfurs are sometimes diluted with 10 to 50 per cent of inert material.[5, 6] It is possible that the so-called "filled" sulfurs will come into more general use, especially where high temperatures prevail, as a means of reducing plant hazard, facilitating distribution and increasing coverage. Blends of 325 mesh and flotation sulfurs are superior to the latter alone. The blended sulfurs distribute uniformly in various types of carriers, including the airplane, and are less subject to drift and dissipation in convection air currents. Blended sulfur gives a longer period of sublimation than does flotation sulfur used alone, at maximum field temperatures of 105° to 115°F. Ground sulfurs are readily converted into a wettable form suitable for spraying by the use of casein, sulfite liquor, and other wetting agents.

**Colloidal Sulfur.** This is considered the most toxic of any form of sulfur, but because of its instability, cost and marketing difficulties at satisfactory concentration, it has not come into general use. Preparations of colloidal sulfur have been found very active as fungicides when prepared in an acid condition (pH range 4.2 to 5.4). Sulfur precipitates rapidly from the solution at a pH value of 5.8 and above.[9, 12] The superiority of colloidal sulfur to other forms has been demonstrated in the control of the red spiders, *Bryobia praetiosa* and *Tetranychus telarius*.[11] Glue, gelatin and weak alkalies (sodium carbonate) have been found to be of distinct value as stabilizers of colloidal sulfur made with sodium thiosulfate (hypo) and concentrated sulfuric acid[12], and also that prepared from the combination of hydrogen sulfide and sulfur dioxide.

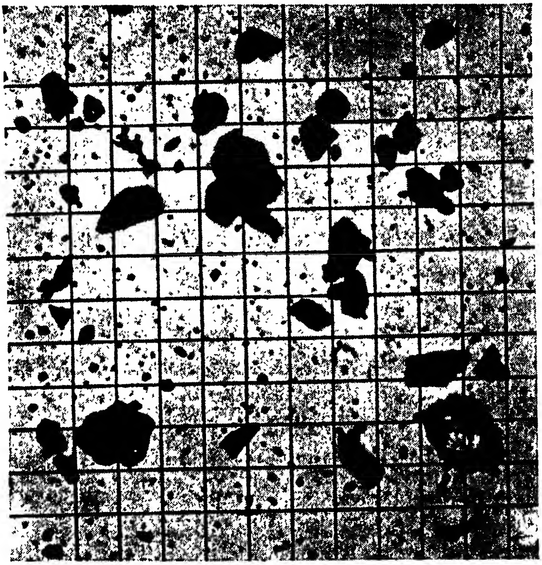

FIGURE 5. Blend of flotation and ground yellow sulfur, 325 mesh. The squares are 16.6 microns in size. (X 325)

**Micronized Sulfur** is a finely divided form produced by the Micronizer Reduction Mill. The process is a combination of the impact system combined with the air-separation principle. The particles are reported to be quite uniform in size, ranging from 3.5 to 5 microns.[13b]

**Flotation Sulfur** is a chemically produced sulfur for dusting and spraying purposes, which is characterized by extremely fine particles and a grayish color varying in intensity with the amount of carbon and other impurities present. It is usually produced by recovering the hydrogen sulfide present as an impurity in illuminating gas manufactured from coal or petroleum, which contains small percentages of sulfur. Flotation sulfur is also produced from the waste gases of oil refiners and may be prepared artificially. (See Figure 5.)

The recovery process was developed by Rosenstein in the gas plants of the Pacific Gas and Electric Company. The process consists of an alkaline wash for removing the hydrogen sulfide from the manufactured gas. The absorbed sulfur, in the presence of nickel sulfide or other suitable catalyst, is precipitated in the elemental form as a spongy mass floating in the water; hence the name "flotation" sulfur. The material was developed commercially[8a, 8b] in a partially dehydrated product which was ground with crude yellow sulfur. The advent of natural gas in the California fields stopped the manufacture of illuminating gas; the process was taken over by the Koppers Company of Pittsburgh, Pennsylvania, which has extended the use of the process, with arsenic as the catalyst, under the name of the "Thylox" process.[11a]

A second method of gas purification known as the "iron oxide" process is used by the Portland Gas and Coke Company, of Portland, Oregon. In this process the impure gas is passed through boxes containing a mixture of wood chips and iron oxide. Elemental sulfur is deposited on the chips, from which it is washed off and purified. The finished product contains about 80 per cent of free elemental sulfur, with small amounts of lime, wood fiber and other impurities. It is an extremely free-flowing, dusty product, free from aggregates and distributing readily from power machines and airplanes.[8c]

The value of flotation sulfur is not only that of very finely divided particles; the dull grayish-colored sulfur tends to absorb heat and consequently sublimes at lower field temperatures than does the glossy surface of ground crude sulfur.[2] The accelerated rate of sublimation increases the fungicidal value, particularly in the cool weather of early spring.

## Sulfur as an Insecticide

The use of free or uncombined sulfur either as a dust or spray is a common method of control of certain plant feeding mites[10] commonly known as "red spiders", as well as of the tomato mite[15a] and the citrus bud mite.[35] Such control measures are equally common both in the greenhouse, orchard and garden. Effectiveness of control varies with the type of sulfur used, manner of application, wind currents, temperatures and timeliness of control measures. Serious consideration has been given to the use of uncombined sulfur as a control for a number of sucking insects, including plant bugs, thrips and the larval stage of scale insects, leaf hopper and psyllids. Successful use of sulfur for such purposes has been associated with high field temperatures. Other sucking insects reported as being controlled by sulfur applications include the young stages of the black scale[15b] *Saissetia oleae*, potato leaf hopper[16c] *Empoasca fabae*, potato psyllid[16d] *Paratrioza cockerelli*, sheep tick[16e] *Melophagus ovinus*, chicken lice[16f], and the hop aphid[16g] *Phorodon humuli*. Control of the latter insect, from the action of sulfur dust alone, occurred at field temperatures of 77° to 101°F. The tarnished plant bug *Lygus elisus* has been found very susceptible to sulfur dust at maximum temperatures of 102 to 116°F.[14] Control of this insect in alfalfa was obtained by the use of six pounds of sulfur per acre. The practice of using finely divided dusting sulfurs as a control for Citrus thrips has also resulted in checking the gray citrus scale *Coccus citricola* while in the larval state on lemons and oranges.[4, 15] The close relationship between temperature and the toxicity of sulfur dusts to the larvae of the Citrus scale is shown in Table 19 [4], with corresponding effects of temperature on untreated larvae.

Dusting sulfur at the rate of 20 pounds per acre is the accepted method of control for the cotton fleahopper, *Psallus seriatus*, in Texas. The dropping of the small cotton squares, resulting from the insect's feeding, is checked within a few days after applying the sulfur, followed shortly by a normal bloom. The dustings are made at one week intervals[16] at daily maximum temperatures ranging from 98 to 104°F. The effect of the sulfur is principally noted on the immature stages of the insect, the nymphs beginning to drop to the ground in 30 to 60 minutes after application. The adult fleahoppers show little, if any, effect from the sulfur. This same difference between nymphs and adults in susceptibility to the effect of sulfur has been noted on bean thrips.

Table 19. Toxicity of Sulfur Dust to Larval Stage of the Citricola Scale (Three commercial dustings made over entire block. Dates: May 6, May 22, and June 11)

| Dates on which counts were made | Materials used | Maximum temperature ranges | Number of scales counted | | Total mortality per cent |
|---|---|---|---|---|---|
| | | | Alive | Dead | |
| 6/17/29 | Flotation & ground sulfur | 6/11–6/17 inclusive, 65–90°F | 128 | 735 | 85.1 |
| 6/17/29 | *Check* | | 1896 | 331 | 14.8 |
| 6/22/29 | Flotation & ground sulfur | 6/18–6/22 inclusive, 82–101°F | 28 | 513 | 94.8 |
| 6/22/29 | *Check* | | 499 | 961 | 65.8 |
| 6/25/29 | Flotation & ground sulfur | 6/23–6/25 inclusive, 102–107°F | 11 | 724 | 98.5 |
| 6/25/29 | *Check* | | 293 | 876 | 75 |

The length of time that a sulfur application remains effective and the spacing of dustings depends upon the amount of sulfur retained on foliage, particle fineness, and maximum temperatures. Susceptibility of the insect species concerned is probably also a factor in the duration of the period of toxicity. Sulfur has been found to kill bean thrips, *Heliothrips fasciatus*, larvae during a period of 10 days at maximum temperatures of 100 to 118°F, followed by a lessened rate for 7 to 10 days. The cotton fleahopper, *Psallus seriatus*,[16] showed an 80 per cent control with 7-day intervals between dustings. The larvae of citricola scale, *Coccus citricola*, showed[4] a mortality ranging from 92.6 per cent on the twenty-second day following dusting, to 96.8 per cent on the day of dusting, as shown in Table 20. Maximum temperature range during the 22 days was from 66 to 105°F.

Sulfur, as a stomach poison to a number of defoliating caterpillars, has been noted by MacLeod[19] in 1937 and later by Dickinson *et al.*,[50] experimenting with the southern army-worm, *Prodenia eridania*, and other *Noctuid* larvae. This group of caterpillars was more susceptible to sulfur than were the Mexican bean beetle, the Colorado potato beetle and the Catalpa sphinx larvae. Dosages of 1 to 1.5 milligrams of sulfur per larva resulted in mortalities ranging from 46 to 100 per cent. Commercial supplies of sulfur showed as high a mortality as specially prepared forms. Field experiments with dusting sulfur used at the rate of 75 pounds per acre gave promising results in the control of the alfalfa butterfly, *Colias eurytheme*.[51]

Table 20. Length of Period of Efficiency of Sulfur Dust on Citricola Larvae[4]

Scale placed on tree 7/1/29 Counted 7/4/29

Material used: Flotation and ground sulfur (25–75 per cent)

| Date of dusting | Time between dusting and placing of scale on leaves (days) | Number of scales counted | | Per cent mortality |
|---|---|---|---|---|
| | | Alive | Dead | |
| 7/ 1/29 | 0 | 18 | 536 | 96.8 |
| 6/29/29 | 2 | 14 | 467 | 97.1 |
| 6/27/29 | 4 | 21 | 510 | 96.0 |
| 6/25/29 | 6 | 11 | 374 | 97.1 |
| 6/23/29 | 8 | 15 | 550 | 97.3 |
| 6/21/29 | 10 | 32 | 516 | 94.1 |
| 6/19/29 | 12 | 4 | 229 | 98.2 |
| 6/17/29 | 14 | 25 | 542 | 95.6 |
| 6/15/29 | 16 | 18 | 463 | 96.2 |
| 6/13/29 | 18 | 11 | 303 | 96.5 |
| 6/11/29 | 20 | 24 | 513 | 96.5 |
| 6/ 9/29 | 22 | 36 | 448 | 92.6 |

**Sulfur Dusts Combined with Other Materials.** Sulfur dust is used as a diluent and carrier for the arsenicals, both calcium arsenate and lead aresenate in the control of cabbage worms, corn earworms, and other caterpillars. Sulfur and lead arsenate mixtures should be used soon after mixing to avoid the possibility of foliage injury. Sulfur-calcium arsenate mixtures, in 2-to-1 combinations, are used in the control of cotton boll weevil and the cotton fleahopper.[43] Mixtures of sulfur and tobacco dust[15] have also been reported as valuable in cotton fleahopper control. A dusting compound made of equal parts of sulfur and naphthalene, melted together, cooled and ground has been found effective against aphids and decidedly more toxic to red spider, *Tetranychus sp.*, than sulfur alone. Ground sulfur is frequently combined with ground derris, *Derris sp.*, and pyrethrum powders, the sulfur not only acting as a carrier or diluent but contributing directly to the value of the mixture in controlling the Mexican bean beetle and the potato leafhopper.[48] Blends of dusting sulfur and rotenone dusts are commonly used in controlling "cattle grub" or ox warble,[47] *Hypoderma lineatum*, as well as cattle lice. A standard control measure for cotton insects is a mixture of sulfur and Paris Green. This is used in the southwestern United States as a control for a group of sucking insects including the stinkbugs, *Chlorochroa ligata* and *Thyanata custator*, and the tarnished plant bug, *Lygus sp.*[47b] A similar formula is used in Peru as a control for the cotton leafworms, *Anonmis texana and Alabama argillacea.*[47a]

**Sulfur as a Fungicide**

The use of sulfur in the control of plant disease has been commonly recognized for many years, particularly in the treatment of mildews. Such use has included both sulfur in its uncombined form and sulfur compounds, especially those with alkalies, including lime-sulfur solution, ammonium, barium and potassium compounds. The action of elemental or uncombined sulfur as a fungicide is just as closely related to temperatures as is the insecticidal action, but in addition it varies in its effect both on different fungi and the various types of spores. The variation in susceptibility to sulfur of some common fungi is shown in Table 21.[17]

The comparative fungicidal value of sulfur is reported[39] by Barker *et al.*, to be in the following order: *Sclerotinia fructigena*, 100 per cent inhibition of spore growth; *Cladosporium fulvum*, 50 per cent inhibition; *Nectria ditissima*, *Botrytis cinerea*, and *Verticillium sp.* are totally unaffected. The author has found, however, that the more active form of sulfur is decidedly toxic to the spores of *B. cinerea*, but that this fungus is much more resistant to the action of sulfur than are the spores of *Monila*. His results are in accord with Barker[39] in that sulfur has a more toxic action when in contact with individual spores than when contacting dense clusters of spores.

The data in Table 21[17] give the maximum temperature range and time of exposure at which the spores of certain fungi are killed by the action of sulfur. The effective time of three to five hours at a temperature range of 21 to 26.5°C (70 to 80°F) corresponds to the warmest part of the day. Comparing these with meteorological data of our fruit regions in the spring, when diseases are most prevalent, shows conclusively the limits at which common ground sulfur is an active fungicide. Sulfur may still be active as a fungicide at slightly lower temperatures than those noted, if accompanied by longer exposures, and the reverse, *i.e.*, shorter exposures and higher temperatures accomplish the same results.[20] Bourcart[5] has also noted the relation of temperature to time as limiting fungicidal activity, giving a range of one to three days at 30 to 40°C (86 to 104°F), four to five days at 25 to 30°C (77 to 86°F), and longer at 25°C (77°F).

Precipitated sulfurs as fungicides have shown the same increase in toxicity[17] over ground sulfurs as noted in insecticidal studies. Dark-colored precipitated sulfur has been found more active than yellow sulfur in the control of apple mildew in the cooler portions of the coastal district in California and in portions of Canada.[24a]

Table 21. Effect of Temperature and Time of Exposure on the Toxicity of Sulphur to Spores

| Temperature (°C) | Duration of Experiment (Hours) | Relative number of spores germinating | | |
|---|---|---|---|---|
| | | *Alternaria solani* | *Sclerotinia fructigena* | *Venturia inaequalis* |
| 10.0 | (Check) | 100 | 100 | 100 |
| 20.0 | 5.0 | | | 72 |
| 21.0 | 4.0 | | 76 | |
| 23.0 | 3.5 | 100 | | |
| 25.5 | 2.0 | | | 70 |
| 26.0 | 5.0 | | | 0 |
| 25.5 | 4.0 | | | 10 |
| 26.5 | 1.5 | | | 100 |
| 26.5 | 3.5 | | | 36 |
| 26.5 | 5.0 | | 0 | 0 |
| 30.0 | 6.0 | 100 | | |

The fungicidal value of sulfur alone has been most noteworthy in the powdery mildew type of infection—fungi which grow on the leaf surface rather than those which are buried within the leaf tissue except in the fruiting stage, for example, peach leaf curl. Powdery mildew, *Uncinula necator*, of the European type of grape is controlled almost entirely by dusting sulfurs.[18] Apple mildew and rose mildew are other examples of fungi susceptible to free sulfur. The powdery mildew of canteloupes, *Erysiphe cichoracearum*, and other cucurbits is quite susceptible to the action of sulfur; but because of the intolerance of the plant to the action of sulfur, especially on slightly injured leaves, such treatment is considered impractical.[21] Sulfur dusts have been reported successful in the control of apple scab when five applications were used beginning with the pre-pink stage.[20] Certain rusts including asparagus rust, *Puccinia asparagi*, are also readily controlled by sulfur dusting.[19]

**Sulfur Compounds.** The boiling of lime with sulfur to form soluble compounds has been generally used in orchard practice since 1880. Its use as a sheep dip for the control of the scab mite is even earlier. Today "lime-sulfur" solution is still a widely used spray material, but has been supplanted in part by sulfur dusts, petroleum-oil sprays, newer types of copper sprays, and certain of synthetic organic compounds.

Calcium hydroxide, $Ca(OH)_2$, is the common base of alkali used in making soluble sulfurs, but all alkalies cause similar reactions. Thus sodium, ammonium, potassium, magnesium and barium may all be substituted for calcium hydroxide (lime).[22] The usual proportions of lime and sulfur are 1 part of burned stone lime ($CaO$) to 2 or $2\frac{1}{2}$ parts of sulfur. The two chemicals are boiled in the proper amount of water for 30 to 45 minutes.[32] The compounds formed are first the calcium polysulfides ($CaS_5$), and lesser amounts of calcium thiosulfate ($CaS_2O_3$); on prolonged cooking calcium disulfides and even monosulfides result. Too great an excess of the base or alkali also tends to form disulfides.[22] Both these and the thiosulfates are less active insecticides and fungicides than are calcium pentasulfide ($CaS_5$). More recent studies of compounds resulting from the hydrolysis of sulfur classify the principal derivatives as follows: "(1) the sulfoxylate, sulfite and thiosulfate, (2) the sulfide, and (3) the polysulfides of the alkali or alkaline earth metal present."[24] The conclusions reached were that "derivatives of sulfoxylic and sulfurous acids are without marked fungicidal action."[24] This confirms earlier studies showing that both calcium sulfate and sulfite were non-toxic to the spores of *Venturia inaequalis.*[17]

The fungicidal action of hydrogen sulfide on spores has been frequently reported, but no effect was noted on the hop powdery mildew, *Sphaerotheca Humuli.* The fungicidal action of sodium sulfide was apparently that of the alkalinity of the solution. The polysulfides were considered to be active fungicidally as such with a protective action from the deposited sulfur.

Formulas used for making lime-sulfur solution vary owing to the concentration of the finished product desired.[25]

| | | |
|---|---|---|
| Formula 1. | Stone lime*. . . . | 80 pounds |
| | Sulfur (ground). . . . | 160 pounds |
| | Water to make the finished product 50 gallons. | |

This formula gives a finished product 32° to 34° Baumé. Careful cooking is required; otherwise a heavy sediment will result.

| | | |
|---|---|---|
| Formula 2. | Stone lime. . . . | 50 pounds |
| | Sulfur (ground). . . . | 100 pounds |
| | Water to make the finished product 65 gallons. | |

---

* Hydrated lime may be substituted for the stone lime by increasing the amount by $\frac{1}{3}$. Avoid air-slaked lime and that with a high magnesium content.

Formula 2 requires less care in cooking and gives a product of 23° to 24° Baumé.† The mixture is agitated while being boiled for 45 to 50 minutes, strained and settled. The density or gravity is measured with a Baumé spindle (heavier than water). Do not allow the lime-sulfur solution to stand exposed to the air.

Standardization of commercial lime-sulfur solutions has been established in California by requiring that such solutions "shall have a density of not less than 31° and not more than 33° Baumé† at 60°F and shall contain not less than 29 per cent of calcium polysulfides."[23]

The fungicidal action of the polysulfides of lime-sulfur solution and dry lime-sulfur is eradicative, whereas that of elemental sulfur is preventive. The solution penetrates the lesions of apple scab, killing the fungus wherever in contact and "prevents sporulation of the onion-and-hopmildew organisms,"[39a] where Bordeaux mixture and sulfur dust fail. The eradicative action of the polysulfides lasts but a short time after application as a spray; free sulfur is precipitated in a form which is more active and adhesive than ground sulfur dust. This has been noted not only in fungicidal applications but also when it acts as a control for the larval stage of plant mites, *Bryobia praetiosa.*[10]

Lime-sulfur solution for cattle and sheep dipping have been made by slightly different formulas from those used for horticultural sprays, namely, 8 pounds of quick lime or 10.5 pounds of hydrated lime and 18 pounds of sulfur, boiled to a finished volume of 10 gallons.[40] Animal dips require careful adjustment of the amount of sulfide sulfur and are made according to standard dilutions without the possibility of excess lime. "The finished solution, drawn off from the sediment, should theoretically contain 18 per cent of sulfide sulfur, but probably will contain somewhat less."[40] For dipping sheep it should be used at a dilution of 1 volume of concentrate to 9 or 10 volumes of water and for cattle 1 to 7 or 8 volumes of water. Dipping baths, to be effective, must be maintained at uniform strength;

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† The relation between the "Baumé Test" and the sulfur in solution in the commercial or home made concentrated lime-sulfur wash can be determined thus:[57]

| Density | Total sulfur (%) | Pounds of sulfur in 1 gallon of solution |
|---|---|---|
| 33 | 26.0 | 2.7 |
| 31 | 24.0 | 2.5 |
| 29 | 22.0 | 2.3 |
| 27 | 20.0 | 2.1 |
| 25 | 19.0 | 1.9 |
| 23 | 18.0 | 1.8 |
| 21 | 17.0 | 1.6 |
| 19 | 16.25 | 1.5 |
| 17 | 15.5 | 1.4 |

this is done by using field-testing outfits and adding additional concentrate as needed.[41]

**Dry Lime-Sulfur.** (Dehydrated lime-sulfur solution.) This form has been evolved by the industry to eliminate the necessity of packing and shipping large quantities of water present in lime-sulfur solution.[55, 56] "Stabilizing" substances such as cane sugar are usually added to the solution, which is then evaporated to dryness in the presence of an inert gas. Commercial dry lime-sulfur "contains a relatively large percentage of insoluble matter, consisting chiefly of free sulfur and smaller amounts of calcium sulfite and lime."[29] Such insoluble matter is objectionable, as it tends to wear or clog the spraying apparatus.[29]

Comparative amounts of poly and monosulfide sulfur, calcium thiosulfate, sulfur and calcium are shown for lime-sulfur solution and dry lime-sulfur in the following table.[29, 32]

| | Calcium polysulfides | Calcium monosulfides | Calcium thiosulfate | Total calcium | Free sulfur |
|---|---|---|---|---|---|
| Lime-sulfur solution | 30–32 | (a) | 1.5–2.5 | (b) | — |
| Dry lime-sulfur | 64.9 | (a) | 8.3 | (b) | 9.8 |

(a) Monosulfide sulfur combined with the polysulfide sulfur.

(b) Not determined.

The use of dry lime-sulfur has been particularly helpful as a fungicide. In the control of apple scab dry lime-sulfur, 6 pounds per 100 gallons of spray proved to be the best substitute for lime-sulfur solution, 1 gallon to 60 gallons of spray. "It is apparently moderately eradicative, being about midway between liquid lime-sulfur and the dry wettable sulfurs. . . . It caused somewhat less injury than lime-sulfur and left a very good finish of fruit."[30]

Satisfactory control of the rust mite, *Phyllocoptes oleivorus*, on citrus trees is reported with 5 pounds of dry lime-sulfur per 100 gallons of spray. Less leaf drop resulted from dry lime-sulfur applications than from the use of other sulfur sprays.[31]

**Ammonium Polysulfide** has had limited use in England as a control for American gooseberry mildew.[52] The compound was produced by passing hydrogen sulfide into saturated ammonium hydroxide (28 per cent) and dissolving an excess of sulfur in the sulfide solution. Experiments with ammonium sulfide in the control of plant mites in the greenhouse have shown it to be quite effective, but too hazardous to many types of plants.

Potassium-ammonium-selenosulfide has been found to be very effective in the control of plant mites (red spider) in greenhouse work, the best results being obtained with combinations of karaya gum as a spreader.[53] Satisfactory control of different species of plant mites has been reported in California both on grape and citrus.[54]

**Calcium Sulfide** (CaS) "is manufactured from anhydrous sulfate by reduction with charcoal and starch or with powdered coal alone in a reverberatory furnace at a temperature of approximately 1800°F (982°C). The material as used in spraying contains from 60 to 65 per cent calcium sulfide. It is used as a suspension in the spray tank at the rate of 16 pounds per 100 gallons of spray. Better control of apple scab has been obtained with calcium sulfide than with lime-sulfur solution used at the rate of 1 gallon to 40 gallons of spray. No chemical reaction occurs in combinations of lead arsenate and calcium sulfide as happens with lime-sulfur and lead arsenate."[33]

Field studies under Eastern United States conditions indicated "that calcium sulfide is a comparatively non-caustic spray material and that it can be used throughout the season on varieties susceptible to spray injury."[33]

**Lime-Sulfur Solution Combined with Other Spray Materials.*** Petroleum-oil combinations with any sulfur compound are attended with a certain amount of hazard. Some of the more stable oil emulsions, combined with low concentrations of lime-sulfur, are used freely on citrus trees with little danger unless the temperature rises to 95°F or above. Dormant sprays of lime-sulfur solution and petroleum oil are used very commonly on deciduous trees. Bordeaux mixture and lime-sulfur solution are seldom combined, because of chemical reactions which may result in the formation of dangerous amounts of copper sulfate.

The alkalinity of lime-sulfur solution is beneficial in combining with nicotine sulfate, but harmful to pyrethrin and rotenone combinations. It is not compatible with soap, cryolite, certain of the dinitro dusts, and tartar emetic. Sodium fluoaluminate and sodium fluosilicate should not be combined because of chemical reactions.

**Effect of Sulfur on Plants.** The use of lime-sulfur solution on foliage has long been associated with injury both to leaves and fruit, particularly if applied at high temperatures, 90 to 105°F (22 to 40°C). The association of lime-sulfur injury with high temperatures is naturally more frequent in the semi-arid regions of the Pacific Slope than under Atlantic Coast conditions. The direct correlation between safety of lime-sulfur to the host and normal temperatures has been based on the theory that, according to physical laws, an increase in toxicity of 1½ to 2 times must be expected for every increase of about 18°F. Hence at high temperatures, lime-sulfur may cause more injury to the foliage than has been caused by the fungus.[34] The author's experiments under the prevailing high temperatures of California confirm the above findings. Summer application of lime-sulfur

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* Lead arsenate combinations, see p. 24 (Chapter on Arsenic).

solution at 2 per cent concentrations had been repeatedly applied to almonds, a hardy foliage, at maximum temperatures of 85 to 90°F without any indication of injury; but with a sudden rise in temperature to 105°F, severe burn resulted. Similar application of lime-sulfur solution at 2 per cent concentration on French prune resulted in severe burn of both foliage and fruit where application was made on the sunny side of the tree, but there was no injury on the shady side with an air temperature of 103°F. Citrus trees in Southern California are subject to the same hazard of high temperatures following lime-sulfur sprays, it being generally recognized that a "hot spell" coming within four days after the application will result in injury. An outbreak of citrus bud mite, *Eriophyes sheldoni*, in Southern California where sulfur applications were desired has led to the same conclusion, namely, that "all sulfur-containing materials used are hazardous to the fruit and foliage (citrus) under conditions of high temperatures. Ammonium polysulfide is significantly safer under such conditions than lime-sulfur or wettable sulfur."[35]

Lime-sulfur solution injury to foliage is more pronounced when applied after a severe attack of apple scab than when used on normal foliage. The cuticle of the leaf, when unbroken, protects the inner leaf tissue from lime-sulfur injury. When the cuticle is injured by the scab fungus or the feeding of aphids, the lime-sulfur penetrates into the interior of the leaf and destroys a certain amount of leaf tissue and the mycelium of the fungus.[34] This caustic or burning effect of lime-sulfur lasts but a short time (about 1 hour), after which the sulfides break down and free sulfur is precipitated.

Other types of injury from lime-sulfur in addition to that from sulfide sulfur, as mentioned above, are a desiccating or drying action on the foliage, yellowing and stunting of growing leaves, lowering the set of fruit and a decrease in weight and size of sprayed plants and fruits.[30, 35, 37] The apricot is particularly susceptible to all forms of sulfur and should not be sprayed or dusted with sulfur or its compounds.

Sulfur dusts have been shown to prevent pollen (apple) germination and may reduce or prevent the setting of fruit. "In order to be injurious, however, the sulfur must be on the stigmas (outer tip of pistil) before fertilization has taken place, or at least before the pollen tube has entered the style a sufficient distance to be out of reach of the sulfur."[33] "Field experiments indicate . . . an allowance of one day (at most two) of favorable pollinating conditions was sufficient to obtain a good fruit set. . . . The practice of spraying during bloom for apple scab control appears feasible from a commercial point of view."[30]

**Sulfuric Acid as a Herbicide.** Diluted with water sulfuric acid is a cheap and quickly acting herbicide especially valuable for annuals. By repeated applications it will control Johnson grass and other weeds with extensive rootstocks. The acid quickly reacts with the soil chemicals and, except for very acid soils, will not be harmful; it has no sterilizing action when used at a recommended strength. Dosages recommended are 2 per cent for puncture vine, mustard, and careless weed; $3\frac{1}{2}$ per cent for lambs quarter and yellow sour clover; 5 per cent for sunflower, horse nettle, dodder, and sow thistle; 8 per cent for foxtail grass; and 10 to 15 per cent for Johnson and nut grass. Based on an average of 200 gallons of spray per acre the amounts used ranges from 4 to 20 or 30 gallons per acre.[23]

Metal parts of spray apparatus should be protected with heavy grease or oil during the application and carefully washed after use.

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# Chapter 5

# Miscellaneous Inorganic Compounds

A few well known chemicals, including copper, arsenic, sulfur, and certain organic compounds have been for many years the principal weapons of both entomologists and plant pathologists in combating insects and plant diseases. In addition, there is a constantly growing list of materials which may be grouped as the "minor" insecticides and fungicides. The fluorine compounds lead this list because of their popularity, principally as a substitute for arsenic. Selenium, a close relative of sulfur, has been found valuable, especially for the control of certain plant-feeding mites (red spider). Zinc, in the metallic, oxide, and sulfate form, has a dual role: as a fungicide, usually in combination with copper, and also for correcting certain physiological troubles, such as chlorosis of the Citrus. Mercury compounds, both organic and inorganic, are increasingly popular as fungicides for certain pathogens attacking lawn grasses and as seed disinfectants. The chlorates are one of a very small group which, like the carbon compounds, depend for their toxic action upon a definite group formation of otherwise harmless elements. Dust applications of inert materials, generally considered harmless in themselves, have been found useful in checking the attacks of insect feeders on grain and seeds. They include calcium carbonate, talc, and lime, all in a finely divided form.

## Fluorine Compounds

The fluorides are salts of hydrofluoric acids having a wide commercial use. They are generally fine, crystalline compounds which vary greatly in their solubility.

**Sodium Fluoride** is a clear, lustrous crystal or white powder, of specific gravity 2.76 and a melting point of 980°C (1814°F). It is readily soluble in cold water and slightly soluble in alcohol. It is too dangerous to use on foliage in treating plants, but its toxic value has led to its general use as a household insecticide, especially in the control of roaches and ants. For this purpose it is blended with pyrethrum powder, borax, aluminum oxide and sulfate[4a] and certain inert powders to form a dusting powder. Sodium fluoride is a dangerous poison to humans[1], and the resemblance of the finely ground powder to baking powder has led to serious accidents.

Fluorides and other white, powdered insecticides that might be confused with food materials are now being colored as a precautionary measure.

Sodium fluoride, for insecticidal purposes, is marketed in a highly purified form ranging, as shown in Fig. 7, from 93 to 99 per cent pure. The particle size of commercial products (1941–42) ranges from 5 to 10 microns with a very few showing coarser particles, as indicated in the figure. "The average particle diameter (surface mean diameter) for each sample was determined by the air-permeation method of Gooden and Smith[1a] with the modification described by Gooden[2a]" (see Fig. 6)[3a].

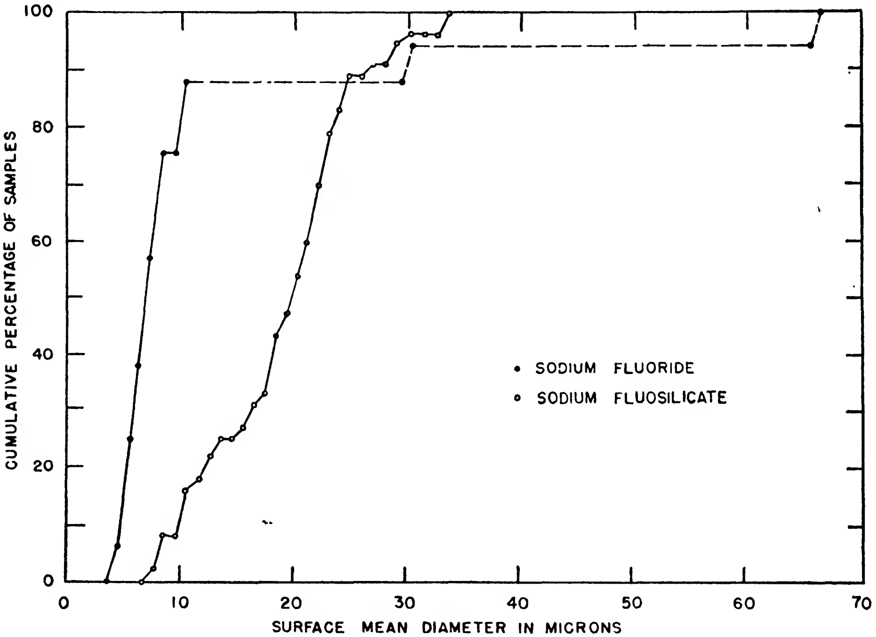

FIGURE 6. Average diameters of samples of sodium fluosilicate and sodium fluoride as determined by air-permeation method.

Sodium fluoride may act both as a stomach poison and by contact in the control of different species of roaches, *Blatta orientalis*, *Periplaneta americana*, and *Blattella germanica*. Hockenyos[4] has shown the possibility of absorption through the body integuments of the cockroach, and Griffiths and Tauber[5a] have given evidence of the toxic action of sodium fluoride both in the food and by contact while walking through the powder. The latter plan is usually followed, the blends being dusted over runways and as also suggested[6a] in marking infested areas with "crayons" made of wet sodium fluoride.

A combination consisting of sodium fluoride 1.5 per cent and nicotine sulfate 0.5 per cent "gave a quick knock-down and actual kill of the wood ticks, *Dermacentor variabilis* and *Ixodes scapulanis*." The spray is injurious to foliage and should not be used on valuable plants.[7a] The value of sodium fluoride as a control for body lice on poultry and cattle lice has been frequently demonstrated. A lethal bait for the silver fish, *Lepisma saccharina*, is made by combining 5 per cent of sodium fluoride with 95 per cent of wheat flour.[3]

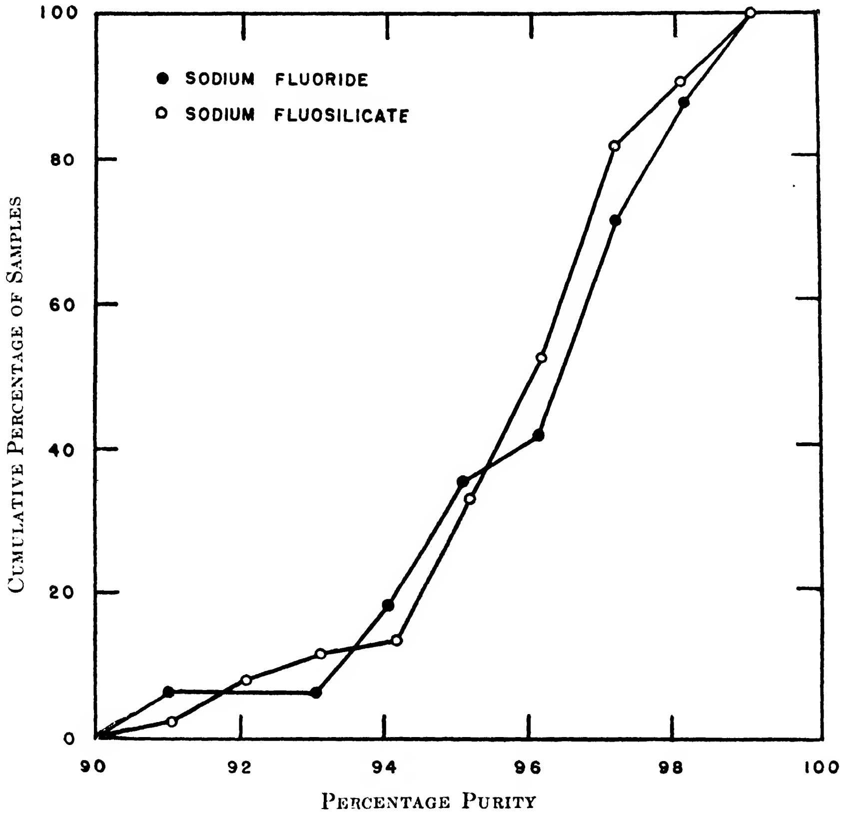

FIGURE 7. Distribution of samples of sodium fluoride and sodium fluosilicate according to their purity.

Sodium fluoride may be used as a selective herbicide in a dust form on tobacco and as a 2 per cent solution for crab grass and oxalis in lawns.[8a] Water-soluble fluorides including the sodium compound are of value as defoliants.[9a]

Equal parts of sodium fluoride and borax are used as a permanent protection to joints of wooden window sash and other joints exposed to weather. Two methods of application are used. A hole is bored in the tenon of the joint large enough to hold 3 grams of the chemical mixture. The parts of the sash are assembled and the chemical is leached out into the wood only by the entrance of water. Paint is then applied over the entire joint surface and sash. (2) Assembled sashes and other joints and the faces of construction timbers where joined may be treated with a saturated solution of the sodium fluoride-borax combination and the material applied with a brush, followed by the usual paint treatment. This treatment has been found to prevent both decay and stain.[5] A 3 per cent sodium fluoride solution is also recommended for treating framing timbers, subflooring, and basement floors.[5]

**Fluosilicates.** These compounds are salts of hydrofluosilicic acid. They are usually crystalline or amorphous powders somewhat more soluble than the corresponding fluoride and give an acid reaction in solution. "There are only three fluosilicates whose solubility is low enough to permit of their use as insecticides on field crops. They are the fluosilicates of barium, potassium and sodium."[6] Sodium ($Na_2SiF_6$) and barium fluosilicates ($BaSiF_6$) are the commonest forms of insecticides and are used principally as dusts. Potassium fluosilicate ($K_2SiF_6$) is less soluble than sodium fluosilicate and more expensive. "All fluosilicates in solution give an acid reaction and for this reason even the less soluble ones may cause foliage injury."[7]

Sodium fluosilicate should not be diluted with hydrated lime unless the latter is used in large proportions. Mixtures of 1 part of sodium fluosilicate with 9 parts of hydrated lime gave no foliage injury when applied on dry foliage. Hazard to the foliage apparently increased with the presence of dew. Moist bean foliage was severely burned when dusted with 1 part of sodium fluosilicate to 2 parts of lime. In the latter proportion soluble calcium fluosilicate and sodium fluoride are probably formed, and this may explain the cause of the foliage injury in the presence of moisture.[8]

"Other carriers, such as talc, sulfur, calcium carbonate, barium carbonate, and flour, were also tried out. In the presence of moisture, calcium carbonate and barium carbonate produced only slight injury on beans when used at the rate of 2 parts to 1 of sodium fluosilicate. The sulfur and talc mixtures produced very little or no injury, while flour seemed to be the next best. A dust composed of sulfur—about 3 parts by weight or 6 parts by volume—should be satisfactory from the standpoint of preventing foliage injury on beans. The sulfur has also the advantage of being repellent to the bean beetle, *Epilachna varivestis*, and may aid in the control of the bean leaf hopper, *Empoasca fabae.*"

Cotton is quite tolerant of sodium fluosilicate, and so to a less extent are apple, bean, and peach; but tomatoes and tobacco have been reported to be more or less readily injured.[8]

The fluosilicates, particularly the sodium compound, are very effective in controlling the striped cucumber beetle, *Diabrotica trivitta*, the flea beetle, *Phyllotreta sinuata*, blister beetles, *Epicauta* and *Macrobasis*, and tobacco hornworm, *Protoparce quinquemaculata*, using dusting powders with sulfur or hydrated lime as the carrier and diluent. This compound has also been found of value in controlling bacterial spot of peach, *Bacterium pruni*.[9] A $\frac{1}{2}$ per cent solution of sodium fluosilicate dissolved in water killed the larvae of the clothes moth, *Tinea pellionella*, in 6 hours when fed on raw wool dipped in the fluosilicate solution.

The red-legged grasshopper, *Melanoplus femurrubrum*, and certain species of cutworms have been controlled by baits using 1 part of sodium fluosilicate to 10 or 20 parts of bran.[9] The Mormon cricket, *Anabrus simplex*, was more effectively controlled with a bait of 3 pounds of sodium fluosilicate, 10 to 16 gallons of water and 100 pounds of bran, then with liquid sodium arsenate, the latter acting as a repellent.[10]

Grain infested by weevil and beetles may be controlled by dusting the sacked grain with one pound of sodium fluosilicate to ten tons of sacked grain. Fairly satisfactory control of mice and rats present in the grain also resulted from the dust application.[11] No effect on the germination of the grain was noted when the fluosilicate was dusted on the sacks at the dosage noted above, but mixing the compound directly with the grain resulted in a lowered germination rate. Grain for use as food is not permitted, under United States Federal laws, to show a residue greater than .049 grain per pound, and if so is subject to seizure. Sweepings from the floor of treated warehouses should not be fed to stock, as serious results have occurred from this practice.[12]

**Compatibility of Sodium Fluosilicate.** A difference of opinion exists as to the safety of combining lead arsenate with this compound of fluorine, so it should be considered as of doubtful value. Calcium arsenate is not considered compatible with sodium fluosilicate, and a combination with Bordeaux mixture would also be somewhat hazardous, particularly with excess lime. As sulfur is precipitated out of lime-sulfur solution in the presence of sodium fluosilicate, this combination should not be used, especially on apples.[9] Uncombined sulfur is compatible with sodium fluosilicate.

**Calcium fluosilicates** ($CaSiF_6$). The calcium compound hydrolyzes in water "with the liberation of much free acid and precipitation of calcium, fluoride and silica. . . . The large amount of acid liberated is indicated by the pH value, which may be as low as 1.5 or less. In the making of calcium fluosilicate, precaution must be taken to keep the compound from going over to calcium fluoride."[4]

**Barium fluosilicate** ($BaSiF_6$). The barium compound has a lower solubility than other fluosilicates and consequently is less injurious to foliage.[6] "A saturated solution shows a pH of 3.4. One gram of material will require 110 cc of 0.1 normal sodium hydroxide solution for neutralization."[13] It is available as a light, fluffy dust which is used both in spraying and diluted with sulfur, talc and diatomaceous earth. Hydrated lime is sometimes recommended as a diluent, but may react in the presence of moisture, reducing the efficiency of the fluorine and increasing the danger of foliage injury. Fish oil has been recommended to increase the adhesiveness of barium fluosilicate, using 1 pound of fish oil to 4 pounds of the fluosilicate in the spray.[13] A bait containing 4 per cent of barium fluosilicate was effective in controlling one of the silver fish known as the "firebrat", *Thermobia domestica.*[10a]

**Compatibility of Barium Fluosilicate.** Sulfur, talc and diatomaceous earth are recommended as diluents for this compound. Hydrated lime and gypsum, and Bordeaux mixture with excess lime and lime-sulfur solution should not be used as a diluent, nor in combination with barium fluosilicate. Nicotine sulfate or other sulfates should be avoided, but pyrethrins are considered safe to use with this compound.[20]

The action of barium fluosilicate in the soil has been studied with the following conclusions: "Since the fluorine content of added barium fluosilicate ($BaSiF_6$) is converted into calcium fluoride by the soil's supply of calcium, continued insecticidal and bactericidal effects of the fluorine addition would depend upon the effectiveness of calcium fluoride ($CaF_2$). Although of low solubility, considerable quantities of calcium fluoride appear in the leaching from the units that did not receive limestone. Since the magnesium content of dolomite increases the outgo of fluorine, the use of this supplement may increase for a time the biological efficiency of added fluorine materials, but the more rapid outgo would also shorten the period during which the fluorine addition would be effective. On the other hand, the depressive effect that added calcium exerts upon the solubility of calcium fluoride, formed within the soil, may conserve the added fluorine to the point where it is not biologically effective.

"The ultimate fate of the added fluorine—formation of calcium fluoride—would be the same for additions of sodium silicofluoride, cryolite, and and other fluorine compounds. It is therefore apparent that no deleterious effect is to be expected from the amounts of fluorine that are used as sprays and dusts, and that no cumulative effect could result from their continued use."[14]

These findings have been corroborated by Scott and Karr in soil studies in the orchard districts of the state of Washington, where cryolite is commonly used as a control for codling moth.[15a]

**Cryolite** ($Na_3AlF_6$). This compound is one of the fluoaluminates—another group of fluorine compounds that are promising as insecticides.

"If aluminum oxide or hydroxide is treated with hydrofluoric acid in excess, the aluminum fluoride first formed is soluble in the excess acid, so that in effect we have a solution of $H_3AlF_6$. . . . Salts of this acid may be formed in the same way as with any other acid, *viz.*, by treatment with a base or a solution of another more soluble salt. The natural mineral cryolite, or sodium fluoaluminate, is an example of this class of compounds. It occurs in nature as a well-defined form."[6] "Cryolite is found in commercial quantity and mined at only one place, Irigtut, Greenland."[11a]

"Cryolite or sodium fluoaluminate, besides occurring in nature, may be made by several wet processes, and synthetic cryolite of a high degree of purity is sold commercially. Synthetic cryolite is a white amorphous powder, but natural cryolite occurs in monoclinic crystals."[15]

Table 22. Titratable Acidities and pH Values of Several Samples of Foreign Synthetic Cryolite

| | Titration in | Per Cent | |
|---|---|---|---|
| I.D. No. | Titration in (cc. of 0.01*N* NaOH) | Per cent Acidity (Calc. as $H_2SO_4$) | pH |
| 4361-37 | 0.05 | 0.0 | 5.60 |
| 4361-38 | .05 | .0 | 6.10 |
| 4330-17 | .2 | .1 | 4.75 |
| 4330-16 | .3 | .1 | 4.40 |
| 4308 | .3 | .1 | 4.25 |
| 4389 | .5 | .2 | 4.10 |
| 4306-C | .7 | .3 | 4.25 |
| 4392-B | 2.3 | .9 | 3.85 |
| 4392-A | 2.8 | 1.1 | 3.70 |
| 4038 | 3.6 | 1.4 | 3.80 |
| 4094 | 4.9 | 1.9 | 3.85 |
| 4119 | 6.7 | 2.6 | 3.90 |
| 4298 | 4.7 | 1.8 | 3.80 |
| 4250 | 6.2 | 2.4 | 3.90 |
| 4310-A | 6.7 | 2.6 | 3.60 |

Decided variations in the recommended dosages of sodium fluoaluminate are indicated in both the domestic and imported materials. It is suggested "that, for insecticidal use on field crops, cryolite products should contain very little, if any, material that is more soluble than cryolite itself. . . . It appears that the solubility figure should not exceed approximately 0.028 gram of fluorine per 1300 cubic centimeters at 23 to 25°C, (73.40 to 77°F), equivalent to 0.053 gram of sodium fluoaluminate."[23]

A study of a number of synthetic cryolites from the standpoint of titratable acidity and the pH values showed that "all the domestic synthetic material were alkaline to methyl red without the addition of sodium hydroxides, and the pH values ranged from 7.45 to 8.10.

"The titratable acidity of 15 samples of the foreign synthetic material varied considerably, and the pH values were for the most part considerably lower than for the other classes, as shown by the data in Table 22.[24]

The titratable acidity and low pH values of some of these samples may be partially responsible for the burning that sometimes follows the application of cryolite insecticides. Two samples (I.D. 4392, A and B) were reported to have caused excessive burning when used on vegetation such as beans, corn, peas, cotton, and peanuts. However, other samples having a greater titratable acidity have not been reported as causing burning."[24]

**Cryolite (Sodium Fluoaluminate) as an Insecticide.** The use of fluorine compounds, including both cryolite and barium fluosilicate, as a control for codling moth on apples in the Pacific Northwest was begun by the United States Department of Agriculture in 1925. This study was begun principally in the effort to find a satisfactory substitute for arsenicals because of the danger of residual deposits from the use of arsenic and lead in the control of codling moth in apples and pears. After several years study it was reported that the fluorine compounds studied are apparently not so toxic as lead arsenate on the basis of equal weight. This may be due in part to a lack of adhesiveness. Because of their cheapness, however, larger quantities may be used without increasing the cost. The lack of adhesiveness may be overcome by using a fish-oil or mineral-oil emulsion with them.

Tests of barium fluosilicate, potassium fluosilicate and sodium fluoaluminate (cryolite) at the rate of 3 or 4 pounds to 100 gallons of water, plus 1 pint of fish oil or $\frac{3}{4}$ gallon of emulsified mineral oil, reduced the wormy fruit in about the same percentage as lead arsenate did at the rate of 2 pounds to 100 gallons of water, without a sticker, except in one experiment, and reduced the quantity of stung fruit by a greater percentage.

"Except in some of the tests conducted in 1927, no fruit or foliage injury resulted from any of the experiments. In the limited number of analyses made to determine the residue on the fruit at the time of harvest, the residue from these materials was less than that left by lead arsenate and was as easily removed."[6]

The use of cryolite in codling moth control is usually restricted to late-season applications, using 3 pounds per 100 gallons of spray and 4 ounces of blood albumin as a spreader. For boll weevil control cryolite used in spray applications with a sticking or binding agent gave control similar to that of calcium arsenate, and both were superior to nicotine bentonite. Applications of cryolite, with good dusting qualities, were comparable in efficiency to calcium arsenate dusts. The Mexican bean beetle has been controlled with cryolite used at the rate of 6 pounds to the acre when mixed with 12 pounds of a suitable diluent. Caterpillars attacking tomatoes, including the pin worm, *Keiferia lycopersicella,* the potato tuber moth, *Gnorimoschema operculella,* tomato hornworm, *Protoparce sexta,* and the corn earworm, *Heliothis armigera,* are controlled by dust applications of 30 pounds per acre of cryolite at concentrations of 40 to 70 per cent in a diluent of talc, sulfur or diatomaceous earth. The use of dust applications, under the semi-arid conditions of California, is favored because of the speed and economy of application. Control of tomato insects in humid climates is more frequently accomplished by liquid sprays, using 6 pounds of cryolite per 100 gallons of water.[28] Because of the intolerance of citrus trees for arsenical applications, cryolite has become the standard control chemical for insects attacking foliage and fruit, both in southwestern United States[12a] and in South Africa.[13a] It is also a standard control for defoliators of cotton in southern United States and in Peru.[14a]

**Compatibility of Sodium Fluoaluminate (Cryolite).** Alkaline materials are generally considered incompatible with cryolite either as a spray or dust. For this reason lime-sulfur solution is not recommended for combining with this compound because of the presence of excess lime. Nicotine sulfate is combined with cryolite in sprays and also dust carriers if the base is not lime. Petroleum sprays may be used both before and after cryolite applications. Sulfur, zinc oxide and certain dinitro compounds are considered safe for use with cryolite. The question of the type of emulsifier used should always be considered in the interests of safety.

The removal of fluorine residues from fruits sprayed with such compounds is required, to conform to the present ruling of the United States of America Federal Security Agency of .049 grain of fluorine per pound of fresh fruit. A number of chemical formulas have been used in the removal of fluorine residues, but a 1.5 per cent solution of hydrochloric acid is generally favored over the sodium silicate wash.[30]

**Toxicology of Fluorine Compounds.** The comparative toxicity to the honey bee of cryolite, calcium arsenate and lead arsenate has been determined and the following median lethal dosages established:

"The median lethal doses of the arsenicals and of cryolite, in micrograms of active ingredient per bee, were as follows: Calcium arsenate (As), fine and medium 0.7, commercial 0.6, coarse 1.3; acid lead arsenate (As), fine 5.0, commercial 13, coarse 185; synthetic cryolite (F), fine 4.2, medium 5.5, coarse 13.0."[31]

Studies of the toxicity of sodium fluoride, cryolite and potassium arsenite "show that for potassium arsenite 5 mg. per kilogram of body weight is the minimum lethal dose for dogs, while sodium fluoride has a M.L.D. of 200 mg. per kilogram. An acute dose of cryolite appears to be incapable of causing death, as 13,500 mg. per kilogram was fed without fatality."[32]

**Drinking water containing fluorine in solution has been shown to have a**

mottling effect on the teeth of those using such contaminated water over a considerable period of time. "Fluoride concentrations in the drinking water supply, in the range from 2 to 3 parts per million seem to have a variable effect. This is probably the borderline range of concentration which produces mild mottling in some cases, characterized by dull white flecking of the enamel without stain, more severe mottled enamel in other cases, and no mottling in perhaps 50 per cent of the cases."[33]

"The average acutely fatal dose of fluoride for mammals is about 0.5 gram per kilogram of body weight, when taken by mouth, and about 0.15 gram per kilogram when injected hypodermically or intravenously." "Experimental chronic intoxication in animals may be produced by daily administration of 15 to 150 mgm. of sodium fluoride per kilogram of body weight, depending on the species used and the severity of the symptoms produced."[34]

It should be noted that statements concerning the toxicology of fluorine and its compounds usually refer directly to water-soluble fluorine or compounds which are quite soluble in water. By contrast, the fluorine compounds used in treating plants are chosen because of a high degree of insolubility in water, and comparisons between these and other fluorine compounds must be made with reference to variation in solubility.

### Selenium (Se)

One of the more rare elements, commonly found associated with sulfur and usually grouped with tellurium, another rare element, selenium has a specific gravity of 4.26, a melting point of 217°C (422°F), and a boiling point of 690°C (1274°F). It occurs in the form of steel-gray rods and as dark red crystals or powder, the latter form being soluble in carbon disulfide. Selenium burns in air to form selenium dioxide, analogous to sulfur dioxide.

Selenium occurs both with sulfur and the sulfides, such as pyrites. It is recovered in the "flue dust" of pyrite smelters and also in the refining of certain copper ores. In semi-arid areas selenium may be found whereever the sulfur content is high in the material from which the soil is formed. In humid regions the selenium content of the soil is comparatively low, even though the parent materials are relatively rich in this element.[36]

A study of the use of selenium as a parasiticide began in comparatively recent years. Reports of its value as a fungicide were made in 1925, but injury to the treated trees restricted its use.[37] Red spider control with this material was noted in 1933.[38] A thorough study was made of the value of a proprietary selenium spray material having a 30 per cent concentration of a mixture of potassium hydroxide, ammonium hydroxide, sulfur and selenium, according to the formula $(KNH_4S)_5Se$. Successful control was reported from the use of this solution diluted at from 1:500 to 1:800, and combined with a spreader, on the Pacific red spider, *Tetranychus pacificus*, on grapes. This mite is quite resistant to sulfur as a control agent, and since petroleum sprays tend to injure the bloom on the grape and check new growth, much attention has been given to the development of the selenium compound for the control of red spider.[35] Its effectiveness is increased by the addition of lime-sulfur solution (1:300) and the use of a light medium oil (1:300).[38] Where either of these materials is objectionable, wettable sulfur at the rate of 6 pounds to 100 gallons of spray may be added to the selenium compound. Similar results have been noted in the use of the proprietary selenium spray in controlling red spiders in greenhouses.[96]

Selenium is reported to be of value as a herbicide. "The toxicity of sodium selenate is determined by the amount of sulfur available to the plants. In water cultures selenium concentrations as low as 0.1 part per million produced distinct injury after a few weeks with nutrient solutions containing no sulfate, whereas a concentration of 18 parts per million was required for this degree of injury in solutions containing 192 parts per million of sulfur. There was no visible injury to the plants where the proportion of selenium to sulfur was 1:12 or less, the point of minimum detectable injury lying between the 1:9 and 1:11. Where the ratio was 1:8 or greater the plants were chlorotic and stunted, and when the ratio was as high as 1:2, growth was almost completely inhibited."

Attention has been called to the danger of using selenium as an insecticide because of the tendency of many plants to absorb it, resulting in chlorosis and stunting as well as danger to animals feeding upon the selenized plants. Quantities as small as 1 part per million of the absorbed selenium do not injure the plant but produce toxic symptoms and even death in experimental animals feeding upon them.[44]

The tendency of plants to absorb toxic amounts of selenium, when grown in soil containing this substance, led to studies of the effect of such absorbed amounts on aphids and red spider. Aphids placed on wheat plants supplied with concentrations of selenium greater than 3 parts per million all died within a few days, while those feeding on plants with lower concentrations lived for a week, but without active reproduction.[45]

Studies on the effect of absorbed selenium on ornamentals has shown that chrysanthemum foliage containing 45 parts per million practically eliminated the chrysanthemum aphid, *Macrosiphoniella sanborni*. Reduction in numbers of both aphids and plant mites *Tetranychus telarius*, occurred with the absorption of one-half this amount of selenium in the foliage. Caution is urged in experiments of this nature because of the danger to higher animals.[46]

## Mercury and Its Compounds

**Mercury** (Hg) is a bright, metallic liquid, also known as qucksilver; it is volatile at all temperatures; it has specific gravity 13.59 and boiling point 357.3°C (675°F); it is insoluble in water, but soluble in acids. It alloys readily with most metals. Metallic mercury enters into certain proprietary materials, but its efficiency is probably due to the formation of oxides ($HgO$ and $Hg_2O$) or other chemical compounds. Mercury vapor itself has been found toxic to germinating tobacco seeds, the toxicity varying directly with the temperature.[46a]

**Mercuric chloride** ($HgCl_2$), also known as bichloride of mercury and corrosive sublimate, has a specific gravity of 5.32, a melting point of 265°C (509°F) and a boiling point of 303°C (577°F); 5.7 parts are soluble in cold water and 54 parts soluble in boiling water; it is also soluble in alcohol, ether, and pyridine, and without decomposition in sulfuric, hydrochloric and nitric acids. It decomposes in the presence of the hydroxides, including sodium, potassium, calcium, and magnesium. Many organic substances decompose it into mercurous chloride or mercury, especially in the presence of sunshine.

Solutions of mercuric chloride in water (1 to 2000 or stronger) give good control of the disease of club root on cabbage and cauliflower. The disease is caused by a fungus, *Plasmodiophora brassicae.* Two applications are generally successful on seedbeds, although when the fungus is distributed through the field soil, control is not so certain. Good control has also been obtained with similar application of mercuric chloride solution for the diseases black-leg, *Phoma lingam,* and a black rot or blight, *Pseudomonas campestris,* on cabbage, cauliflower, and brussels sprouts. Surface molds on germinating pea seed were eliminated by a dip in a concentration of 0.18 per cent of this mercury compound.[48]

The cabbage maggot, *Phorbia brassicae,* is also commonly controlled by 2 or 3 seedbed treatments with mercuric chloride solutions ranging in concentration from 1 to 200 up to 1 to 1500. Plant injury is sometimes noted from such treatments, especially brussels sprouts. Organic mercury preparations were as effective as mercuric chloride against clubroot and were safer to the plant but were of less value in checking the cabbage maggot.[47]

Fungus infections of lawns and greens by *Rhizoctonia solani* (commonly known as "brownpatch") and by *Rhizoctonia sp.* causing "dollar spot" are controlled by applications of mercuric chloride in solution at the rate of 1⅕ pounds of the compound to 6000 square feet of lawn. Combinations of ⅓ mercuric chloride and ⅔ mercurous chloride ($HgCl$) gave better control of brownpatch than the former used alone. These materials used together showed less injury to the turf and gave more lasting results than either one used alone.[49]

Mercuric chloride in combination with mercuric cyanide, $Hg(CN)_2$, is a standard disinfectant for treating tools and pruning wounds in fighting pear blight. One-fourth ounce each of the two mercury compounds is dissolved in one gallon of solvents, composed of 7 pints of water and 1 pint of glycerin. The solution should be made up and stored only in glass or earthenware containers.[48a]

**Mercuric Oxide** ($HgO$). Both the yellow and red forms of this compound lie between mercuric chloride and mercurous chloride as to effectiveness in control of lawn diseases and as to injury to the turf from overdose. Mercuric oxide at 0.5 per cent concentration is a common ingredient of antifouling paints for ships' bottoms. It serves to protect against algae, tube worms and certain mollusks.[20a]

**Mercurous chloride** ($HgCl$), also known as calomel, has a specific gravity of 7.1. As respects melting point, it sublimes at from 400 to 500°C (752 to 932°F); its boiling point is 383°C (721°F). It is practically insoluble in water, alcohol, and ether.

Bottom rot of lettuce caused by the fungus *Rhizoctonia solani* has been partially controlled by applications of calomel at from 10 to 20 pounds per acre. All dosages, even the smallest, caused so much injury to the lettuce that its use has been discontinued in favor of an organic mercury compound, ethyl mercury phosphate.[50] Mercurous chloride is reported as very satisfactory in the control of the root maggot on cabbage and cauliflower' It is no more effective than mercuric chloride in the control of this insect, but because of its insolubility it can be used at the rate of 3 or 4 ounces as a suspension in water. Dust applications may also be made using an inert carrier such as gypsum or hydrated lime. Heavy treating of seed with calomel is also suggested as a control for the maggot.[51]

## Chlorates and Chlorites

**Sodium chlorate** ($NaClO_3$) consists of colorless, odorless crystals, which are very soluble in cold water. It is characterized by a high fire hazard both from the dried solution and from the crystals when in contact with any dry organic matter. Containers should be stored in a cool place with good air circulation. Mixtures of sodium chlorate and arsenic trioxide result in spontaneous combustion; these compounds should never be stored together.

Experimental work with sodium chlorate in Idaho in the control of several species of wild *Ribes*[57] (includes both currants and gooseberries) and also in Washington on the bind weed or wild morning glory, *Con-*

*volvulus arvensis,*[58] during the period from 1926 to 1928 attracted general attention to the value of this chemical as an herbicide. Many of the chemicals tested as controls for the shrub *Ribes* gave quick but only temporary action, including defoliation and the killing of young growth. Sodium chlorate, in a 25 per cent solution, was the only one generally effective in killing not only the top of the shrub, but the entire root system. Decided varietal variation was noted in the susceptibility of different species of *Ribes.* A 10 per cent solution of sodium chlorate, made slightly acid (pH 5.0 to 6.5), gave complete eradication of *R. petiolare.* For other species solutions ranging from 25 to 50 per cent were required for control. The solutions are sprayed on, using light-weight power outfits and applying about one quart of solution per bush. Best results were obtained by by spraying in cloudy, humid weather.[57]

Bindweed or wild morning glory, *Convolvulus arvensis*, may be eradicated by proper applications of sodium chlorate. One pound of the chemical is dissolved in a gallon of water and used at the rate of 3 gallons per square rod of infested area. The best results are attained by applying from midsummer to late fall. The plant is storing starch in the roots at this time and the chlorate is apparently carried downward by this movement. Heavy growths of tops should be mowed and raked off or heavier dosages will be required. Sprouts which appear the second year should be treated in the same way. Calcium and magnesium chlorate are also used in the same manner, but less commonly than sodium chlorate.[58]

"Sodium chlorate, acting through the soil, is very poisonous to both annuals and perennials. It is very soluble and is readily leached. For highest success consideration should be given to the rainfall between the time of application of chlorate and the season of active root absorption. The depth of penetration of the chemical into the soil should coincide with the depth of the main root system at the time of maximum root activity in the spring."[59]

The toxicity of chlorate to plants is not affected by the texture of the soil, but is greatly dependent upon the chemistry of the soil—particularly the anions, chlorides, sulfates, bicarbonates, and nitrates. The first three are important in arid regions, but the nitrate content of the soil is by far the most important in reducing chlorate absorption by plants. The other anions hinder the absorption of chlorates and reduce toxicity, but without the stimulating action of the nitrates. Water adsorption of chlorate, in certain types of soils, has been shown by Crafts.[16a]

Dosages recommended vary with the susceptibility of the plant, degree of penetration into the soil as determined by rainfall, and soil type, particularly the presence of nitrates. High temperature, such as occurs in late summer and fall, also tends to decompose chlorate and reduce its toxicity. The range for plants susceptible to chlorate, such as morning glory, St. Johnswort, Russian knapweed, Canada thistle, and Johnson grass, is 1 pound per square rod for favorable conditions, and up to 8 pounds for very fertile soils, or where other conditions may interfere with chemical action. The latter dosage is almost as expensive as the use of carbon disulfide; in view of the long sterilizing action of chlorate it might be advisable to use carbon disulfide, since it leaves no sterilizing residue.[60]

Chlorate, because of its high solubility and ease of leaching in the soil, kills annuals only during the year of application, but is of more value for killing deep-rooted perennials. It is not a successful soil sterilizer except in combination with slower-acting chemicals, such as white arsenic and borax. The latter two chemicals are unsatisfactory for quick killing of annual weeds. The combination of chlorate and white arsenic is preferable as a sterilizing agent for most soils, since the borax-clorate combination is antagonistic in many soils; that is, they tend to retard each other's activity. The mixture does have some value because (1) it is not as poisonous as arsenic, (2) the fire hazard of the clorate would be reduced, and (3) the effect is more durable than that of chlorate alone.[61]

**Sodium hypochlorite** solution, containing 0.4 per cent of available chlorine, has been found very effective in reducing blue mold, *Penicillium expansum*, infection of apples. The fruit is exposed for at least one minute in the 0.4 per cent solution, and this same concentration is sprayed on picking boxes and about the packing house. Best results in box and house treatment are obtained by closing the treated rooms for several days following the application.[62] Similar results in the use of hypochlorite solutions were obtained in the control of the blue and green molds, *Penicillium italicum* and *P. digitatum*. The concentrations tested were 0.4, 0.6, and 1.0 per cent solutions of sodium hypochlorite, all three being fatal to spores of both fungi at 2 minute exposures.[63]

**Borax** ($Na_2B_4O_7 \cdot 10\,H_2O$), also known as sodium tetraborate decahydrate, is an effective control of the blue and green molds, *Penicillium italicum* and *P. digitatum*, at a range of concentration from 4 to 12 per cent varying with the temperature and length of exposure. A temperature range of from 66 to 120°F with an exposure of 2 to 16 minutes has been found effective. The longer the exposure, the higher the temperature and the greater the concentration of the chemical, the more effective was the solution in reducing viability. A mixture of borax and boric acid ($H_3BO_3$) gave results similar to borax used alone, although a slightly greater toxicity was noted to *P. digitatum*.[63] Control of the stem-end rots of Citrus fruits caused by *Diplodia natalensis* and the **Phomopsis** stage of *Diaporthe citri* is accomplished by a borax bath at 8 per cent concentration immediately upon arrival at the packing house.[64] Powdered borax and solutions are recommended as preventives of wood decay in window sashes and other jointed woodwork.[5]

**Boric acid** ($H_3BO_3$) has been recommended for use in the control of fleece-worm infestation in Australia caused by the flesh fly, *Lucilia cuprina.* Under American conditions, it has been found that boric acid is toxic to the more important fleece worms, the black blowfly, *Phormia regina,* the secondary screwworm fly, *Callitroga macellaria,* and *Lucilia sericata,* a greenbottle fly, but a number of synthetic organic compounds equal or exceed this material in toxicity.[65] Borax is combined with sodium fluoride in cockroach baits (see p. 86).

### Thallium (Tl)

Thallium is a soft white metal with a grayish tinge, resembling tin in appearance. The usual source of supplies of thallium in the United States is from central Europe, particularly Germany and France. Small supplies of low grade ore are produced in the United States, Canada and certain South American states. It has a specific gravity of 11.8 and a melting point of 301.7°C (575°F). Thallium forms two series of salts, thallous compounds, in which the metal is monovalent, and thallic compounds, in which it is trivalent.[67]

Thallous sulfate ($TL_2SO_4$) and thallous acetate ($TLCOOCH_3$) are the forms commonly used in ant sirups and rodent baits. (Both compounds are sold commercially as thallium sulfate and thallium acetate, terms which are commonly used in the literature.)[68]

Thallium acetate at concentrations ranging from 0.5 to 4.0 per cent, dissolved in a sirup of water, cane sugar, and cane sirup (10–10–1 parts), was fed upon readily by the fire ant, *Solenopsis geminata.* At concentrations of 2 per cent and higher a mortality of 85 per cent and above was obtained in cage tests. Tartaric acid and benzoate of soda added as preservatives were repellent. Thallium sulfate tested at concentrations ranging from 0.125 to 2.0 per cent dissolved with difficulty at the higher concentrations. Mortalities of about 86 per cent were obtained at 1.0 per cent concentrations in cage tests.

Field tests against the fire ant with thallium acetate bait at the same concentrations used in the cage tests gave effective control. The bait was taken most readily following rains and as long as the ground remained moist. Thallium sulfate baits were not satisfactory in field tests[68] as reported in 1939, but later work showed almost equal value for the sulfate and acetate forms.

Successful use of thallium sulfate baits in suitable containers as a control for the fire ant has been reported in the Citrus groves of Texas. The recommended concentration of thallium sulfate is 1.2 per cent concentration. The formula used in preparing the bait is as follows:

| | |
|---|---|
| Water | 4½ pints |
| Thallium sulfate | 2 ounces |
| Sugar | 5 pounds |
| Honey | ½ pound |

Dissolve the thallium sulfate in the water by boiling, being careful not to breathe the fumes. After the chemical is dissolved add the sugar and honey and stir until dissolved. Add enough water to bring the total to one gallon.[69]

The control of house ants, *Monomorium pharaonis*, *M. minimum*, and *Lasius interjectus*, is reported to be successful with a smaller concentration of thallium sulfate than is recommended for the fire ant. The suggested formula is 1 pint of water, 1 pound of granulated sugar, 27 grains of thallium sulfate and 3 ounces of honey.[70]

Rodent control by the use of thallium sulfate baits began about 1920 in Germany and in the United States about 1924. The use of thallium sulfate at one per cent by weight in grain baits in controlling ground squirrels, prairie dogs, and rats is principally as a supplement to strychnine, because of the great danger to operators and others handling the baits.[71]

The use of thallium sulfate in rodent control work increased so rapidly in the ten years following its introduction that the question of its action on vegetation and soil sterilization arose. Laboratory and field studies of the action of thallium sulfate gave the following results: Germination of the seed of *Vicia faba*, (beans) *Lupinus albus*, and *Zea mays* (corn)was completely prevented by the addition of 340 parts of thallium per million in pot cultures. The injury was greatest in sandy soils. Leaching did not prevent the harmful action. "In soils containing 100 mg. per kilogram or more, toxic effects were noted with all seedlings. A concentration of 1000 mg. per kilogram stopped the germination of timothy, and 10,000 mg. per kilogram stopped the germination of corn and clover.

"Field studies with thallium sulfate-treated grain, using the customary formula of 1 pound of thallium sulfate to 99 pounds of grain, showed that injury to vegetation occurred only from the use of 2000 to 3000 pounds of treated grain per acre. Since the maximum application of treated grain in the original treatment is only 1 pound per acre, it was concluded that no danger existed to vegetation or as a soil sterilant."[72]

Further studies of the action of thallium on soil show variation in toxicity according to the soil type, it being greatest in soils of low fertility. The fixation of thallium in clay loams was particularly noted. Confirmation was noted of other research,[72] namely that 100 parts per million of thallium sulfate on a dry weight basis, should be completely toxic. "At least

5000 pounds of squirrel bait, carrying 1 per cent thallium sulfate uniformly distributed, would be necessary to sterilize an acre completely."[73] Considering the difference between the sterilization mentioned and the actual rate of use, there is little fear of the sterilization of soils by thallium-treated squirrel bait.[73]

**Toxicology of Thallium.** Limited use has been made of thallium in medicine at the rate of 8 milligrams per kilogram of body weight, but this use is considered so dangerous as to be on the decrease. "Thallium affects the sympathetic nervous system, thereby producing general alopecia (loss of hair), pains in the muscles and nerves of the legs, and disturbances of the endocrine glands (particularly the ovaries and testicles and the thyroid, suprarenal, and pituitary glands). Calcium metabolism is upset and leads to rickets."[67]

The minimum lethal dose of thallium fed as the sulfate to wild rats, or to white, and injected into rabbits intravenously is, in both instances, 25 milligrams per kilogram.

"Thallium is among the most toxic substances recommended for rat control; comparative tests with other rat poisons by the same feeding method give the following minimum lethal doses:

| | mg. per kg. of body weight |
|---|---|
| Thallium | 25 |
| Strychnine | 20–25 |
| Arsenious oxide | 100 |
| Red-squill powder | 250 |
| Barium carbonate | 750 |

"Thallium is a cumulative poison of high toxicity and is without taste, smell, or other warning property. It should not be recommended to the public as a rodent poison. Where the use of thallium is found necessary for the control of highly resistant species of rodents, it should be entrusted only to persons who understand its dangerous qualities and who will exercise appropriate care in handling it."[67]

## Potassium Antimony Tartrate

This compound, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, also known as tartar emetic, has a specific gravity of 2.6. Antimony is produced in small quantities in the United States, but is principally an import, much of the supply coming from Mexico. The solubility in cold water is 5.6 parts in 100 and 35.7 parts at 100°C (212°F). The value of this compound as an insecticide has been recognized for a number of years in ant control. A common formula is one part of tartar emetic to 20 parts of honey, or grease and lard may be substituted for the honey.[74]

Horticultural work with potassium antimony tartrate as the control material began with experiments in the control of the gladiolus thrips, *Taeniothrips gladioli*. The formula developed at that time has been modified and the cost reduced, the recommendation being 2 pounds of tartar emetic, technical grade, and 4 pounds of brown sugar to 100 gallons of water. This formula is considered safer to the plant than Paris Green and sugar. Calcium antimony tartrate, containing 10 per cent less antimony than does tartar emetic, used at the rate of 4.4 pounds per 100 gallons of spray gave similar control to the potassium compound. "Calcium antimony tartrate is slowly soluble in water and must be finely powdered so that it will go into solution readily or hot water must be used. Tartar emetic is more readily soluble, but it also should be finely divided to accelerate solution."[76]

Combination sprays containing spreaders gave poorer control than the tartar emetic-brown sugar sprays that are applied as droplets.

Attempts to control the greenhouse thrips, *Heliothrips haemorrhoidalis*, by the use of practices similar to those used for the gladiolus thrips gave unsatisfactory control. Chemicals tested included potassium antimony tartrate, calcium antimony tartrate, zinc antimony tartrate, potassium antimony citrate, together with cryolite and barium fluosilicate.

"As a group, the antimony compounds were much more toxic to the greenhouse thrips than were the fluorine compounds. Tartar emetic was the most effective material tested, but the toxicity of this compound was not of sufficient magnitude to offer much promise in field control. It has been demonstrated since, in field tests, that tartar emetic is not effective for the control of greenhouse thrips."[77]

The tartar emetic-sugar spray (1–2 pounds tartar emetic, 2 pounds sugar, 100 gallons of water) has become a standard field control for the citrus thrips *Scirtothrips citri* in California citrus groves[79] and in the present shortage of supplies of tartaric acid has led to a study of potassium antimony citrate as a substitute compound. Field applications of the citrate compound gave somewhat erratic control of the insect and studies of the two compounds in spray mixtures showed significant variations in the pH values. Field mixtures of tartar emetic had a pH near 6.1, while that of potassium antimony citrate was in the region of 4.4. Raising the pH of the tartar precipitate to a pH of 8.0 resulted in a lowering of toxicity, while a similar lowering of toxicity was also noted when the pH of the tartar emetic solution was lowered beyond the normal pH of 6.0.

"The toxicity of residues from potassium antimony citrate solutions was affected by the pH to a much greater degree than in the case of tartar emetic. The highest toxicity was reached at a pH of 6.0 and 7.0. The toxicity was greatly reduced in the lower pH values. Residues from the solution of pH 3.0 were relatively nontoxic and at a pH of 8.0 they were less toxic than at values of 5.0, 6.0, and 7.0."[78]

Tolerance or resistance to the toxic action of tartar emetic is apparently increasing in certain limited areas in southern California where this type of spray has been in use for about three years. Sucrose has been substituted for sugar because of the food shortages, and dosages of 12 pounds of tartar emetic and 12 pounds of sucrose per acre have failed to control the citrus thrips.

Additonal values for tartar emetic as a control agent are found in reports of the successful control of the tobacco hornworm, *Protoparce quinquemaculata*, moth and the greenhouse leaf tier, *Phlyctaenia rubigalis*.[19a]

**Toxicology of Tartar Emetic.** The use of sweetened tartar emetic solutions as orchard sprays during the blooming season has led to a study of the possibility of killing honey bees by such applications. The data resulting from these investigations indicate "that the minimum lethal amount of tartar emetic was between 3 and 6 micrograms per bee and that death resulted over progressively longer periods as the concentrations were decreased. At the weaker dilutions, the symptoms of poisoning were not so definite as at the higher concentrations."[81] "While the minimum lethal dose of tartar emetic was found to be between 3 and 6 micrograms per bee, the tartar emetic-sugar spray applied in greater concentrations in the control of the citrus thrips in California, did not cause noticeable loss this year to colonies in the vicinity of treated fields."[81]

Food contamination with antimony present in enameled cooking vessels is reported following tests showing the extraction of antimony by hot 2 per cent tartaric acid and even by cooking saurkraut in enamelware. Illnesses have been traced in England to lemonade prepared in buckets containing antimony in the enamel.[82]

## Zinc and Its Compounds

Zinc production in the United States has ranged from 20 to 65 per cent of the world's supply during the last 40 years. Mining is well distributed, at least one-half of the states producing in commercial quantities. The chemical element zinc is recognized, in certain districts such as parts of California and Florida, as a specific for correcting a physiological disturbance of Citrus[83] and other orchard[84] trees, apparently due to a nutritional deficiency. Metallic zinc dust and a number of compounds, principally zinc oxide ($ZnO$), but also zinc sulfate ($ZnSO_4 \cdot 7H_2O$), have been used interchangeably, so that it is apparently zinc itself that is required.

Metallic zinc and sodium fluoaluminate, in the proportions of 1 to 2 pounds of the former to 3 pounds of the latter, are frequently applied to Citrus groves, either suspended in 100 gallons of water or as a dust mixture.

Zinc oxide, being insoluble in water, is combined in spray applications of lime-sulfur solution, nicotine, and petroleum, the latter combination being dependent on the emulsifier in regard to safety on foliage.

Zinc sulfate is soluble in water and hence is usually applied as a spray. Applications on dormant trees may be made without lime, but on Citrus trees they are usually carried out with lime to reduce danger of injury.

Further usage on Citrus trees of zinc compounds—sulfide, sulfate and oxide—have resulted in decided scarring of both orange fruits and foliage. The injury has been traced to zinc oxide-lime-sulfur applications and light dosages (2.5 to 3.5 pounds) of zinc sulfate. Increasing the amount of zinc sulfate to 7 pounds, used with 2 gallons of lime-sulfur solution, has eliminated the injury. This is explained by the fact that zinc sulfate reacts chemically with the lime-sulfur solution and the 7-pound dosage apparently neutralizes the 2 gallons of solution.

Combinations of zinc sulfate with lead arsenate and lime are used on peaches to reduce the danger of foliage injury. Water-soluble arsenic may form as a result of combining lead arsenate and lime, but in the presence of zinc sulfate an insoluble zinc arsenate is formed. The usual recommendation is 1 pound in 100 gallons of water with 3 pounds of acid lead arsenate and 3 pounds of hydrated lime. Zinc sulfate is not recommended as a fungicide, although value has been shown in controlling apple scab, *Venturia inaequalis*, and brown rot, *Sclerotinia fructicola*. It is not recommended as a bactericide for the bacterial spot, *Phytomonas pruni*.[85]

Zinc sulfate is used in a limited way as a fungicidal spray in Citrus groves because of its compatibility with hydrocyanic acid gas commonly used in fumigation. The value of zinc sulfate alone is not sufficient to control the brown rot of the lemon and the *Dothiorella* rot of the avocado, except at concentrations injurious to foliage; but in zinc-copper combinations the latter may be reduced to a point where safe fumigation with hydrocyanic acid is possible. The combination treatment for *Dothiorella* rot and mottle leaf recommends 16 pounds of zinc sulfate, 1 pound of copper sulfate, 8 pounds of hydrated lime, 6 pounds of sulfur to 100 gallons of water.[86] The formula used for brown rot control on lemons is 1 pound of copper sulfate, 12 pounds of zinc sulfate (23 to 24 per cent), 6 pounds of hydrated lime to 100 gallons of water with blood albumin or casein spreader. This is stated to be of similar effectiveness to a 6-6-100 Bordeaux mixture.[87]

Zinc oxide has been found of value as a seed disinfectant, preferably for broccoli, brussels sprouts, cabbage, cauliflower, endive, kale, kohlrabi, lettuce, parsley, radish, and turnip. Two teaspoonfuls of the zinc compound is used with 1 pound of seed, or 1½ to 2 per cent by weight for large lots of seeds. It is also recommended as a soil surface treatment for damping-off fungi. This treatment is in addition to disinfecting the seed. The zinc oxide is spread as a white layer over the surface of seedling trays and allowed to remain while the young plants are developing.[88]

Weed control in seed beds, where Engelmann Spruce and Western White Pine are being grown, is reported from the use of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) or "Zinc vitriol" at the rate of 3½ ounces of the chemical to 1 quart of water to every 4 square feet of seed bed. A new application of the zinc salt is needed for each successive crop of trees. The second dose should be only half the quantity of zinc originally applied. The treatment does not kill well-established weeds or underground runners, but it does prevent the germination of most of the weed seeds.[89]

Zinc chloride is a water-soluble compound used as a wood preservative, particularly where not exposed to the leaching action of rain or soil water. It has the advantage of cheapness, availability, lack of odor and of fire hazard. Chromated zinc chloride is now being tried as a substitute for zinc chloride as being less subject to leaching. Both zinc compounds are recommended as preventives of termite attack[22a] Tree injections of zinc chloride, 1 per cent water solution, have been recommended as a method of treating chlorosis of the orange.[23a]

## Dust Barriers

Artificial applications of finely divided inert dusts and even material accumulations of road dust on foliage have been recognized as of value in repelling or reducing the number of insects feeding or ovipositing on foliage, twigs or even grain. Such effect on the presence or activity of insects may, in the broad sense of the term, be classified as insecticidal. A good illustration is the use of a thorough coating of talc on the foliage of Elberta peaches as a control of the Oriental Peach Moth, *Laspeyresia molesta*. Nine applications of the dust during July and August were found necessary because of redusting after rains. Fruit infestation by the moth was reduced from 40 to 50 per cent for the season, but further control in the infestation was not possible because of a similar reduction in the numbers of the parasite, *Macrocentrus ancylivora*, which was attacking the moth.[90]

The pepper maggot, *Spilographa electa*, has been prevented from ovipositing in the pepper fruit by keeping the plant coated with talc during the season when the fly is abundant. Practical control will require about 10 dustings per season.[91]

**Calcium carbonate,** $CaCO_3$, in a very finely divided form, has been found to retard greatly the breeding of the rice weevil, *Sitophilus oryza*, in rice stored for a period of one year at a temperature ranging from 50 to 75°F. Proper humidity was maintained throughout the period to give optimum conditions for feeding and breeding. Calcium carbonate was added to the rice in the proportion of 1 per cent of the weight of the grain. Over a period of one year the rice weevil barely maintained its numbers while the number of insects in the uncoated rice increased 1000 per cent. This amount of calcium carbonate is not objectionable from the standpoint of flavor; in fact some markets prefer rice with the slight flavor which calcium carbonate imparts. This preference has probably developed because of the use of very small amounts of calcium carbonate in rice to reduce friction and consequent heating during the milling process.[92]

A study of various types of inert dust insecticides has shown that activity is associated with certain physical attributes; particle size and hardness were found to be the most important, though not the only factors in killing the granary weevil, *Sitophilus granarius*. Silicon carbide particles "larger than 15 microns were without action . . . the effectiveness increased as the size was reduced from 10 microns to about 2 microns. . . . Adsorbent dusts, like charcoal, were much more effective on larvae than were mineral powders."[33a]

**Barium carbonate** ($BaCO_3$) has been in use for many years as a rodent poison, particularly for rats and mice. Its general use for this purpose is probably due to a lower toxicity to humans than is found with strychnine and arsenic. Barium carbonate baits may be prepared of many substances, the usual proportion being 4 parts of a cereal (corn meal, rolled oats), or bread, ground meat or fish, to 1 part of the dry powdered barium compound. Dry materials are mixed with the barium carbonate and then moistened with water or milk.[93]

The Mexican bean beetle, *Epilachna corrupta,* may be controlled by applications of barium carbonate at the rate of 0.25 to 1.0 pound per gallon of water. The action is slower than standard materials, including cryolite and barium fluosilicate, but is useful in light infestations. No toxic action was noted from the barium carbonate application to any of the caterpillars.[94]

**Sodium carbonate** ($Na_2CO_3$) is used at a concentration of 6 to 10 per cent in the control of blue and green molds, *Penicillium spp.*, on citrus fruits. A temperature of 120°F increased the effectiveness of the sodium carbonate solution as applied to spores. Solutions of sodium bicarbonate ($NaHCO_3$) were not commercially effective in mold control.[63]

## Phosphorus ($P_4$).

Yellow phosphorus is of regular crystalline formation with a melting point of 44.2°C (111°F) and a boiling point of 290°C (554°F). It is very slightly soluble in water, alcohol, and ether. This is in contrast with the amorphous, red form ($P_4$) with a melting point of 725°C (1337°F) and insoluble in the three above solvents.

A study of the toxicity to the American cockroach, *Periplaneta americana,* and the German cockroach, *Blatella germanica,* of yellow phosphorus with particle size ranging from 2.5 to 10 microns has established the dose required to kill 50 per cent of the insects (the median lethal dose) as being close to 0.020 mg. per gm. of the weight of the nymphs of the American cockroach. Similar tests with the nymphs of the German cockroach showed the median lethal dose of phosphorus to be 0.13 mg. per gm., 6.5 times greater than the median lethal dose for the American cockroach. Studies of the toxicity to the American cockroach of sodium arsenate and sodium fluoride compared to phosphorus showed that the median lethal dose of sodium arsenate "in water in terms of $As_2O_3$ probably lay between 0.04 and 0.3 mg. per gm." Sodium fluoride was fed in diluted paste to nymphs of the American cockroach in doses ranging from 0.12 to 0.55 mg. per gm. "Only three of these insects were killed. The toxicity of sodium fluoride in diluted paste was much lower than that of phosphorus, but the median lethal dose was not determined."[95]

Phosphorus is a common ingredient of rat baits, but requires much more careful handling than is necessary with squill or barium carbonate.

**Zinc Phosphide.** This chemical has come into general use for rodent control; in England as a raticide and in the United States for controlling both rats and ground squirrels. Zinc phosphide has been found stable up to six months storage in burlap bags, but it decomposes, somewhat readily under field conditions. Baits for use against ground squirrels are prepared with either hull-less grains or whole barley and oats. It is more adaptable to different baits than any of the other toxic agents used on this rodent.[25a]

Poultry has been found quite susceptible to the action of zinc phosphide, the minimum lethal dose being approximately one grain for a 5-pound bird.[26a]

## Ammonium Sulfamate

This compound, $(NH_4)_2O \cdot SO_2NH_2$, has been reported as an effective control for the Klamath weed or St. Johnsworth, *Hypericum perforatum,* when used both as a spray and as a dust. It was quicker in its action as a control agent than was borax and also was active afterward as a fertilizing agent.[27a] The material is reported as of little value as a translocation spray and gives satisfactory kills under humid conditions. Death may result through root absorption if the chemical is carried downward by rainfall or irrigating water. Breakdown occurs rapidly after application and without permanent injurious action.[28a]

## Ammonium Thiocyanate ($NH_4CNS$)

Being a water-soluble compound, this is an active herbicide, but because of the rather large dosages required and the cost it has not come into general commercial use. Limited use for the compound is reported for certain of the lawn weeds.[29a]

## Sodium Cyanide (NaCn)

At 3 per cent concentration, this substance killed quackgrass, poison ivy, honeysuckle, dandelion and plantain, *Plantago major*.[30a] It is also reported useful as a soil sterilant at concentrations ranging from 50 to 500 ppm of potting soil.[31a] The value of cyanide compounds as soil sterilizers varies with the character of the soil. Clays adsorb large amounts of hydrocyanic acid gas, while sandy soils show practically no adsorption.[32a]

Calcium cyanamide ($CaCN_2$) and iron sulfate (both the ferric and ferrous forms) are used as herbicides and as wood preservatives.

Studies of the fungicidal activity of various silver compounds showed superiority for the oxide, iodide, hexacyanoferrate and the dichromate compounds. Mixtures of iron sulfate and hydrated lime with silver nitrate gave the most adherent combination.[34a]

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# Chapter 6

# Mineral and Other Oils

## MINERAL OIL

Mineral oil, derived from petroleum, has long been recognized as an efficient insecticide on both plants and animals. Consumption has, however been retarded by frequent injury to plants, difficulties of emulsification and variation found both in crude oils and in the distilled fractions—kerosene, Diesel oil and light lubricating oils. Kerosene, when partly refined, has in the past been most commonly used because of plant tolerance. This fraction was first used on Citrus and other trees about 1881, but to a limited extent, since it is too volatile to kill scale insects and mealy bugs. A cheaper and more toxic fraction known as "stove distillate"[1,7] together with crude oil[2,3,8] was recommended. The only specification commonly given for the oil used was the density or "Baumé". "Stove" distillates ranged from 16 to 35° and the crude oil from 12 to 25° Baumé.[9] Many types of crude oils were used, ranging from the natural crude, whose only refinement was the removal of water and sand, to a heavy residual oil with a high content of asphalt. As the oils were emulsified in the field, there was necessarily much irregularity in the final product and frequent complaints of injury.

The many difficulties encountered in handling distillates and crude oil led to experiments with light grades of lubricating oil[4] which had been refined to a certain degree. The first general use,[5,6] of lubricating oil as a tree spray was on dormant apples. The oils used were known as "engine oil" or "red engine oil". The specifications used were those employed in the lubricating-oil trade without reference to their fitness for defining oils to be used on plants.

The value of petroleum as an insecticide was then (1928) generally recognized, but increased consumption depended upon a better understanding of the action of oil upon insects, plants, and animals. Specifications were needed that would define the characteristics of oils for plant use as precisely as those describing oil for lubricating purposes. One of the first and most important of the new specifications is what is known as the "sulfonation test", developed in 1914 and 1915. A report on the value of this specification was not published until 1926,[10] although publicity had been given to the findings. The application of this principle to the refining of light lubricating oils with sulfuric acid and sulfur dioxide increased the tolerance of oils by plants to such a degree as to make possible the general use of refined oils on both dormant trees and plants in foliage.[10] The cost of the first refined "white" oil emulsions restricted their use, but this difficulty was overcome by an increase in volume of consumption and greater efficiency by the use of less stable emulsions.[11] The development of a successful quick-breaking emulsion reduced the necessary concentration of oil, permitting more complete utilization.

## Present Scope of the use of Petroleum as an Insecticide

Petroleum and its derivatives are toxic to insects to a marked degree and rank as one of the most important insecticides. Distillates of petroleum are so varied in character that it is possible to choose fractions with specific characteristics favorable for use in the control of many types of insects, mites, and ticks and over a wide range of conditions.

The lighter and more volatile distillates, such as benzene and gasoline, have properties desirable for the control of certain household pests. The next fraction in the distillation process, kerosene, both in the refined and crude form, has been an important factor in spray practice for the last forty years. Crude petroleums themselves, without any refinement whatever except the removal of sand and water, show a waning use both in orchard work and as dips for cattle, horses, and hogs. Mosquito abatement districts are still using small amounts of crude oils and increasing quantities of unrefined, residual distillates. The latter, together with by-products removed in refinery practice and Diesel oil, are now used in carload lots as herbicides[3] and for poultry parasites. Experience has shown that, although many of these unrefined and consequently cheaper materials are considerably more toxic to insects than refined kerosene, they also are more toxic to vegetation. The use of partly refined petroleum distillates, derived from varying sources, may be attended with little or no injurious effect to plants, but there are many cases on record of grave consequences following their use. Deciduous and citrus orchards have been partly defoliated, and bearing fruit trees killed, following the use of partly refined, unstandarized distillates. Similarly, the major part of the season's fruit crop has at times been caused to drop, and occasionally a considerable percentage of fruit has been rendered unsaleable or reduced in market value. Such injuries are, however, lessening very rapidly with the general use of highly refined and lighter grades of "white" oils for foliage applications. The latter are being marketed under increasing restrictions and under definite specifications as rapidly as these are established.

The research on mineral oil as a plant spray since 1914 has raised its status as an orchard spray from that of a little-used hazard on foliage and one of considerable risk on dormant trees, to that of a major insecticide rivaling in some fields the fumigant hydrocyanic acid gas, and again displacing lime-sulfur solution in the deciduous orchard. Combinations of oil emulsions with other insecticides, such as lead arsenates, and as a carrier for many toxic chemicals, including nicotine, pyrethrins, and copper, have greatly widened its field of usefulness. Beneficial physiological reactions are also being noted with the advent of fractions more tolerable to the tree. Citrus groves recently sprayed with oil have been found to withstand the effect of desiccating winds. The blooming dates of deciduous trees may be either delayed or advanced by properly timed applications of dormant oil sprays. Such reactions are from their nature difficult to understand and require years of effort for confirmation.

## Physical and Chemical Nature of Petroleum

When pumped from the well petroleum is a mixture of crude oil, water, and sand. The first step in the refining process is to separate the water and sand from the oil, the latter being stored in great tanks near the well or pumped directly into pipe lines. Field tests of the character of the oil from a well are of a very general nature, most wells being grouped in one of two classes. All the wells of one class in a field are pumped into tanks of the same series, or a single pipe line. The individual characteristics of any well are thus largely lost through this blending process. Experimental work on any mineral oil, unless brought direct from the well, is always of a blend of several wells and perhaps two or more widely separated fields. This gives permanent value to research on petroleums, for a stock of crude oil of today will probably be very similar to the production of ten years from now.

California oils and those generally produced throughout the Southwest are largely of an asphaltic base, in contrast with the paraffin-base of the eastern states. The California oil usually contains also a considerable proportion of naphthenes and paraffins.[13]

Petroleum is a physical mixture of a large number of organic compounds commonly known as "hydrocarbons." The crude oil is broken up by distillation into a large number of fractions or distillates. The grouping of these is dependent on the nature of the crude oil, the distillation temperature and the number of degrees intervening between the points at which the fractions are cut. The lighter fractions include cymogene, benzene, naphtha, and gasoline, followed by the kerosenes and then the light lubricating oils. The commercial fractions are not, however, pure chemical compounds, but mixtures of two or more series.

The saturated hydrocarbons, the paraffins, have the general formula

$C_nH_{2n}+2$.* The members of this group are incapable of adding any more hydrogen atoms to the molecule; hence they are called "saturated." Included in this series are methane, ethane and propane. The naphthenes behave similarly to the paraffins in their lack of chemical activity.

The earlier work with petroleum as a plant spray was largely restricted to a study of physical attributes, but in recent years Fenske and other workers have made much progress in the study of petroleum chemistry and have developed certain physical and chemical properties useful in identifying and separating fractions containing principally molecules of similar size and type. A combination of fractional distillation and selective solvent extraction has been most useful in the separation and identification of various fractions.[24, 26] Refractive indices, of value in analytical work, are determined by the aid of the Abbe-type refractometer.[24, 30] The aniline point (reaction between oil and dry aniline at definite temperatures),[33] viscosity index,[27] gravity index and the boiling point index are shown to be of value in the examination of petroleum fractions.[28, 29]

### Specific Characteristics of Mineral Oils and Their Significance.

The mineral oils, both crude and refined, first used in the spraying of plants were defined by specifications developed for lubricating oil and kerosene.[28] They included density or specific gravity (Baumé), flash point, color, and sometimes viscosity. Such specifications or characteristics were found inadequate for defining oils to be used on plants in both the dormant and active states; hence it became necessary to develop specifications that would so define oils that refiners generally could produce the desired types. The more important ones developed or given added significance were those of unsulfonated residue,[10] oxidation,[19] viscosity,[45] and the distillation range or boiling point.[14] Certain other chemical and physical properties investigated during recent studies of petroleum oil have been applied by Pearce and co-workers to the selection of oils to be used as insecticides.[36, 37]

**Density.** The density or specific gravity of an oil is commonly expressed in degrees Baumé, or in recent technical papers as A.P.I.† Taken in connection with temperature changes it is an indication of the molecular weight. Its use distinguishes the volatile kerosenes from the relatively slow evaporating lubricating oils. The gravity of oils varies widely with the locality and the degree of refinement. Density is used in determining the refractive index, viscosity-gravity constant and the gravity index.

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* In this formula $n$ is used to indicate the number of atoms. A typical example of a saturated hyocarbons is ethane, which has the formula $C_2H_6$.

† The letters A.P.I. refer to the American Petroleum Institute, which was active in perfecting certain refinements in the measurements of the gravity of oil.

**Uusulfonated Residue.** A method of treating petroleum with concentrated sulfuric acid to separate the saturated hydrocarbons (naphthenes and paraffins) from the unsaturated hydrocarbons and aromatics is based on the difference in chemical activity of these two groups. The naphthenes and paraffins, being largely inert chemically, do not combine with sulfuric acid and are separated in this way from the other components of the crude distillate which have "sulfonated" or combined with sulfuric acid.

This test is now standardized[35] and has become the basis for an enormous expansion in the use of refined petroleum as an insecticide on plants. Its primary importance is as an indicator of plant tolerance, particularly where used in foliage applications. The sulfonation test in connection with other characteristics, including distillation, oxidation, volatility and viscosity, provides an accuracy of evaluation that is practicable and dependable.[10]

**Viscosity** is a measure of movement or flowability of an oil and to a certain extent an index of its molecular structure.[24] The viscosity of petroleum fractions, under varying temperatures, is not constant, but varies with the molecular weight and chemical structure. Such variations are stated in terms of a viscosity index.[27, 31] The importance of viscosity as a method of analysis has led to the development of capillary-type viscosimeters for making very accurate measurements as an aid in analyzing hydrocarbon oils.[25] Viscosity is of value for comparing oils derived from the same region, and taken with the distillation range it forms the basis for classifying western United States spray oils.[14] This system is not applicable, without modification, to the paraffinic oils of eastern United States.

The viscosities of lubricating oils are stated in the United States in terms of the Saybolt Universal viscosimeter, the readings being in seconds of flow at 100°F. The viscosity of kerosenes is measured by the Saybolt Thermo-viscosimeter, which bears no relation to the lubricating oil viscosimeter. Standard tables of viscosities are used for converting readings made on different types of viscosimeters.

Viscosity may be taken as an indicator of volatility, but the two characteristics are not synonymous. Variation is especially noticeable in a comparison of eastern and western oils. The refining process may change the viscosity of an oil materially while the volatility remains constant. Temperature changes in the field cause very great changes in viscosity, as shown in the following examples for certain western oils used as insecticides. An oil with a viscosity of 60 seconds Saybolt at 100°F may change to 146 seconds at 50°F and 48 seconds at 120°F. One of 98 seconds at 100°F may reach 780 seconds at 40°F. It is for this reason that dormant spray oils are now generally marketed at Saybolt viscosities not higher than 100 to 110. If more viscous oils are used at temperatures of 40 to 50°F they become incapable of satisfactory coverage.

Viscosity is an important characteristic of spray oils, as it affects coverage, film structure, penetration and translocation within the leaf structure and the body of the insect.[58]

**Distillation.** The fractional distillation of an oil at stated temperatures determines the quantity and density or "heaviness" of the fractions distilling between ranges of temperature at stated intervals. A standardized method has been developed as a guide for the preparation of plant spray oils.[32] Distillation is sometimes taken as an indicator of volatility and is very closely associated with this characteristic. Boiling points alone are, however, undependable as a basis for classification, as they vary with the structure of the hydrocarbon, including the length and number of side chains, aromatic and naphthenic rings, and unsaturation.[24]

Table 23. California State Department of Agriculture Distillation Rates of Samples of Petroleum Spray Oils Collected in 1941, 1942, and 1943

| Product | Year | Viscosity | ASTM Distillation | | | Per cent at 636°F. | Range |
|---|---|---|---|---|---|---|---|
| | | | 5% | 50% | 90% | | |
| | | | (Unsulfonated residue 92%) | | | | |
| | | (sec.) | °F | °F | °F | | °F |
| Light Medium | 1941 | 68 | 578 | 632 | 702 | 53 | 124 |
| | 1942 | 67 | 571 | 632 | 701 | 56 | 130 |
| | 1943 | 66 | 580 | 629 | 715 | 57 | 135 |
| | 1941 | 68 | 566 | 631 | 690 | 55 | 124 |
| | 1942 | 67 | 563 | 625 | 682 | 60 | 119 |
| | 1943 | 67 | 581 | 629 | 683 | 56 | 102 |
| | 1941 | 73 | 587 | 633 | 695 | 53 | 108 |
| | 1942 | 75 | 582 | 634 | 684 | 53 | 102 |
| | 1943 | 72 | 585 | 633 | 699 | 52 | 114 |
| Medium | 1941 | 74 | 588 | 644 | 720 | 42 | 132 |
| | 1942 | 76 | 586 | 642 | 713 | 44 | 127 |
| | 1943 | 75 | 583 | 640 | 730 | 47 | 147 |
| | 1941 | 75 | 564 | 648 | 730 | 44 | 166 |
| | 1942 | 73 | 557 | 639 | 724 | 48 | 167 |
| | 1943 | 73 | 591 | 645 | 715 | 43 | 124 |
| | 1941 | 76 | 582 | 643 | 707 | 45 | 125 |
| | 1942 | 73 | 581 | 637 | 696 | 48 | 115 |
| | 1943 | 73 | 586 | 641 | 693 | 45 | 107 |
| | 1941 | 79 | 596 | 643 | 701 | 42 | 105 |
| | 1942 | 80 | 600 | 639 | 691 | 45 | 91 |
| | 1943 | 78 | 591 | 640 | 700 | 45 | 109 |
| Heavy Medium | 1941 | 84 | 603 | 651 | 706 | 34 | 103 |
| | 1943 | 84 | 604 | 649 | 710 | 35 | 106 |

The official California regulation governing the classification of western type spray oils grouped as shown in Table 23 is as follows:

"**Sec. 1. Foliage Spray Oils**

Any mineral oil or petroleum oil sold to be applied on foliage for use in pest control, whether or not mixed with other materials, shall be labeled both with the minimum guaranteed percentage of unsulfonated residue as determined by the California State Method, and with the Grade or Class in which it belongs as follows:

*Light*

64 to 79% of the oil distilling at 636°F. Minimum Unsulfonated Residue 90%

*Light Medium*

52 to 61% of the oil distilling at 636°F. Minimum Unsulfonated Residue 92%.

*Medium*

40 to 49% of the oil distilling at 636°F. Minimum Unsulfonated Residue 92%.

*Heavy Medium*

28 to 37% of the oil distilling at 636°F. Minimum Unsulfonated Residue 92%.

*Heavy*

10 to 25% of the oil distilling at 636°F. Minimum Unsulfonated Residue 94%.

"**Sec. 2. Dormant Spray Oils**

Any mineral oil or petroleum oil sold to be applied to dormant trees or plants for use in pest control, whether or not mixed with other materials, shall be labelled with the minimum guaranteed percentage of unsulfonated residue as determined by the California State Method. Statement of the Class is not required, but if the Class is given, it shall be determined by the percentage distilling at 636°F as follows:

*Dormant Light*

64 to 79% of the oil distilling at 636°F.

*Dormant Light Medium*

52 to 61% of the oil distilling at 636°F.

*Dormant Medium*

40 to 49% of the oil distilling at 636°F.

*Dormant Heavy Medium*

28 to 37% of the oil distilling at 636°F.

*Dormant Heavy*

10 to 25% of the oil distilling at 636°F."[14]

**Oxidation.** Petroleum distillates are subject to the action of air and sunlight. The added acidity developed in this way is due to an oxidation process depending on the character of the oil, the amount and type of unsaturates present, temperature, intensity of light and the presence of oxygen. Acidity is produced in measurable amount, and if the reaction is prolonged a black precipitate results. Highly refined oils, which are resistant to the action of concentrated sulfuric, may be sensitive to oxidation reactions, perhaps because certain natural inhibitors have been removed during the refining process and possibly the character of the molecule changed by the acidic reaction. Spray oils, exposed as they are in thin films on foliage and within the leaf, may develop sufficient acidity to cause noticeable injury to foliage, as shown in Figure 6. Unoxidized oils applied in the same way to peach foliage were neutral in their effect.[19] Such results, in slight degree, may appear within 5 to 15 days after application, but injury of this type is much less common than has been suggested.[20] Oxidation of spray oils on foliage is modified by volatility, rate of penetration and translocation within the leaf itself. Properly refined foliage types of spray oils are neutral when applied, and it is only by prolonged exposure to air and sunshine or shorter exposures at high temperatures, that significant amounts of acid are developed, as will be noted in Tables 24 and 25.[21]

Table 24. Oxidation of Oils by the Sligh Method

| Oil No. | Oils used | Unsulfonated Residue | Organic Acid Expressed as Mg. Sodium Hydroxide per gm. Oil | | |
|---|---|---|---|---|---|
| | | | Check (mg.) | 1 hr.* (mg.) | 2½ hr. (mg.) |
| 1 | White western oil | 98 | — | — | 0.18 |
| | Oil #1 plus 10% $SO_2$ extract from kerosene | | 0.022 | 0.32 | 1.20 |
| | Oil #1 plus 1% $SO_2$ extract | | 0.010 | 0.24 | 0.62 |
| | Oil #1 plus 0.1% $SO_2$ extract | | — | — | 0.14 |
| 2 | Eastern stock white oil | 99 | — | 0.006 | 0.12 |
| | Oil #2 plus 10% $SO_2$ extract from kerosene | | 0.026 | 0.35 | 0.96 |
| | Oil #2 plus 1% $SO_2$ extract | | 0.012 | 0.16 | 0.52 |
| | Oil #2 plus 0.1% $SO_2$ extract | | — | — | 0.08 |

* Exposure time at 150°C.

Table 25. Oxidation of Oils by Direct Sunlight (Maximum temperature 65° to 74°F) (15-day exposure)

| Oil No. | Oils Used | Unsulfonated Residue | Organic Acid Sodium Hydroxide mg. per gm. Oil |
|---|---|---|---|
| 1 | White oil | 99 | 0.04 |
| 2 | " " | 98 | 0.10 |
| 3 | " " | 97 | 1.28 |
| 4 | " " | 98 | 1.36 |

Nos. 1 and 2 correspond to the same numbers in Table 27.

Oils No. 1 and 2 are the same in both tables. In addition in Table 25, two oils are included that are known to be decidedly susceptible to oxidation. All samples were neutral at the beginning of the experiments and highly refined, as shown by a range of unsulfonated residue of 97 to 99 per cent. To determine the effect of the presence of unsaturates, measured amounts were added of the residue obtained by the refining of kerosene with liquid sulfur dioxide (commonly known as the Edeleanu process).

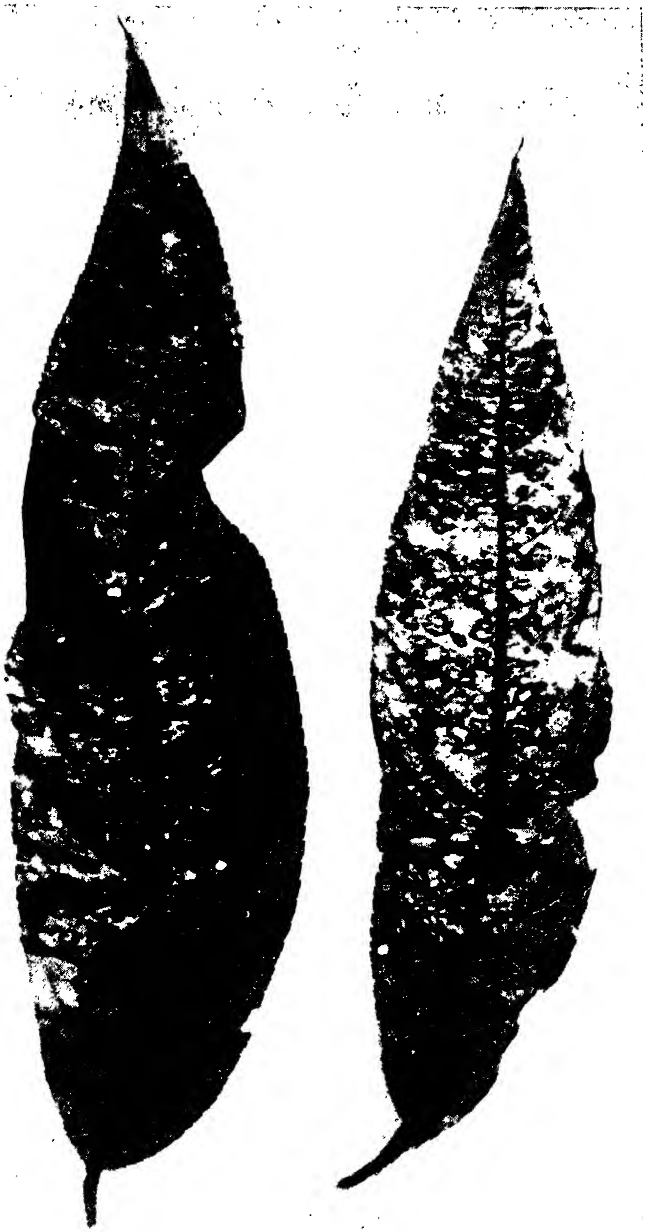

FIGURE 8. Peach leaves treated with refined mineral oil oxidized in two ways. (*right*) Oil heated to 150° C for 2 and ½ hours. (*left*) Oil exposed in open dish to sunlight for 15 days. Leaves treated with the same oil unoxidized were normal. Photographed 10 days after application.

This method of refining segregates the unsaturated hydrocarbons, including olefins, aromatics, sulfur and other impurities, with the least chemical reaction of any commercial method of purification. In these and other experiments the unsaturated residue, obtained by refining operations, is added to the saturated compounds whenever it is desired to compare the action of the two groups, or to simulate unrefined distillates.[46]

The oils and blends in Table 24 were heated for 2½ hours at a temperature of 150°C (302°F) in an oxygen atmosphere. The procedure known as the Sligh test has been developed as a standard practice of testing the rate of oxidation of refined petroleum oils.[18]

The oil samples used in Table 25 were exposed to direct sunlight in uncovered Petri dishes for 15 days. Each dish contained about 20 ml. of the oil indicated. Discoloration, comparable to the degree of acidity developed, was noted.

The effect on peach foliage of the oils oxidized by the two methods is seen in Fig. 8. Unoxidized oils applied in a similar manner to the same type of foliage showed no abnormal effect.

The problem of the oxidation of plant spray oils has been met by the oil refiner in a number of ways:[34] (1) selecting refined oils which show the greatest stability or resistance to oxidation; (2) oxidizing oils followed by repeated neutralization with alkali[36]; (3) adding artificial inhibitors of oxidation, including amines, certain organic sulfur compounds, and halogen and phenolic derivatives.[12]

**Volatility.** This property is closely associated with distillation or boiling range. The two types of plant spray oils, light lubricating oils and kerosene are separated on the basis of volatility, which varies widely, as seen in Table 26.[21]

The total loss of oil in 49 days from No. 2, a commonly used plant spray oil, is only 0.09 gram from a total weight of 2.328 grams. Such an insignificant loss in 49 days' exposure, in a film structure, throws doubt on the significance of volatility as an important factor in the disappearance of the lubricating-oil type of film from the surface of leaves and twigs. A very great contrast is seen in the volatility of the kerosene type, where 84.1 per cent is lost in 8 days, much of the loss occurring in the first 24 hours. A similar difference is noted in the insecticidal action of the two oils. Kerosene volatilizes so quickly that it is ineffective against most insect eggs and resistant scale insects. The light lubricating oil both penetrates the leaf structure and persists in the form of a film over the leaf surface, thus acting over a period of days and weeks both as a toxic agent and as a repellent. The persistence of the film favors penetration into the eggs of insects and mites and closely attached forms such as scale insects and mealy bugs.

The effect, if any, of humidity on the evaporation rate of oils was determined by passing wet and dry air through samples of the same oil and determining the loss of oil by weighing. The oil used had a viscosity of 105 seconds Saybolt and an unsulfonated residue of 98 per cent. The total loss in weight of oil, irrespective of the absorption of water, was 12.5 mg. for the dry air and 12.3 mg. for wet air. It was also found that the oil had absorbed 0.0106 gram of water per 9.12 grams of oil, or 0.11 per cent of water.

Table 26. Volatilization of Light Lubricating Oils and Kerosene
Temperature Range 14 to 23°C (55 to 73°F)
Duration of test 49 days

| Oil No. | Viscosity* | Amount of oil used (grams) | Days exposed | Loss of oil (gram) | Loss per day (mg.) |
|---|---|---|---|---|---|
| 1 | 106 | 1.848 | 8 | 0.0092 | 1.5 |
| | | | 21 | .0160 | 0.762 |
| | | | 12 | .0080 | 0.666 |
| | | | 8 | .0062 | 0.775 |
| 2 | 70 | 2.328 | 8 | .0108 | 1.35 |
| | | | 21 | .0555 | 2.64 |
| | | | 12 | .0167 | 1.39 |
| | | | 8 | .0105 | 1.31 |
| 3 | 330 | 2.125 | 8 | .0022 | 0.275 |
| | | | 21 | .0032 | 0.152 |
| | | | 12 | .0016 | 0.133 |
| | | | 8 | .0004 | 0.05 |
| 4 (kerosene)** | 345 | 2.488 | 8 | 2.0945 | 262. |
| | | | 21 | 0.3676 | 17.5 |
| | | | 12 | .0172 | 14.25 |
| | | | 8 | .0028 | 0.35 |

* Determined by the Saybolt viscosimeter at 100°F.

** Kerosene viscosity determined by Saybolt Thermoviscosimeter.

It is concluded that oil of the volatility used loses equal amounts by evaporation in either dry or wet air; it is also concluded that oil such as the sample used will absorb as much as 0.11 per cent of water from air with 100 per cent humidity.[21]

**Acidity.** Unrefined mineral oil usually contains small percentages of organic acids. Such acidity, measured in equivalents of standardized potassium hydroxide, may not be more than a few milligrams per liter and is easily neutralized by an alkaline wash. Mineral oils refined to the degree necessary to make them safe to use on plants in foliage should not show an appreciable degree of acidity. Oils for use in dormant application should not contain more than a fraction of one per cent of acid.

As previously mentioned, the acidity value of an oil is not a constant factor, but may increase to a dangerous degree after the oil has penetrated into the leaf and under natural field conditions.

**Sulfur.** Sulfur, except certain organic forms, is considered a hazard to the plant. Elemental sulfur, in the experience of the author, may be injurious under certain conditions even in amounts as low as 0.05 per cent. However, the usual refinery practice necessary to raise the unsulfonated residue to a satisfactory point reduces the sulfur to a negligible point in most instances.

## Mineral Oil as an Insecticide

Petroleum or "mineral" oil is an active insecticide, especially in the crude and slightly refined states. Such oil fractions are, however, used for treating poultry houses and similar work, or in a limited way for trees in the dormant stage. The usual high content of the chemically active unsaturated hydrocarbons, organic acid and sulfur in unrefined petroleum make such oils unsafe to use on growing plants and to a large extent on animals. These natural hindrances to the use of petroleum as insecticides have been largely overcome by refining, the process leaving the oil in a bland condition more tolerable by plants and animals, without greatly affecting the physical qualities. The inherent toxic value of petroleum may in certain instances be increased by the addition of oil-soluble chemicals, including nicotine, rotenone, pyrethrum extract, and copper, by which both the insecticidal and fungicidal activity is increased.[72, 73, 93, 94, 138]

The value of mineral oil in spray applications is not alone that of an insecticide but includes a number of valuable physical qualities which are only slightly modified by refining, namely, low surface tension, high solubility and penetrating power. The low surface tension of oil increases the wetting and spreading ability, thus favoring coverages. Oil is especially active as a wax solvent, which is decidedly helpful in spraying and dipping, since most leaves, twigs and fruits, as well as animal hair and wool, are wax-coated. Only liquids which can dissolve or wet a waxy or oily surface can spread uniformly over it. Oils have also a penetrating power greatly superior to water, thus being able to penetrate the minute breathing tubes of insects and the stomata of leaves.

Restrictions on the general use of mineral oils as plant sprays being largely overcome by selection according to the unsulfonated residue test,[10] the way is open for further studies of the chemical and physical properties of the various fractions in relation to their value as insecticides. These properties, varying as they do with the producing sections (differences in volatility of the paraffinic and naphthenic oils and wide fluctuations of viscosity within the range of field temperatures) have led to confusion in the interpretation of results, especially from lack of opportunity for basic studies. Progress in the understanding of petroleum chemistry and the use of physicochemical tests in the selection of fractions is being reflected by improvements in efficiency. A contribution has been made by Chapman *et al.*[36] on the comparative ovicidal value of paraffinic and naphthenic oils, including reference to the unsulfonated value of the oils. Unfortunately the fact that eastern oils (paraffinic) are less volatile, for a given viscosity, than western oils (naphthenic) was not considered, nor were corresponding differences in the ovicidal value for these two types of oils. Comparative ovicidal tests of paraffinic and naphthenic oils are needed

Table 27. Specifications[a] of Oils Tested

| Oil No. | Gravity[b] (°A.P.I.) | Flash point[c] (°F) | Fire point (°F) | Viscosity in seconds[d] at 100°F | Color[e] | Sulfur (%) | Unsulfonated residue of oil |
|---|---|---|---|---|---|---|---|
| | | | *Lubricating Oils* | | | | |
| 1 | 19.2 | 305 | — | 105 | — | 0.7 | 51 |
| 2 | 21.3 | 310 | 350 | 99 | — | .65 | 52 |
| 3 | 22.5 | 310 | 350 | 96 | 6 | 6 | 56 |
| 4 | 22.7 | 320 | 360 | 107 | 2.5– | 6 | 60 |
| $4^x$ | 22.7 | 320 | 360 | 100–110 | 1.5 | 6 | 62 |
| 5[h] | 29.8 | 320 | 360 | 106 | plus 25[f] | .006 | 98 |
| $5^x$[h] | 28–31 | 280 plus | — | 70–80 | plus 25[f] | .015 | 98 |
| 6 | — | 360 plus | — | 330–340 | 3.0 | 6 | 58 |
| | | | *Kerosenes* | | | | |
| $1^a$ | 35.9 | 124CT[g] | — | 375 | — | — | 81 |
| $2^a$ | 41. | 83CT | 125 | 320 | plus 25[f] | 0.016 | 82 |
| $3^a$ | 41.3 | 113CT | 135 | 345 | plus 25[f] | .010 | 93 |
| $4^a$ | 43.3 | 143CT | 175 | 400 | plus 25[f] | .006 | 98 |

[a] The pour point on all oils used was below 0°F.

[b] The A.P.I. (American Petroleum Institute) gravity table is similar to the Baumé gravity table and for all practical purposes they may be considered identical for lubricating oils.

[c] Cleveland open cup.

[d] Viscosity of lubricating oils determined by the Saybolt Universal viscosimeter. Viscosity of kerosene fractions measured by the Saybolt "Thermoviscosimeter" which bears no relation to the lubricating-oil viscosimeter.

[e] A.S.T.M. standards.

[f] A.S.T.M. standards for kerosene by Saybolt colorimeter; the color number plus 25 is an arbitrary value given to the most highly refined kerosenes.

[g] Closed Tagliabue Tester.

[h] Numbers 1 to 4x, inclusive, are samples of commercially distilled petroleum oil fractions showing the changes through varying degrees of refinement as indicated principally by the unsulfonated residue readings. Numbers 5 and 5x are highly refined white oils, used in plant spraying and differing in viscosity. Note the increase in gravity through the refining process. Number 6 is a commercial lubricating oil of high viscosity and low degree of refinement. Numbers 1a to 4a inclusive are kerosenes of varying degrees of refinement, as indicated by the unsulfonated residue readings and the change in gravity.

on oils of similar distillation ranges, the latter having correspondingly higher viscosities than the paraffinic oils. Further studies, of a well rounded nature, are necessary on the chemical and physical attributes of mineral oil, including both paraffinic and naphthenic types, before the insecticidal values can be correctly judged.

In a study of mineral oil fractions to determine the insecticidal values, a series of distillates was used with specifications as given in Table 27.[58]

Table 28. Toxicity of Oils to the Eggs of the Clover Mite *Bryobia Praetiosa* (Applied June 10th, Read June 18th)

| Oil No. | Viscosity* | Concentration of oil (%) | Larvae alive | Number of eggs | Dead (%) |
|---|---|---|---|---|---|
| 4 | 107 | 2 | 0 | 424 | 100.0 |
| 4 | | 2 | 2 | 355 | 99.5 |
| 4 | | 3 | 1 | 123 | 99.2 |
| 5 | 106 | 2 | 69 | 860 | 92.6 |
| 5 | | 3 | 2 | 750 | 99.8 |
| 3a | 320 | 3 | 65 | 194 | 66.5 |
| 3a | 400 | 10 | 18 | 185 | 90.3 |
| Untreated | | | 185 | 190 | 2.7 |

* Numbers 4 and 5 (see Table 27) are lubricating oils with a Saybolt standard viscosimeter reading. Number 3a is a kerosene with viscosity determined on the Saybolt Thermoviscosimeter. The latter instrument bears no relation to the lubricating-oil viscosimeter.

Table 29. Relation of Viscosity of Oil to Its Effect on Red Scale[1]

| No. of test | Description | Viscosity | Percentage of oil in emulsion | Per cent scale surviving test[2] | Remarks |
|---|---|---|---|---|---|
| 1 | No. 6, a heavy lubricating oil | 364 | 2 | 0.0 | |
| 2 | No. 5, (Table 27) | 100 | 2 | 0.0 | |
| 3 | A special light lubricating oil (specifications not given) | 38 | 2 | 2.0 | This oil was just below the lethal viscosity limit. |
| 4 | No. 4a, a refined kerosene. | 400 | 20 | 19.0 | Viscosity determined by Saybolt Thermoviscosimeter. |

[1] California red scale *Aonidiella aurantii*.

[2] The basis for scale counts ranged from 200 to 600 insects.

These were commercially distilled and refined fractions in which increasing amounts of sulfuric acid were used during the refining process. The unsulfonated residue, it will be noted, changes with each acid treatment, as does also the gravity. The most hightly refined, Nos. 5, 5x and 4a, not only have a very high unsulfonated residue value but are neutral and almost entirely free of sulfur.

The striking difference between light lubricating oils and kerosene, as discussed under distillation, viscosity and volatility, is shown in the data in Tables 28[21] and 29.[58] The greater efficiency of lubricating oils is due both to their direct action as an ovicide and to the residual film of oil on the leaf and twig surface, together with that which has penetrated into the leaf structure. The oil film has a lethal action on the newly hatched larval stage of the mite, while the oil present in the leaf structure has a repelling action. The kerosenes, because of their volatility, do not produce such toxic films and what little enters the leaf is soon dissipated by evaporation or translocation.

The superiority of lubricating oils over kerosene is again shown in Table 29, using the Red Scale, *Aonidiella aurantii*, as the test insect. This is a very difficult insect to control either by spraying or fumigation. Neither the "light" grade lubricating oil nor kerosenes will give satisfactory control. In commercial practice the light medium to heavy grades of oil are used (see discussion under Distillation) in preference to the light grade of oil. The heavier oils are used with slightly more hazard to the Citrus tree, which must be balanced against scale injury.

Table 30. Oil Fumigation* with Kerosene and Lubricants
(Test Insect: Ladybird beetle, *Hippodamia convergens*)

| Oil used | Viscosity | Unsulfonated residue | Beetles dead<br>2 days (%) | 4 days (%) | 6 day (%) | 8 days (%) | 9 days (%) |
|---|---|---|---|---|---|---|---|
| 1a Kerosene | 375‡ | 81 | 23.1 | 42.3 | 92.3 | 100 | 100 |
| 2a " | 320 | 82 | 33.3 | 91.6 | 100. | 100 | 100 |
| 3a " | 345 | 93 | 7.7 | 57.3 | 96.0 | 100 | 100 |
| 4a " | 400 | 98 | 3.4 | 21.0 | 69.0 | 100 | 100 |
| 1 Lubriccant | 105§ | 51 | 4.5 | 13.7 | 41.9 | 54.5 | 94.3 |
| 2 " | 96 | 56 | 0.0 | 3.5 | 7.1 | 14.2 | 17.5 |
| Control | — | — | 0.0 | 0.0 | 4.1 | 20.0 | 28.0 |

* Temperature range 46°-78°F.

† Number of days elapsing between observations of test beetles.

‡ Kerosene viscosity determined on the Saybolt Thermoviscosimeter.

§ Lubricant " " " " " Universal viscosimeter.

Other tests used in evaluating the insecticidal action of oils included fumigation of insects in closed containers and immersion of the test insects in the various fractions. It is recognized that such exposures are artificial in character and not comparable with field conditions. They do, however, eliminate certain variants of treatment that occur in both laboratory and field applications. The variants include imperfect coverage, changes in film structure, loss by evaporation and penetration, diurnal changes in the viscosity of the oil, influence of the emulsifier and minimum effects of oxidation on the oil.

In the fumigation experiments the test insects, ladybird beetles, *Hippodamia convergens*, are exposed over 5 ml. of the oil used and all are enclosed in tightly stoppered glass cylinders (for additional oil specifications see Table 27). A striking difference is noted in the lethal action of kerosenes and lubricating oils, as would be expected from their respective rates of volatility. Lethal action is correlated with the unsulfonated residue value. Kerosene 2a has had a slight refinery treatment, as indicated by the unsulfonated residue test, but having a lower boiling point than 1a, the increased volatility may account for the greater toxicity.[21]

Table 31. Time Required to Kill Beetles* by Immersion in Oil

| Oil used† | Unsulfonated residue | Number of seconds in exposure period | | | | | | | | | | | | | | Total No. Beetles |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15–20 | 21–30 | 31–40 | 41–50 | 51–60 | 61–70 | 71–80 | 81–90 | 91–100 | 101–120 | 121–140 | 141–180 | 181–280 | 400 | |
| | | *Number of beetles dead* | | | | | | | | | | | | | | |
| 1 | 51 | 1 | 8 | 9 | 12 | 22 | 16 | 17 | 9 | 13 | 6 | | | | | 113 |
| 2 | 52 | | 45 | 42 | 8 | 3 | — | 2 | — | | | | | | | 102 |
| 3 | 56 | 16 | 75 | 7 | 1 | — | 1 | | | | | | | | | 100 |
| 4 | 60 | — | 5 | 8 | 8 | 41 | 19 | 8 | 8 | 1 | 9 | 3 | 1 | 1 | | 112 |
| 5 | 98 | | | 2 | 11 | 2 | 8 | 10 | 8 | 35 | 15 | 5 | 7 | 5 | | 107 |
| 5x | 98 | | | | 15 | 8 | 2 | 14 | 14 | — | 16 | 7 | 7 | 23 | 1 | 107 |

* Test insect ladybird beetle *Hippodamia convergens*.

† For specifications of oils used see Table 27.

Immersion experiments with the beetles, *Hippodamia convergens*, using the series of lubricating oils with graduated unsulfonated residues, show a correlation between these values and the time required to cause death in the data of Table 31.[21] Confirmation of the slow lethal action of oils with a high unsulfonated residue is shown by de Ong *et al.*[58] Ebeling reports confirmation of the correlation between lethal action and the unsulfonated residue in similar experiments with the larvae of the potato tuberworm, *Gnorimoschema operculella*, but also cites data of a conflicting nature with experiments on other types of insects.[59]

**Dormant Sprays.** Crude oil and slightly refined petroleum distillates[1, 2, 8, 39, 40] were at one time the principal dependence of the orchardist for winter spraying. These were largely displaced by "miscible oils" and commercial emulsions of oils with some degree of refinement. The term "miscible oils"[17, 39, 40] was applied to oils in which a cresylic or carbolic acid soap had been dissolved as the emulsifier, but containing a relatively small amount of water. The "miscible" or "soluble" oil retains its oily appearance, but with the addition of more water assumes the opaque appearance of oil emulsions. Miscible oils usually contain a relatively high content of oil, ranging from 75 to 90 per cent. The emulsion formed is of a decidedly stable character.

Following the work of Yothers[4] on the use of lubricating oil on Citrus trees, "red engine oil"[5] came into general recognition as a dormant spray in the control of San Jose sçale, *Aspidiotus perniciosus.* The emulsion was made by the "boiled process" using a potash fish-oil soap. The difficulty of using soap emulsifiers in hard water and the inconvenience of cooking led to the use[6] of casein, copper sulfate-lime and other emulsifiers in the preparation of lubricating-oil sprays on apples and peaches. The use of the latter types of emulsifiers obviates the need of cooking, the process being spoken of as the "cold-stirred" method. Lower concentrations than 3 per cent show appreciable reductions in the kill of San Jose scale. Oil sprays on the apple[42] in the Pacific Northwest are similar to those used on the peach,[41] except that a 4 per cent concentration of oil is recommended. For heavier infestations, concentrations up to 6 and 8 per cent are used. The same application[43] that is used for San Jose scale is fairly satisfactory in killing the eggs of tree hoppers,* leaf rollers,[44] *Cacoecia argyrospila*, and European red mites. Petroleum oils, when properly emulsified, are generally considered safe to use on dormant trees at concentrations of 2 to 4 per cent. Varietal exceptions to this rule have been noted[47] in the case of sugar maples and black walnut. Further ovicidal tests on the fruit-tree leaf roller, *Caeoecia argyrospila,* are reported with a paraffinic type of oil; the amount deposited is taken as the criterion of efficiency, 1.5 mg. of oil per square inch of bark being given as the minimum deposit to control this insect.[16] Factors affecting the oil deposit include concentration of oil, quantity applied, type of emulsifier, size of the oil droplet in the emulsion as governed by the apparatus used in mixing the emulsion, and the amount applied per tree.[15] Studies of the composition of oils from various regions commonly used for dormant spraying have indicated the superiority of paraffin structures to aromatics as ovicides.[37]

The viscosity of oils used for dormant spraying ranges from 85 to 110 seconds Saybolt. Dormant spraying is usually done at temperatures of 30 to 60°F which in itself changes the viscosity decidedly.

For winter spraying, oil refinement is of less significance than are climatic conditions and degrees of dormancy. In districts where low winter temperatures produce a true dormant condition of deciduous trees, oils with an unsulfonated residue of 55 to 60 per cent are often safely used at tem-

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* About 15 different species are present in the orchard; only *Ceresa bubalus, Stictocephala inermis*, and *C. basalis* are thus far recognized as common enough to be of economic importance.

peratures of 35 to 55°F. Variations and retardations in the growth of apple twigs following oil applications have been noted.[51] Temperatures of 70°F and above increase the hazard, and at such times an unsulfonated residue of 70 per cent is safer. Winter spraying with oil is safer after the danger of zero weather is past.[53] In regions of comparatively high winter temperatures, it is considered safer to use oils of 65 to 70 per cent unsulfonated residue, since spraying frequently extends into the period of growth. Recommendations for dormant spraying naturally vary with the variety of tree. Early blooming varieties, such as the almond, cherry, and plum, require spraying in midwinter, while the apple may be treated at a later period. The French prune is especially sensitive to oil applications as shown by variations in the blooming date[48, 50] and increased growth or "stimulation" of the foliage in the spring following certain of the applications. This series of sprays was applied every two weeks from November 15 to March 15, using a 6 per cent concentration of oil. Retardation of bloom resulted from the November spraying, but the first spraying in December had no noticeable effect on the tree. Stimulation, as manifested by an earlier bloom, resulted from the late December and January sprays. February spraying retarded bloom and foliage, and injury resulted from March applications with the leaf buds opening.

Freezing temperatures and dry soil or drying winds are associated with oil injury. A comparison of the effect on dormant trees of oils of an unsulfonated residue of 53 to 56 per cent, and the effect of comparatively high and low temperatures (30 to 70°F) showed[49] a greater difference from the variable temperatures than from the degrees of refinement used. Trees growing in dry soil were much more severely injured, especially by freezing temperatures, than were those growing in moist soil. Field observations confirmed these findings and established the rule that oil sprays should not be applied to trees growing in dry soil or immediately after drying winds. Oil should not be applied in the late winter and early spring at maximum temperatures of 70°F or above.

The need of an oil for use in the intermediate stage between dormancy and foliage has led to the development in England of the following specifications for such purposes:[52]

(a) Boiling range: not less than 90 per cent by volume to distill above 315°C (590°F), 50 per cent above 350°C (653°F), and 20 per cent above 380°C (707°F).

(b) Viscosity: not less than 100 seconds and not greater than 400 seconds Redwood 1 at 70°F.*

(c) Specific gravity: 0.86–0.92 at 60°F.

(d) Unsulfonated residue: not less than 80 per cent by volume.

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* 100 seconds Redwood 1 at 70°F equals 68 seconds Saybolt at 100°F.
400 seconds Redwood 1 at 70°F equals 165 seconds Saybolt at 100°F.

**Foliage Sprays.** The use of mineral oil fractions on fruit trees and other plants has become a general practice with the development of highly refined light lubricating oils. Oil sprays are commonly included in the second and third codling moth sprays, in combination with lead arsenate, on apples in the northwestern districts. The oils used have a viscosity range of 50 to 70 seconds Saybolt[54, 55] with an unsulfonated residue of 85 per cent and higher. The heavier the oil the higher the unsulfonated residue should be. Oils with a viscosity of 100 to 110 seconds Saybolt reduced the size of the fruit and in many instances produced a darkened area around the calyx of Rome Beauty apples, a brown spotting on the variety Jonathan and russetting on the Yellow Newton.[54] The use of less viscous oils (50 to 70 seconds) has almost entirely prevented such injury. The grouping according to distillation range is from light to light medium. Concentration of the oil is usually 0.5 per cent.

Experiments are reported by Chapman *et al.*, with certain petroleum fractions in controlling the oriental fruit moth, *Grapholita molesta*, the eye-spotted bud moth, *Spilonota ocellana*, and the codling moth on apple trees. Paraffinic oils, as in dormant spraying, are stated to be more effective as ovicides than the naphthenic type. Concentrations of oils giving the greatest efficiency ranged from 0.25 to 1.0 per cent. The oil deposit for this range was from 25 to 32.5 mg. per 100 square inches and upward.[36]

In codling moth control oil sprays are seldom used alone, but rather combined with lead arsenate. Such combinations vary in compatibility, depending on the stability of the arsenical and the emulsifier used in the oil. Unless compounded especially for combination with arsenical sprays, soap should also be used sparingly because of the danger of freeing arsenic. The addition of one-half to one pound of hydrated lime to each 100 gallons of spray is recommended.[56]

The action of mineral oil in codling moth control is largely that of an ovicide. The principal value is on eggs present at the time of application although partial control is obtained on eggs deposited within a few days after the application. The action of the larval stage is not so marked. Besides supplementing the arsenicals in codling moth control work, oil sprays check leafhoppers, aphids, European red mites, and the San Jose scale in the immature stage. Mineral and other oils also control pear *Psylla pyricola*,[57] especially when combined with nicotine.

The applications of mineral oil to Citrus trees has led to a high degree of specialization, due to the variety of scale insects present and the climatic extremes under which the work is done. The range of refinements and the viscosity tolerated by Citrus trees was first determined[58] in California, and modifications of this system have spread throughout the world. The distillation range or boiling point is used as a supplement to visosity and largely in place of volatility. This specification is especially valuable in indicating the proportions of light and heavy fractions in blended oils.[61] Oils for use on Citrus trees are grouped from light to heavy grades (1 to 5).[14] Data on the use of oils in commercial groves show results similar to those noted on apple in codling moth control, namely, that oils of a viscosity of 100 to 110 seconds Saybolt may produce a retarding effect on the tree, although the long-continued, rather high temperatures minimize the effect. Viscosities of 50 to 75 seconds are generally used for most infestations.[61] Distillation ranges for oils usable on Citrus trees ranges from 80 per cent distilling at 636°F (335.5°C) for European red mite to 18 to 30 per cent distilling at 636°F for resistant forms of scale (to be used on lemons only). The oils used for general work in scale control have a distillation range of 45 to 50 per cent at 636°F. Reports of ten years' records of commercial oil sprayings on oranges show little or no deterioration of the tree,[63] although the belief that frequent oil applications are injurious is gaining among the fruit growers.

**Effect of Mineral Oil on Plants.** Liquids of low surface tension, such as oils and possibly their emulsions, readily penetrate very small apertures such as the stomata (breathing pores) of leaves and the tracheal openings of insects, where liquids of higher surface tension, such as water, cannot enter. Oils penetrate leaves principally through the stomata,[1] but entrance also occurs through the epidermis.[91–97] It has been the author's experience, confirmed by Young and Morris,[98] that the rate of penetration is largely dependent on viscosity, modified by field temperatures. Oils applied on the under side of the leaf only penetrate more rapidly than on the upper side because of the greater abundance of the stomata on the lower side. Microscopic studies of oil within a living leaf have shown that the lighter lubricating oils and kerosene move through the water tubes or tracheids as tiny globules of oil. More viscous oils (100 to 120 seconds Saybolt) clog these tubes and prevent the oil from being translocated, leaving it fixed in the leaf blade. Kerosenes may enter the leaf structure, both through the stomata and the epidermis, within a few hours, whereas the period of penetration of lubricating oils of viscosities of 100 to 110 seconds Saybolt may extend over days. The ease of translocation of the very light oils within the structure of leaf and twig is also closely related to the viscosity of the oil.* The movement of oil within the Citrus tree has been shown

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* Laboratory studies of the author's at 65 to 75°F have shown that kerosene penetrates the leaf of nasturtium (*Tropollium sp.*) through the tracheal tubes in two hours. The same degree of penetration on mature apricot leaves required six hours. In a comparison of the rates of penetration highly refined oil of 240 seconds Saybolt, the following differences were noted: In 14 hours kerosene had penetrated

by Knight[91] to be first penetration into the vascular system of the leaf, and then translocation into the storage tissues, pith and xylem parenchyma of the twigs. The slowness with which viscous oils move through plant tissue and the length of time required for translocation to less vital parts of the plant explain the greater injury frequently associated with the use of heavy oils. The penetration of spray oils into foliage may be retarded to a limited extent by the addition of such organic substances as triethanolamine oleate, glyceryl oleate, glyceryl monoöleate, and glycol monoöleate.[92]

The presence of mineral oils of moderate or high degree of refinement (85 to 100 per cent unsulfonated residue) has a physical rather than a chemical reaction. Acute tissue injury seldom occurs in oil-soaked foliage unless oils are used which contain organic acids, dissolved sulfur or other active ingredients, which favor oxidation and thus form dangerous concentrations of organic acid, as illustrated in Figure 8. The physical effects of mineral oils, especially the more viscous ones, within the tissue of leaves are disturbances which include a lowering of the transpiration rate of water;[91] prevention of the movement of gases, including carbon dioxide and oxygen, through the cell walls;[62] and a reduction in the amount of starch normally produced. The latter effect has been shown, by applications of pure oil, to check all starch formation in the leaves affected for weeks at a time, or until the oil is largely eliminated.[21] Pure oils are of course not applied to foliages unless as a fine mist; but a somewhat similar condition may result from too frequent applications of viscous oils, which tend to accumulate in the leaf. A general tendency of this type will hinder starch production to such a degree as to stunt the growth of a crop of fruit as well as buds for the following year. One or two sprayings in a season with oils of moderate viscosity and of the lighter grades seem to have but little, if any, effect on the feeding or photosynthetic power of a tree. The slight retardation of starch formation, under the latter type of application, is rather comparable to that of a few days of continuous cloudy weather. Marked influence on the respiratory rate of the plant has also been noted[91, 95], but this varies with the state of activity. The apple tree in the dormant season showed[96] an acceleration of respiration, but

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the vascular bundles of the apricot leaf and was entering parenchyma while the heavy oil had entered the intercellular spaces; in 17 hours kerosene had diffused through the parenchyma bundles. The path of penetration was through the stomata into the intercellular spaces, thence to the vascular bundles and the parenchyma. The oil present in the vascular bundles formed first a continuous and then a broken stream of oil, with alternate bubbles of oil and water. In the parenchyma cells the oil was diffused in the protoplasm. Viscous oils penetrated more slowly and less uniformly than kerosene. Two per cent emulsions of kerosene did not penetrate leaves as did the pure oils.

in the delayed dormant season when the leaves were unfolding the respiratory rate was retarded. Applications of oil to the leaf and foliage of the apple resulted in injury largely correlated with the degree of unsulfonated residue.[97, 98]

The effect of the relative humidity in which the plant is growing on the absorption of oil has been found by different workers to vary, it being claimed[1] that low humidity favors penetration of oil, and also that[96] the greatest injury occurs at high humidities. This variation in conclusions apparently results from the extremes of humidities under which the different investigations were conducted. Trees exposed to drying wind with relative humidities of 10 *to* 30 per cent wilt to such a degree that oil penetrates freely. Continued exposure to humidities of 80 to 95 per cent may produce a "water-logged" condition in the plant which would intensify oil injury.

The general effect of refined or partly refined oils on plants is to cause some variation in normal functioning, including transpiration, respiration, and starch formation (photosynthesis). Such disturbances are not necessarily serious if the type of oil is chosen carefully and with due regard for the specific need. The details of such choice of oils and time and manner of application are to be determined for local conditions and the desired results. Oils of a viscosity of 90 to 110 seconds Saybolt should be used sparingly, as they have frequently caused defoliation or a reduction in the size of the fruit.[55] Such physiological effects on growing fruit are more noticeable as maturity approaches.[48] French prunes, one-half grown, treated with undiluted oils ranging from kerosene to a Saybolt viscosity of 70 seconds, showed at maturity a change in drying ratio from 3:03 (fresh fruit) to 1 (dried fruit) for the untreated fruit to that of 3:70 to 1 for the heaviest oil used, proving the retarding effect of the heavier oil on the growth of the fruit. Applications of the same oils to very immature fruit showed but little change in the drying ratios. This work indicates the possible danger of petroleum to fruit near maturity. If it is necessary to spray at this time, only light volatile oils should be used.

The physical reactions of oils on plants may be advantageous under certain conditions, when properly understood. Blooming dates may be advanced or delayed, growth stimulated or retarded, and transpiration of moisture may be regulated for short periods.[48] Oil coatings on stored apples and oranges may affect the proportions of oxygen and carbon dioxide and retard the loss of moisture. Loss of weight of fresh ripe French prunes, wiped with oils of varying viscosities and stored at 32°F, varied greatly, as shown in Table 32.

The weight loss is shown to be directly in proportion to the viscosity of the oil. Oil No. 4, which is intermediate between kerosene and the lightest lubricants, is so volatile that a durable film was not obtained.

**Emulsifiers and Spreaders.** The application of oils to living plants and animals in more than minute droplets or thin films of refined oil is in most instances hazardous. Where desirable to apply oils as a control for insects or fungi, it is necessary to dilute the oil or break it up in a way that will prevent the deposit of large amounts at any one place. This is accomplished in two ways: first, by applying the oil in very fine droplets by the use of a strong blast of air from an airplane or a power blower; and second, by diluting the oil with water. Being immiscible, oil and water, cannot be combined uniformly except by the use of a third substance of varying solubility in the oil and water, known as an emulsifier. The oil and water mixture are violently agitated or forced through minute apertures, thus breaking the oil into minute globules around which a thin film of the emulsifier forms. The oil globules usually range in size from 2 to 20 microns (0.001 mm) in diameter. The larger globules or droplets of oil (7 to 12 microns in diameter) have been found more toxic to aphids, *Aphis fabae* (*A. rumicis*), than the smaller ones (2 to 4 microns or less in diameter).[72] The film of emulsifier prevents the oil globules from coalescing, thus aiding in keeping the oil suspended in the water. The emulsion may be broken by rupturing the film surrounding the oil droplets, using a strong acid solution or freezing, thus freeing the oil, which floats to the surface of the water. Another type of oil-in-water emulsion is made by the use of continued violent agitation in the spray tank, as is developed in certain types of power-driven sprayers.[76] Such a mechanical emulsion is maintained only long enough for immediate application from the tank where it is produced.

Table 32. Weight Loss of French Prunes Treated with Oils of Varying Viscosity

| Oil No. | Type | Viscosity (Sec. Saybolt) | Per cent Loss in Weight | |
|---|---|---|---|---|
| | | | 23 days | 46th day |
| 1 | Heavy white oil | 240 | 13.5 | 15.1 |
| 2 | Light " " | 105 | 14.1 | 15.2 |
| 3 | Very light white oil | 76 | 15.7 | 17.9 |
| 4 | Light distillate (white) | 55 | 18.8 | 21.2 |
| 5 | Untreated | — | 21.5 | 24.1 |

Emulsions of oil and water may be of two forms: oil suspended in water or water in oil. The latter is known as an "invert" emulsion. Since oil is the external phase of the invert emulsion it can be diluted in the spray tank only by oil or one of its solvents; the inversion may, however, be completed after leaving the spray nozzle. A modification of this principle, known as the "inverted spray mixture," is made by adding lead arsenate to a somewhat unstable type of emulsion; this results in flocculation and suspension of the lead compound, cryolite, or other electrolyte in the oil phase instead of the water, giving a heavier deposit of the lead arsenate when applied to the tree.[71, 82, 83, 84] To facilitate application of this mixture, a special type of applicator or sprayer has been developed which is capable of applying the invert emulsion when formed in the spray tank.[83]

Sodium- or potassium-base soaps should be used with caution for emulsification in regions where hard water prevails, as such alkaline bases react with calcium and magnesium salts dissolved in the water to form insoluble soaps which tend to break the emulsion. The addition of a small amount of free alkali, such as sodium hydroxide, to the water used in diluting emulsions may aid in stablizing an emulsion; it acts both to soften the water and also to prevent the hydrolysis or breaking down of soap, when it is used as an emulsifier.

Besides soap, casein and glue, waste sulfite material or lignin from wood pulp mills has been recommended both as an emulsifier and spreader.[85]

Table 33. Amount of Oil in Run-off from a Two Per Cent Emulsion Made with Varying Amounts of Emulsifier

| Formula | Calcium-casein mixture (%) | Ratio of emulsifier to oil (%) | Ratio of conc. of oil in run-off to conc. in emulsion (%) | Oil in run-off (%) |
|---|---|---|---|---|
| 1 | 5.0000 | 250.00 | 125.0 | 2.50 |
| 2 | 4.0000 | 200.00 | 120.0 | 2.45 |
| 3 | 3.0000 | 150.00 | 120.0 | 2.40 |
| 4 | 2.0000 | 100.00 | 122.0 | 2.44 |
| 5 | 1.0000 | 50.00 | 112.0 | 2.30 |
| 6 | 0.5000 | 25.00 | 106.0 | 2.20 |
| 7 | 0.2500 | 12.50 | 92.0 | 1.82 |
| 8 | 0.2000 | 10.00 | 86.0 | 1.70 |
| 9 | 0.1000 | 5.00 | 63.0 | 1.32 |
| 10 | 0.0500 | 2.50 | 63.0 | 1.24 |
| 11 | 0.0310 | 1.50 | 31.0 | 0.64 |
| 12 | 0.0078 | 0.39 | 17.0 | 0.34 |

The next important development was the use of organic bases such as triethanolamine which, when combined with the fatty acids, form emulsifiers capable of making very stable emulsions. Sulfonated vegetable oils, or more accurately speaking, sulfated oils and esters of the fatty acids, either in the normal or sulfated form, are good emulsifiers and in certain instances excel as spreaders.[12, 70] The sulfonated oils and esters are also active as insecticides and fungicides. The above organic compounds may be used in hard water and in some instances even in sea water. The sulfonated products break down at temperatures of about 160°F (71.1°C) but are very stable at normal field temperatures. In addition to the emulsifiers mentioned, there are an increasing number of organic compounds and proprietary materials available for the preparation of any desired type of emulsion. The stability of the emulsion varies with the size of the oil droplet and the type and concentration of the emulsifier. Size of the oil droplet is affected both by the type of emulsifier used and the mechanics of the manufacture, *i.e.*, type of agitation and size of aperture through which the mixture is forced.[60]

The concentration of the emulsifier affects both the oil deposit and correspondingly the insecticidal value, as shown in Tables 33 and 34.[58] The profound influence which the physical qualities of an emulsion, including size of oil globule, stability, oil deposit and run-off, may have on the insecticidal value has been generally recognized.[15, 58, 72, 76, 86, 87]

Spreaders vary in their action both in regard to the type of material and the amount used. The so-called "tank-mix"[75] emulsion, in which dried blood is used as a spreader and emulsifier, is an example of a special field developed for one type of product which, when properly used, results in a satisfactory application of oil, but may lead to an excessive "run-off" of oil and insufficient coverage.

Table 34. Relation of Scale Mortality to Concentration of Emulsifier in a Two Per Cent Emulsion of Oronite Crystal Oil

| No. | Concentration of calcium caseinate (%) | Scale surviving at end of test* (%) | Remarks |
|---|---|---|---|
| 1 | 2.0 | 32.3 | Many young alive. Oil absorbed by emulsifier. |
| 2 | 1.0 | 49.5 | Many young alive. Oil absorbed by emulsifier. |
| 3 | 0.5 | 38.3 | Many young alive. Oil absorbed by emulsifier. |
| 4 | .25 | 7.5 | Sprayed surface slightly greasy. No young alive. |
| 5 | .125† | 0.0 | Oil film just visible on sprayed surface. |
| 6 | .0625 | 0.0 | Oil film distinct on sprayed surface. |
| 7 | .031 | 0.0 | Well developed oil film present. |
| 8 | .015 | 0.0 | Well developed oil film present. |
| 9 | .0078 | 0.0 | Well developed oil film present. |

* The usual natural mortality, about 40 to 50 per cent, is necessarily included in the counts.

† This corresponds to 1 pound of calcium caseinate to 100 gallons of spray.

**Emulsive Oils.** The use of emulsifiers dissolved in the oil[75] offers a number of advantages in commercial practice: (1) it eliminates the necessity of emulsification as a separate process, together with freight charges on water incorporated in the emulsions; (2) it gives greater control of penetration of the oil spray into foliage by an increase of viscosity or "apparent gelatinization," and by preferential wetting of suspended solids such as lead arsenate and cryolite;[73] (3) it also gives superior spreading qualities of oil containing oil-soluble spreaders compared with those of oils applied as emulsions with water-soluble emulsifiers.[62]

A preliminary to the use of the oil-soluble emulsifier is the use of an oil-soluble fatty acid such as oleic[70] or lauric acid, to which is added an amount of alkali necessary to form a soap in the solution, water being added to form the type of emulsion desired. Organic compounds containing oleic acid are commonly used in making the emulsive type of oil.[75]

**Oil Deposit Measurements.** Since the thickness of oil deposits on leaves and twigs varies, and since the permanence of such films differs with the type of oil used, it becomes necessary to have accurate methods of measuring these deposits. The problem is complicated by the presence of naturally occurring gums and resins on both leaves and bark. The methods adopted are similar, but vary in detail. They include recovery of the oil present by digestion or the use of suitable solvents, including ethyl and petrolic ether, acetone and methylene chloride; removal of the solvent by evaporation or distillation; and measurement of the recovered oil.[60, 77, 78, 79, 80, 81,]

**Repelling Action of Oil-treated Foliage.** Foliage sprayed with light lubricating oils, 50-60 to 90-100 viscosity Saybolt, and showing oil penetration into the intercellular spaces was not fed upon by aphids, sow bugs, *Porcellio loevis Koch*, or snails. As the oil volatilized or was translocated from the intercellular spaces into the xylem tubes, normal feeding was resumed by the species concerned. The repelling action continued over a period of two to four weeks with oils of viscosities of 70 to 100 seconds Saybolt at the low temperatures of early spring (maximum range 55 to 73°F).[21]

Greenhouse and field observations confirm the above laboratory findings on the attacks of plant mites, *Tetranychus sp.*, on the French prune and with the red scale, *Aonidiella aurantii*, on lemon and orange[105] trees. Potted French prune trees in the greenhouse were sprayed with petroleum fractions ranging from kerosene through light lubricants with viscosities of 50–60, 70–80, 100–110, to 220–230 seconds Saybolt. The kerosene was sufficiently volatile to be largely lost from the foliage within ten days. The mites, which had escaped the oil application and those hatching from the eggs, increased very rapidly on these trees, and within three weeks after spraying the trees were almost completely defoliated. The lethal and repelling effect of the lubricants used was directly proportional to their viscosity, much of the foliage treated with the heaviest oil (220–230 seconds Saybolt) being present on the trees four months after application.[21] The two heavier oils had a retarding effect on the growth of the tree. Similar results are reported by Ebeling on the repelling action of oil on newly hatched red scale insects.[105]

**Oil Carriers of Toxic Chemicals.** Mineral oil, in addition to its innate value as an insecticide, has certain physical qualities that make it valuable as a carrier for many toxic chemicals. These qualities include low surface tension, wetting, spreading, penetration and film-building qualities.

The custom of combining nicotine sulfate and dilute oil emulsions in the spray tank has been established for many years.[9] Free nicotine in concentrated form has been shown[93, 94, 113] to be useful when dissolved directly in the oil and the latter emulsified or applied in the pure form. Commercial application of this principle is now common.[105, 109, 110] Besides codling moth and red spider work, this combination has been found useful for a number of sucking insects.[111, 112, 113]

Nicotine sulfate, being less soluble in mineral oil than the alkaloid nicotine, is less efficient for such combination. However, the alkalinity of the water carrier or of the spreader may break down the nicotine sulfate compound and permit a larger amount of nicotine to dissolve in the oil. In Table 35[93] different solubility rates for various petroleum fractions are given. The solubility rate increases, it will be noted, in the lighter oils, and since they are usually safer to use on foliage that type of combination is preferable.

Table 35. Distribution of Nicotine in Oil and Water Mixtures*

| Oil used | Viscosity at 100°F. (38°C.)† (Seconds) | Total Nicotine in: Oil layer (%) | Total Nicotine in: Water layer (%) |
|---|---|---|---|
| Kerosene | 345 | 54 | 46 |
| Lubricating oil, very light | 50 to 60 | 48 | 52 |
| Lubricating oil, light | 75 to 80 | 44 | 56 |
| Lubricating oil, light | 100 to 110 | 42 | 58 |

* Equal volumes of oil, containing 1 per cent of nicotine, and water were shaken together at room temperature for 5 minutes, and the amount of nicotine determined in each layer.

† Viscosity of kerosene determined by Saybolt Thermoviscometer; that of lubricating oils determined by Saybolt viscometer.

Extracts of pyrethrum flowers (*Pyrethrum cinerariaefolium*) by means of the lighter petroleum fractions, *e.g.*, kerosene, was first generally utilized in "fly sprays," the earliest formulas calling for proportions of one-half to one pound of ground pyrethrum flowers to a gallon of the petroleum solvent. The present tendency is to use slightly larger proportions of pyrethrum in the solvent. To this basic mixture may be added small proportions of organic compounds, pine oils or perfumes, which supplement the action of the pyrethrins, disguise the kerosene odor, and sometimes act as repellents.

The value of sesame oil for increasing the efficiency of oil-pyrethrin fly spray has been shown by Eagelson.[121] A crystalline compound called sesamin, $C_{20}H_{18}O_6$, has been isolated from certain fractions of the oil and is apparently one of the principal ingredients causing the synergistic action between the oil and pyrethrins.[122] The combination of kerosene oil, sesame oil, and pyrethrins has proved to be a satisfactory formula for aerosol applications for mosquitoes and flies.[123]

Gasoline was first used as the solvent, but it was found too volatile for the customary application of a light mist, while fractions heavier than kerosene leave too much oily residue for use in the home. The "fly spray" type of pyrethrum application, with slight variations in the formula, has become the common household insect spray for moths, mosquitoes, and cockroaches. The oil extract of pyrethrum, when emulsified, has also been found of value in controlling the larval and pupal stages of the mosquito.[101, 116]

Refined mineral oil,[117] and later pyrethrum-oil extracts, have been established by Barber[119] and are now generally recommended[125] in horticultural work as a control for the corn earworm, *Heliothis armigera.* Scarcity of pyrethrum led to experiments with substitutes. Davidson and Barber report[118, 120] that the use of styrene dibromide ($\alpha$-$\beta$-dibromoethylbenzene) at 0.75 gram per 100 ml. of highly refined petroleum oil gave protection, in the control of the corn earworm, equal to the addition of 0.2 per cent of pyrethrins. Dichloroethyl ether at a concentration of 2 per cent in mineral oil (viscosity Saybolt seconds from 125–210) is reported as effective as pyrethrins and less expensive.[119] The greatest success obtained thus far in field spraying with oil-pyrethrins is in the control of the sugar beet leafhopper, *Eutettix tenellus*, and the grape leafhopper, *Erythroneura comes.* For this work solutions of very light, refined petroleum oil are used without dilution, applying with a blower at the rate of 5 to 10 gallons per acre.[124] Attempts to control various moth larvae have not been very successful, with the notable exception of the prune worm, *Mineola scituella.*[127]

Ground roots of rotenone-bearing plants combined with low concentrations of oil (1.0 per cent or less) have been used successfully as a spray for black scale, *Saissetia oleae.*[73] Solutions of rotenone and rotenoids in oil are more effective than ground suspensions, especially for the California red scale, *Aonidiella aurantii.* However, rotenone is only sparingly soluble in petroleum; this had led to the use of a third substance, a mutual solvent for both oil and rotenone, which makes possible a true solution or stable suspension of the toxicant in the oil. Such mutual solvents are termed "solubilizers." Three materials have been found useful as solubilizers for the Derris extractives (including rotenone) and spray oils, for use against the black scale; they are dibutylphthalate, 2(4-tertiary butylphenoxy) ethanol, and an oil-soluble phenolic resin known as "Cardolite 627,"[129] a formaldehyde reaction product of cashew nut liquid. In red scale control, which requires a high dosage of oil regardless of toxicity, "Cardolite" alone was found satisfactory from all standpoints.[73] In further studies on solubility it has been found that pure rotenone is more soluble in solutions of a light-medium petroleum oil and 2(4-butylphenoxy) ethanol than when other derivatives of derris are present.[129] Cressman and Broadbent have shown an increased toxicity to the California red scale with a minimum of 0.57 per cent of derris resins in the mineral oil.[131] In further studies it is stated that the scale population 6 to 12 months after spraying is decidedly heavier in localities where oil alone was used than in those where derris resins were included in the oil.[132]

Certain oil-soluble dinitro and thiocyanogen compounds have received much attention during recent years for increasing the ovicidal value of mineral oils and giving better control of scale insects.[74, 114, 115] The individual compounds will be discussed in Chapter 9.

**Animal Dips.** Crude oil dips for cattle have been used very generally in controlling the tick instrumental in carrying Texas fever. This fight, which was waged for years in the Gulf States and on the Mexican border, is an outstanding case of a successful campaign against a serious cattle disease. A crude oil from the Beaumont oil fields which contains from 1 to 15 per cent of sulfur and has 40 to 50 per cent of the fraction boiling below 300°C (572°F), has been recommended[64] for this purpose; the oil is emulsified with soap. This emulsion is used at a 10 per cent concentration for cattle mange and sheep scab as well as ticks. Kerosene, emulsified in a similar way, and also used at a 10 per cent concentration, is applied as a spray to animals. Higher concentrations of oil in the dip are recommended[65] in a later paper; the amount of oil per 100 gallons of dip is given as 40 gallons for mange or scab and as 25 gallons for lice and ticks. Detailed directions for building a vat are given.

**Repellent Sprays.** For protecting dairy cattle against flies have been developed to be used both alone and as carriers for pyrethrins and other toxics.[66] Experiments with the above methods resulted in a rise of temperature[67] and a decrease in milk production in the sprayed animals compared with the control cows. Two types of oil spray were used: the first was a white mineral oil and the second a blend of two parts of the first oil and one part of a household spray containing pyrethrum extract.[66] The heavy white oil caused a decrease of 11.7 per cent in milk production, while the blended oil containing pyrethrum caused a 4 per cent decrease in production. Later experiments indicate a definite relationship between viscosity plus the unsulfonated residue and the effect on the animal. An oil with a visosity below 40 seconds Saybolt may injure the animal; an oil with a viscosity of 65 seconds Saybolt may also cause injury if the unsulfonated residue is much below 90 per cent, but can be tolerated with a higher unsulfonated residue.[67]

Combinations of oil of tar and fish oil with mineral oil have shown[99] a prolonged repelling action for dairy flies on cattle. Kerosene pyrethrum extract has for many years been the base for dairy fly and hog barn sprays as well as for the household type of insect spray. This combination is of greater value as a paralyzing agent than as a toxic material. The rather low kills sometimes secured with pyrethrum extract alone have led to the inclusion of more toxic agents, such as rotenone and a number of the synthetic organic compounds.

**Mosquito Larvicides.** The use of mineral oil, both in the "crude" form and distillates of varying density and volatility, has been common for many years in the control of mosquitoes in the larval and pupal stages. Quayle[100] describes the oil used in an early California campaign as a blend of four parts of a heavy oil (18° Bé) and one part of light oil (34° Bé). This was later modified to include oils with a Saybolt viscosity range from 25 to 40 seconds and a boiling range of 200 to 600°F.[102] Murray has shown the advantage of certain soluble substances developed during the cracking of the oil and by irradiation as an aid to permanent film formation.[103]

A study of the way in which petroleum fractions affect mosquito larvae was made by Freeborn and Atsatt.[104] They showed that the confined oil vapors of volatile fractions such as kerosene were capable of killing larvae as well as the liquid oil which penetrated the body of the insect. Their conclusions were remarkably similar to later studies[58] on the California red scale. The addition of 0.07 per cent of pyrethrins to kerosene has been found superior to kerosene alone for killing mosquito larvae.[102]

**Herbicides.** Chemical control of weeds is highly developed in the semiarid region of the Pacific Coast. Because of the availability and low cost of oil refinery by-products, petroleum has come into general use in weed control.[130] A common by-product known as "acid sludge" has received considerable attention, but its corrosive action on spray pumps has limited its use. A cheap grade of fuel oil, commonly sold as "Diesel oil" is now generally used for large-scale operations, such as municipal campaigns of eradication of introduced species of weed. Diesel oil is sold on gravity specifications of 24° to 35° Bé. A small amount of asphalt in the mixture has also been found advantageous in the emulsification. Diesel oil is a fraction intermediate between kerosene and the lightest lubricants; for herbicidal purposes it is used unrefined. The author has found that the unsaturated hydrocarbons present in Diesel oil are the most active in killing plant tissue; hence oils carrying the highest amounts of such compounds are the most efficient. Kerosene has also been recommended as a cheap control measure for the barberry bush. For such work a gallon or more is poured about the base of the plant.[133]

The selective use of oil herbicides (applications which kill weeds but are tolerated by the crop plant) has become a general commercial practice in certain districts. Carrots in particular are known to be tolerant to aromatic compounds. Celery is also quite tolerant to certain so-called "stove oils." In commercial practice the pure oil is applied as a fine mist at the rate of about 150 gallons per acre to young seedling carrots. Studies on the chemistry of petroleum herbicides, for selective purposes, show that oil containing a high concentration of toxic olefins and aromatics will kill almost all species of plants; but by altering the proportions of these to the less toxic compounds a mixture results which is tolerated by certain plants, and selective action results.[134]

**Fungicidal Combinations of Mineral Oil and Copper Compounds.** A noticeable weakness of mineral oil in controlling plant pests is its low fungicidal value. The chemically active unsaturated hydrocarbons show a certain degree of fungicidal activity, but since such compounds are largely removed from oils applied to foliage this value is largely lost. Combinations of oil and Bordeaux mixture (copper sulfate and slaked lime) are suggested[135] as more stable than emulsions made with soap, and they also preclude the necessity of a second spraying with oil following a Bordeaux application to control plant diseases. Later work[58, 136] showed that the lime of the Bordeaux mixture combined with a part of the oil present, thus lowering the efficiency of the spray.

The commonly used fungicides, sulfur and copper, are occasionally combined with oil, especially in oil-soluble forms such as copper oleates,[137] naphthenates, and resinates. Lime-sulfur solutions have been combined with oil emulsions, using other compatible types of emulsifiers than sodium soap. Such combinations of oil and sulfur are principally for dormant sprays, but are also used in weak concentrations on Citrus foliage. Copper resinate,[138] $Cu(C_2OH_{29}O_2)_2$, has been found to be a very useful oil-soluble compound for use both with pine-tar oils and mineral oils. In its dry form it is very light and fluffy and somewhat difficult to dissolve, but when dissolved in the safer types of pine-tar oils it offers a satisfactory method of applying copper to either dormant trees or those in foliage. There is this marked difference in the application of copper in the Bordeaux form and in an oil-soluble form: the former method forms a deposit on the surface of leaf and twig little of which can be absorbed; but the oil-soluble form is carried into the tissue of leaf and twig and a comparatively small amount remains on the outer surface. The use of this penetrative power makes possible action on fungi and bacteria within the tissue of the plant. Such forms of oil-soluble copper may be blended with petroleum fractions when desired for use on resistant scale insects. Oil-soluble coppers dissolved in tar oils have also been found of value in preserving fish nets[139] attacked by certain slime molds.

Copper combinations with the oil used in treating wrapping paper[141] for pears in the prevention of "scald" is now practiced commercially. The inclusion of copper in this way reduced decay caused by the fungus *Botrytis.* Such copper-treated wrapping papers are of value principally in preventing the spread of decay from one fruit to another in packed boxes.

## Vegetable and Animal Oils

The glyceride oils include both the principal animal oils and the following vegetable oils: coconut, palm, cottonseed, soybean, corn, sesame, and a number of others of lesser volume. They differ from mineral oils in their structure, glycerides being compounds (esters or salts) of a fatty acid and glycerol, one of the higher alcohols (glycerin being the commercial term). Glyceride oils and fats may be split by steam, yielding free glycerol and the free fatty acids. Decomposition is also accomplished by saponification with an alkali, thus forming soap, breaking down the soap with dilute sulfuric acid and then separating the fatty acid.

A number of vegetable oils, including soybean, maize, cottonseed, rape, and sesame are fungicidal on the hop powdery mildew *Sphaerotheca humuli* at 0.25 and 0.5 per cent concentration. The fungicidal value of the oils was shown to be largely that of the glycerides themselves rather than that of the glycerol.[147] Similar fungicidal values have been reported in the control of onion mildew, *Peronospora destructor*.[148]

The fatty acids derived from glyceride oils may act as insecticides, fungicides, and bactericides. Dills and Menusan report that capric and lauric acids are more toxic as insecticides than oleic, caprylic, myristic and palmitic acids when the acid was applied as an emulsion. When soap was made from the acids, the oleate was more toxic than the laurate and caprate.[145] Such acids are entirely too dangerous to foliage to be used in the raw form. The sulfonated refined fatty acid, which is entirely miscible with mineral oils, may be used as a plant spray without more hazard than that of the mineral oil itself. The toxicity of derris powder to certain plant bugs was increased by the addition of one per cent of sulfonated soybean oil, coconut oil, castor oil or linseed oil, to the spray mixture. Better suspension of the powder was obtained in this way as well as increased insecticidal efficiency. The sulfonated form of the oils was superior to that of the untreated oil because of its natural miscibility with water.[149]

Fish oils are derived from white-fish, menhaden and sardine. They are used principally as adhesives for arsenical sprays.[157] In the form of sodium and potassium soap the fish oils and whale oils have had very extensive use as spreaders, particularly for nicotine sulfate sprays and lead arsenate. Chemical reaction with many of the lead arsenates has restricted this use. Fish-oil and whale-oil soaps have been used very generally in the control of aphids and similar types of insects, but because of variability of composition and mild efficiency they have been largely displaced by other insecticides.

**Pine Oils and Pine-tar Oils*.** Certain of the pine-tar oils (derived from destructively distilled pine wood rich in rosin) have been found to have distinct fugnicidal properties in themselves even after treatment to in-

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* The term "pine oil" is applied to fractions produced by steam distillation. "Pine tar oils", ranging from "wood turpentine" to heavy tar, are produced by a process of destructive distillation where charcoal is the final residue; hence the term "d.d. oils."

crease plant tolerance. Such refined oils may be used alone on plants both as insecticides and fungicides or in combination with mineral oil as carriers for copper resinate[140] and nicotine. Free nicotine is soluble to a greater degree in pine oils and pine-tar oils than in petroleum and may be used to hold large amounts of nicotine in the oil phase of the emulsion. The increased wax solubility and spreading qualities of the pine oils over that of mineral oils make them valuable for many types of combinations.[144] Unrefined pine-tar oils may be used in borer treatment, for which they are very useful because of their penetrating and toxic qualities.[154] The addition of naphthalene, nicotine or benzyl chloride, $C_6H_5CH_2Cl$,together with an oil-soluble copper, gives a preservative action as well as that of an insecticide.[153]

The fly-repelling values of pine tars, pine-tar oils, and certain of the pine oils has greatly stimulated the use of these materials as livestock and dairy sprays. They are also used in the kerosene pyrethrum type of fly spray to increase toxicity and to reduce the necessary amount of pyrethrum and derris extract in the combination.[146]

**Essential oils** are a volatile group of oils distilled or expressed from certain aromatic plants. The insecticidal value of these oils is confined largely to their use as mosquito repellents. They are now being displaced for this use by certain synthesized organic compounds such as dimethyl phthalate.

Oil of citronella has proved one of the most effective as an insect repellant[150] and has been used for this purpose for many years. Other essential oils used as repellents include: oil lavender, oil rosemary, oil pennroyal and steam-distilled pine oils.

**Miscellaneous Uses of Mineral and Vegetable Oil.** Oil emulsions used as a dip for seed corn [142] gave almost perfect protection against various insects attacking stored products. Germination was found uninjured with certain types of emulsifiers but with others germination was retarded.

Oxidized products of certain mineral oil[143] fractions have been found useful as insecticides, but principally as an aid to the spreading and penetration of nicotine and other toxic chemicals.

Chemically treated bands for killing migrating codling moth larvae are made of solutions of beta or alpha naphthol dissolved in mineral oil.[151] Applications of moderately heavy pine-tar oil used alone, diluted with equal parts of water, and also as a carrier and solvent for paradichlorobenzene and other salts proved very effective against overwintering larvae of the codling moth.[152, 156] The oil is in a water-soluble form and may be used alone or diluted one or two times with water. At the latter strength satisfactory control of codling moth larvae was obtained in the protective silken covering which they spin.

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# Chapter 7

# Fumigants and Fumigation

The first use of a toxic gas to control insects and mites, and as a disinfectant, was that of fumes from burning sulfur. Many other volatile insecticides developed by the joint efforts of chemists, entomologists, and plant pathologists are now in general use. The earlier studies were begun about 1880, in an effort to find a gas sufficiently poisonous to kill the scale insects on Citrus trees and yet be tolerated by the tree. These studies were sufficiently developed by 1886 so that directions were given[1] for the use of hydrocyanic acid gas (HCN) in the control of these insects on orange and lemon trees. The gas was produced in a crude generator outside of the tented tree, but this method was soon supplanted by the use of an earthenware pot beneath the tent. The latter method was used until 1914, when the outside generator again came into use,[2] not only as a tree fumigant but also for treating greenhouses and ships. The plant pathologist has been slower to adopt volatile gases as fungicides. Not until 1923 was the use of sulfur dioxide ($SO_2$) officially recommended as a preliminary treatment of grapes prior to shipment or storage.[3] Formaldehyde has been found useful in soil and seed disinfection as a protection against "damping off" fungi such as *Fusarium*, and for general work in disinfecting rooms and clothing.

Successful fumigation involves not only a lethal vapor concentration but certain physical attributes of the fumigant, including vapor pressure, molecular diffusion, penetration, sorption of the gas by the walls and contents of the fumagatorium, and the modifying effects of temperature. Time of exposure, leakage rate, air currents, and the physiological reaction of temperature and humidity on insects and fungi are all very important. Fumigation is usually practiced at temperatures which normally range from 12 to 38°C, but which may extend as low as 7°C and as high as 48°C. These limits are established principally by the physiological response of the insect since, being cold-blooded, they are almost inactive below 7°C. Prolonged exposures to either extreme of temperature may have a lethal effect that probably blends with that of the fumigant. The order of toxicity varies with the species of insect, as shown in Table 36[4a], and may change even more strikingly among less closely related groups.

The choice of commercial fumigants is made largely among volatile chemicals that would produce a lethal concentration at the temperature range indicated above. Artificial temperatures are sometimes used as an aid to dissemination of vapors, as from liquefied sulfur dioxide and nicotine, which has a high boiling point. Paradichlorobenzene, with a moderately toxic vapor and boiling point of 172°C, has been restricted in use as a soil fumigant to the warmer seasons of the year. Less toxic chemicals may, however, require more than a vapor-saturated atmosphere to give a lethal concentration; for these the aerosol method of distribution is used. By this method chemicals of a lower toxicity and vapor pressure may be used effectively as fumigants. Naphthalene[131] and certain of the halogenated naphthalenes[96] have been found successful as aerosol fumigants.

Table 36. Median Toxicity to Certain Insects of the Various Chemicals Used or Suggested for Use as Insect Fumigants (Temperature, 25°C; Exposure Period, Five Hours).

| | | Mg./Liter to Kill 50 Per Cent | | |
|---|---|---|---|---|
| Fumigant | Boiling Point (C) | *Tribolium confusum** | *Sitophilus granarius*† | *Sitophilus oryzae*‡ |
| Hydrocyanic acid | 26 | 0.6 | 5.8 | — |
| Chloropicrin | 112 | 4.6 | 5.0 | 2.0 |
| Sulfur dioxide | −10 | 5.7 | 5.7 | 17 |
| Ethylene oxide | 11 | 18 | 5.6 | 5.7 |
| Carbon disulfide | 46 | 61 | 40 | 26 |
| Methyl formate | 32 | 23.5 | 20 | — |
| Ethyl formate | 54 | 24.5 | 29 | 17.5 |
| Methyl bromide | 5 | 11.2 | 7.4 | 4.0 |
| Methyl acetate | 57 | 82 | 88 | 63 |
| Ethyl acetate | 77 | 83 | 86 | 49 |
| Ethylene dichloride | 84 | 37.5 | 138 | 31 |
| Propylene dichloride | 97 | 40 | 118 | 44 |
| *tert.*-Butyl alcohol | 83 | 43 | 73 | 32 |
| Trichloroethylene | 87 | 108 | 335 | 196 |
| Carbon tetrachloride | 76 | 185 | 360 | 160 |

* Confused flour beetle.

† Granary weevil.

‡ Rice weevil.

## Hydrocyanic Acid (HCN) (Hydrogen cyanide, prussic acid).

Hydrocyanic acid is a colorless liquid with a boiling point of 26.1°C; specific gravity 0.6967 at 15°C; vapor density or specific gravity of the gas 0.934 at 15°C; and range of flammability from 5.6 to 40 per cent volume of the gas in the air.[5] In fumigation practice, however, the concentration of the gas seldom reaches 2 per cent. The liquid is miscible with water in all proportions, and the gas also is readily soluble in water. The freezing point is −15°C. The stability of liquid hydrocyanic acid is variable when stored in closed containers. Decomposition is favored by high temperatures (33°C and above), the presence of 5 per cent or more of water, contamination by residue from decomposed liquid, all alkalies, sodium cyanide and nitric acid. Sulfuric acid and metallic copper are listed as contributing to the stability of the material.[2, 6]

The commercial form of liquid hydrocyanic acid is produced from the gas generated by combining sulfuric acid with sodium cyanide. The gas is liquefied by cooling and purified by distillation to remove excess water. One ounce of sodium cyanide (51 to 52 per cent cyanogen) yields the equivalent of 20 cc. of liquid hydrocyanic acid. The purity of the commercial material is 97 to 98 per cent, the remainder being water. Liquid hydrocyanic acid is usually sold by weight, but difficulties in handling the volatile liquid have led to the use of special gravity tables for determining the purity [7] (see Appendix[7]). Transportation of liquid hydrocyanic acid is by truck in strong steel cylinders.

Table 37. Pressure of Hydrocyanic Acid (About 97% HCN) in a Closed Container at Different Temperatures.

| Temperatures (°C) | Temperatures (°F) | Pressure (pounds per sq. in.) |
|---|---|---|
| 30.5 | 87 | 3.4 |
| 34.4 | 94 | 4.9 |
| 37.8 | 100 | 7.9 |
| 40.5 | 105 | 9.8 |
| 43.3 | 110 | 11.8 |
| 46.1 | 115 | 13.3 |
| 48.9 | 120 | 15.7 |
| 51.7 | 125 | 17.7 |

I.C.C. Specifications No. 33, Interstate Commerce Commission U.S.A.

*75-lb. cylinder:* approximate gross weight 245 lbs., tare 170 lbs., net 75 lbs. Size: 10½ inches diameter, 53 inches high.

*30-lb. cylinder:* approximate gross weight 130 lbs., tare 100 lbs., net 30 lbs. Size: 7½ inches diameter, 48 inches high.[9]

The full cylinders should be left in an upright position and stored at temperatures not higher than 15°C in well ventilated places, away from the sun. Storage longer than six months is considered dangerous because of slow decomposition, indicated by a slight yellowish color, which results in the formation of ammonia, carbon monoxide, hydrogen and nitrogen. Pressure increases rapidly with rising temperature as shown in Table 37.[2]

## Potassium Cyanide (KCN)

This is the earliest form of cyanide used for fumigation purposes. It contains 40 per cent of cyanogen when in the pure form. The commonest impurities are sodium cyanide and sodium chloride. When chlorine, even as low as 0.4 per cent, is present, it results in the decomposition of the HCN as generated, with the formation of ammonia, which is converted into ammonium sulfate in the generating jar. Commercial potassium cyanide, as commonly sold for fumigation purposes, is about 98 to 99 per cent pure. Hydrocyanic acid gas is produced by combining potassium cyanide with sulfuric acid and water.* The common formula is:

Potassium cyanide, 1 pound
Sulfuric acid, 1 pint
Water, 3 pints

The formula gives a slight amount of surplus acid over that actually required to break down the cyanide, but this excess has been found necessary in field practice.

### **Sodium Cyanide** (NaCn)

The commercial grade used for fumigating purposes usually contains 98 to 99 per cent of sodium cyanide, with a cyanogen content of 51 to 52 per cent. It is marketed in the form of "eggs" weighing approximately one ounce each. Sodium cyanide contains 33 per cent more cyanogen than that found in commercial grades of potassium cyanide. The larger amount of cyanogen in the sodium compound necessitates a corresponding increase of sulfuric acid required for releasing the gas; hence the formula in general use is:

Sodium cyanide, 1 pound
Sulfuric acid, 1½ pints
Water, 3 pints

The same care in avoiding cyanides carrying one per cent or more of chlorides should be used as noted under potassium cyanide.

The methods used in generating hycrocyanic acid gas from both sodium and potassium cyanide are the same, the only variation being in the proportions of acid and cyanide in the two formulas. The acid is extremely corrosive and should be used with care to avoid spattering. The water is placed in the generator first, followed by the acid; if the reverse order is used so much heat will be generated at the surface of the two liquids as to cause severe spattering. No hydrochloric or nitric acid should be used as a partial substitute for sulfuric acid, nor should there be chlorides or nitrates in the chemicals used, as these impurities will cause decomposition of the

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* Water is a necessary ingredient of the formula, as the use of concentrated sulfuric acid results in the formation of carbon monoxide, the amount increasing with the concentration of the acid. Ammonia and sulfur dioxide are also formed by the combination of concentrated sulfuric acid and hydrocyanic acid. Excess water prevents the solidification of potassium sulfate as it is formed in the generator.

hydrocyanic acid with a corresponding loss of efficiency.[18] The cyanide is weighed into double paper bags to delay the action of the acid, and is then placed in the hot acid solution. All operators should leave quickly to avoid breathing the concentrated gas. Do not allow the cyanide to stand exposed to the air or in paper bags any longer than is absolutely necessary. Observe all precautions in handling or fumigating with cyanide, as it acts quickly and is very toxic to human beings. The residue left in the generator after fumigating should be disposed of carefully, as it contains small amounts of hydrocyanic acid in solution, and possibly undecomposed cyanide.

### Calcium Cyanide [$Ca(CN)_2$]

Calcium cyanide is a loose combination of calcium and cyanogen which releases hydrocyanic acid upon exposure to atmospheric moisture. It is marketed as a fine powder or coarse granules. Friction-top metal containers are used for storage. A commercial product, formed by fusing calcium cyanamide ($CaCN_2$) with sodium chloride, became available about 1916; its cyanogen content ranges from 27 to 30 per cent. This form came into limited use in the United States as a general fumigant and for rodent control. In Australia it was used as a Citrus fumigant, preferably on oranges, and was found to be quite safe to the tree except during the rainy season; under California conditions, however, it has proved too dangerous to use on Citrus trees. It was also used extensively in Australia for the control of rabbits.[22]

In 1925 another and safer form of calcium cyanide was developed. The cyanogen content of the latter ranges from 52 to 58 per cent, averaging about 55 per cent. This form is made by combining hydrocyanic acid, calcium carbide and about 2 per cent of water. It is marketed as a fine powder, the commercial grades having 30 to 50 per cent or more of cyanogen, respectively.[23] A dosage of 1¼ ounces of the 30 per cent calcium cyanide has been found to be the equal in efficiency to 20 cc. of liquid hydrocyanic acid. This later form came into extensive use as a fumigant for Citrus trees in California, but has been largely supplanted by liquid hydrocyanic acid. It was used as a building fumigant[23] and has been found effective in the control of chinch bugs.[25] A dosage of 5 to 7 grams of 28 per cent calcium cyanide per 1000 cubic feet of space was found to be effective for greenhouse fumigation, but for more resistant insects this may have to be raised to as high as 2 ounces per 1000.[24a]

### Hydrocyanic Acid as a Fumigant

Hydrogen cyanide or hydrocyanic acid, as it is usually termed by the fumigator, has been for many years the most widely used fumigant and is the standard to which all gases are compared. It diffuses readily at room temperature, is very active in penetration, and is used generally against all types of insects and rodents attacking stored products, as well as for bedbugs, lice, moths and ants in the home. Its toxicity to humans requires great care in manipulation and aeration following treatment. As an orchard fumigant it has had very limited use on deciduous trees and to a much larger extent for leafhoppers on vineyards, but it is as a Citrus fumigant that it has attained greatest popularity and developed into a highly specialized mode of treatment. A peculiar advantage of HCN for such work is the minimum amount of disturbance which it causes to biological control. As the commercial use of both parasites and predators against the insect enemies of Citrus trees is common practice, this feature is a valuable one.

*(Courtesy Dr. D. L. Lindgren)*

FIGURE 9. Fumigation tents as used in a citrus grove. Numbers on the tent are for determining the dosage. Machine in the center foreground is for generating the charge of hydrocyanic acid gas.

The literature on the use of cyanide compounds as insecticides is voluminous and a comprehensive review has been compiled by Cupples.[17a]

Orchard fumigation of Citrus trees with liquid hydrocyanic acid has now become a general practice in the semiarid districts of the world. The usual means of application in southwestern United States is with a small machine mounted on a one wheel frame which is readily pushed through the orchard by the operator. The desired dosage is measured in the machine, pumped into coils in a steam boiler where it is vaporized and passed through a hose and nozzle under the tented tree. The diffusion of this warm gas throughout the tented tree is rapid. In tent fumigation the usual time elapsing between setting off the charge and pulling the tent off the tree is 45 minutes, since effective concentrations of gas cannot be held in a tent for longer periods of time. Fumigation is done at night, the work beginning about an hour after sunset and ceasing about the same length of time before sunrise. Severe injury both to foliage and fruit will result from fumigation with heavy dosages either during the day or immediately prior to or for an hour after the sun has been shining on the trees. Temperatures below 70° but above 40°F are considered safest. The red scale, *Aonidiella aurantii*, is most susceptible to HCN at low temperatures. It is more easily killed at 75°F than at 90°F and is even more susceptible at 50°F than at 75 or 90°F. The tent used for covering citrus trees during fumigation is a flat, octagon cloth with measurements marked at one foot intervals running over the tent in both directions. A good quality of duck or drill, preferably of a very close weave to reduce leakage, is used in the tent, see Fig. 9. The difficulty of compensating for these variables has led to general uniformity both in dosage and length of exposure with but little departure from the established custom. Gas tight fabrics are being experimented with as a means of overcoming much of the variables experienced in using cloth tents but have not come into general use.[21]

Dosages of liquid hydrocyanic acid for citrus trees in southwestern United States are based on a unit of 20 cc. (equivalent of 1 ounce of sodium cyanide containing 51 to 52 per cent cyanogen) to 100 cubic feet. This rate is taken to be "100 per cent dosage schedule". A 50 per cent dosage is 10 cc. per 100 cubic feet and a 110 per cent dosage is 22 cc. per 100. Knight was the first to study gas concentrations under fumigating tents and correlate the data with effective concentrations of HCN in scale insect control.[11] In commercial fumigation the mean concentration of gas under a fumigating tent, for 45 minutes varies with the dosage, temperature and the tent used. See Fig. 10, showing data with a 100 per cent dosage and a temperature range of 55° to 64°F. Dosages under field conditions may be varied with the tolerance of the tree and the susceptibility of the insect. Higher dosages or other means of treatment are used for the "resistant*" type of insects.

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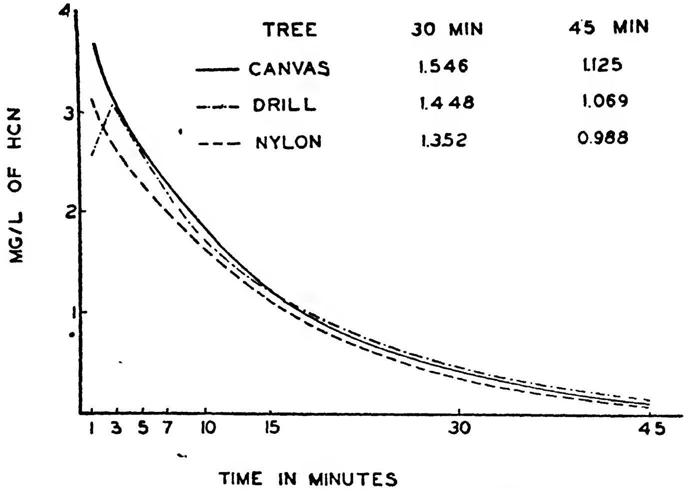
* Resistant is used in the sense that the scale insect requires such a high concentration of gas to give a satisfactory kill that the host plant may be injured.

The effect of different types of concentration curves of HCN resulting from "interval shooting" (two gas generations instead of one in the 45 minute period) and high versus low initial concentrations of gas have been studied by Pratt et al,[12] Cupples,[13] and Lindgren.[15] There is general agreement that in commercial work a single application of HCN is desirable and that the type of curve is not as important as a good distribution of gas. Good results are secured both by a well maintained low concentration and a quick high concentration. Lindgren made further determinations of the mean gas concentrations in the fumigating tent by sampling at 1, 3, 7, 15, 30, and 45-minute intervals from the release of the charge (see Fig. 10). He reports a range in concentration of mg/l from 0.299 for a 4-cc. dosage to 1.215 for a 24-cc. dosage, the kill of red scale being from 98.44 to 100 per cent for the various dosages.[15]



(*Courtesy Dr. D. L. Lindgren*)

FIGURE 10. Mean average concentration of HCN under different types of fumigating tents for the periods of time indicated.

Quayle shows that a decided degree of resistance to HCN has been developed by the common scale insects of Citrus trees; the red scale, *Aonidiella aurantii;* the black scale, *Saissetia oleae;* and the citricola scale, *Coccus pseudomagnoliarum,* from certain localities in California. His studies over a period of years show that higher dosages than normal are necessary to give satisfactory control of these insects in the districts in which the resistant scale predominate. Similar degrees of resistance to the use of methyl bromide and ethylene oxide as fumigants are indicated in limited experiments with these chemicals.[16]

Greenhouse fumigation with hydrocyanic acid is subject to the same precautions as field fumigation, in that the work is usually done at night or at least on cloudy days. House temperatures should be between 60 and 70°F.[24] High humidities during fumigation are not necessarily dangerous unless accompanied by temperatures of 70 to 75°F. Dosages in the greenhouse are usually $\frac{1}{4}$ ounce of sodium cyanide, or corresponding amounts of liquid hydrocyanic acid, per 1000 cubic feet.[24]

Liquid hydrocyanic acid has come into general use for fumigating mills, warehouses and ships by either air-pressure distributors or the discoid method. For the pressure system a portable unit of charged cylinders of hydrocyanic acid and supplemental air pressure is used, or permanent installations of suitable size pipe with specially designed nozzles are set up, through which liquid HCN is forced. For small buildings or compartments of larger buildings the discoid method may be used. In this process, measured amounts of liquid HCN are absorbed on an inert solid substance from which it volatilizes quickly on exposure to the air. The absorbent material is pressed into thin discs or discoids, each of which carries approximately $\frac{1}{2}$ ounce of HCN. Sealed metal cans are used for storing the prepared discoids. The proper number of cans are distributed to a room, the tops cut out by one operator and the discoids distributed on pads. Properly charged gas masks should be worn by all operators. Dosage is based on 1 pound of sodium cyanide to 1000 cubic feet of space, and is increased according to the amount of material stored in the room. Corresponding dosages for liquid hydrocyanic acid are given by the manufacturer.[10, 58]

**Compatibility of Hydrocyanic Acid with Other Insecticides.** Fumigation with hydrocyanic acid is commonly practiced either immediately prior to or following the application of nicotine, pyrethrum, rotenone, dinitro dusts, cryolite, sulfur, tartar emetic, oil, zinc oxide and soap. The exceptions are copper sulfate, Bordeaux mixture, manganese sulfate and lime. Fumigation of Citrus trees with HCN is said to be dangerous at any time within a few months after applications of copper or manganese.[19, 20] If it is necessary to apply a fungicide to Citrus groves that may soon require fumigation, certain of the organic forms may be employed after proper testing; or use may be made of the zinc-copper "Bordo" formula, which is considered safer than the usual Bordeaux mixture. The formula is as follows:[18a]

| | |
|---|---|
| Zinc sulfate (23 to 25% metallic zinc) | 12 pounds |
| Copper sulfate | 1 pound |
| Hydrated lime | 6 pounds |
| Water to make | 100 gals. |

The same tendency to plant injury with HCN fumigation, following copper applications, has been noted in greenhouse treatment. Basic copper sulfate and carbonates have been found safer than Bordeaux mixture applications.[21a]

**Sorption of Hydrocyanic Acid by Foods.** Fumigation with HCN being a very general practice, it is sometimes necessary to expose foods to high concentrations of gas. Since HCN is readily absorbed by water, care should be used in exposing foods of a high moisture content. Many types of food with low moisture contents do not absorb large amounts of the gas, and a few hours' aeration is usually sufficient to remove the danger.[26, 27] For very high dosages—10 to 20 ounces of sodium cyanide per 1000 cubic feet—the aeration period should be extended to 24 hours. The gas does not impart an objectionable odor to tea and tobacco, but the above-mentioned heavy dosages may injure leafy vegetables such as lettuce, celery, cabbage, and soft fruits, including strawberries and bananas. Careful tests on the baking qualities of fumigated flour showed only the slightest effect from such treatment and no effect on the finished loaf.[28] Fumigation tests on the absorption of HCN by fresh meat showed as high as 90 ppm immediately after treatment and only 9.7 ppm 24 hours later. Milk absorbed 13.5 ppm at the surface, which dropped to 1.0 ppm after 24 hours. Dried fruits absorbed from 10.8 ppm for raisins to 8.6 ppm for figs; these amounts dropped to 4.8 and 3.7 ppm, respectively, after 24 hours.[27] Cheddar cheese, both whole and sliced, made with different proportions of cream and skim milk and fumigated for 24 hours at a dosage of 10 ounces of sodium cyanide per 1000 cubic feet, showed only slight absorption of HCN. The slight odor of the gas disappeared within two hours after treatment and neither odor nor flavor could be detected when the cheese was eaten at this time.[29] Bananas fumigated in refrigerator cars with sodium cyanide at the rate of 5 pounds per 1000 cubic feet have shown serious injury. No injury resulted with the recommended dosages of 6 ounces per car of 2600 cubic feet capacity. The amount of HCN absorbed by bananas at the latter dosage was about 10 ppm, all of which was dissipated by a few days' exposure.[30a]

Citrus fruits absorb varying amounts of HCN, the green fruits being more susceptible than the mature ones.[17] Lime fruits taken direct from refrigeration were injured by all dosages of HCN. This was probably due to condensation of moisture on the chilled fruit, as at normal temperatures this type of injury did not appear, even at the 25-cc. dosage.[30]

**Soil Fumigation with Hydrocyanic Acid.** Experiments with HCN generated both in the soil and on the surface indicate limited possibilities of this practice, under favorable conditions, as a control of soil-inhabiting insects. HCN diffuses slowly through loose soil, with almost no penetration into heavy damp subsoils. Diffusion in moist soils apparently occurs only after saturation of the soil water. Clay soils absorb much greater quantities of HCN than do sandy soils or sand itself. The gas absorbed by clay soils is largely retained in spite of all efforts to remove it by aeration. The variability of the soil structure under field conditions makes it extremely difficult to estimate dosages which are toxic to insects and yet tolerated by growing plants. Fumigation is practical only where growing plants are not present, or for treating potting soil of a uniform nature.[31]

Larvae of the Japanese beetle, *Popillia japonica*, which were feeding near the soil surface have shown an 80 per cent control by a dosage per acre of 165 pounds of sodium cyanide dissolved in 12,000 gallons of water. Experiments with dry cyanide were promising; in these a combination of 400 pounds of sodium cyanide and 500 pounds of ammonium sulfate were added to the soil. The latter chemical decomposes quickly, giving an acid reaction which aids in releasing the HCN.[32]

Sodium cyanide solutions varying in concentration from 0.5 to 1 gram per pint of water were used in treating the roots of young apple seedlings for the control of the woolly apple aphid, *Erisome americanum*. The young trees tolerated dosages of not more than 1 gram of sodium cyanide each. This dosage killed the greater proportions of aphids present on the roots. The hydrocyanic acid gas was released from the aqueous solution by the action of the acid soil, the pH being 4.6 to 6.0.[32a]

**Vacuum Fumigation with Hydrocyanic Acid.** The use of vacuum was found of little advantage in treating soil for controlling the larvae of the wheat wireworm, *Agriotes mancus;* the white grub, *Lachnosterna sp.;* and the Japanese beetle, *Popillia japonica*, present around the roots. Complete kills were never obtained in wet soils with dosages ranging from ½ to 3 ounces of sodium cyanide per 100 cu. ft. of space, the necessary amounts of water and acid for generating the gas being used in all experiments. Since larvae in soaked soil were not killed with dosages as high as 3 ounces per 100 cubic feet, it was not considered possible to prevent the introduction of such pests by fumigating potted or balled plants with dosages that would be tolerated by the plant.[33]

Control of lice in clothing and baggage is greatly aided by the vacuum method of applying HCN. A high vacuum is superior to a low vacuum, as it gives quicker and deeper penetration. Both adults and eggs are easily killed by HCN and the cyanogen-chloride mixture with a 15-minute exposure. For routine delousing work on clothing, a dosage of 143 to 285.7 ounces of sodium cyanide per 1000 cubic feet, or from 72 to 143 fluid ounces of liquid hydrocyanic acid, is recommended, the initial vacuum to be 26 inches with an exposure of at least 30 minutes.[34]

Vacuum fumigation of baled cotton with HCN to control the pink bollworm, *Pectinophora gossypiella*, present in the cotton seed has been a customary method; but recently control methods have been developed for fumigation at atmospheric pressure. A dosage of 3 ounces of liquid hydrocyanic acid per 100 cubic feet of space, including the cotton, gave a complete kill of larvae at a depth not greater than 3 inches within the bale. Below this depth the pressure was so great as to crush the seed and kill all larvae present. Fumigation should always be carried on at temperatures above 51 °F.[35]

**Self-warning Gases.** Because of the extreme danger of exposure to even rather low concentrations of HCN and the lack of irritating qualities or recognizable odor, small quantities of other and more easily identifiable gases are sometimes combined with HCN. Such gases are usually of an irritating quality, or of an offensive odor which makes them self-warning even in small amounts. Chloropicrin, an active fumigant itself, but of a self-warning character, is added to HCN in an amount of about 5 per cent of the total gas volume. Cyanogen chloride is another gas commonly used in low concentrations, with HCN as the principal fumigant. The formula for the latter mixture is 4 ounces of sodium cyanide and 3 ounces of sodium chlorate added to an amount of hydrochloric acid and water sufficient to keep all in solution.[26]

**Auxiliary Gases.** Pratt and co-workers, in a study of auxiliary gases to be combined with HCN, showed that an increase of toxicity was possible by the addition of certain gases, with a corresponding decrease in the necessary time of exposure. A basic concentration of 0.20 per cent HCN was used, since this dosage gave a 100 per cent kill of the test insect, *Hippodamia* spp., a common lady-bird beetle, in 20 to 30 minutes' exposure. The concentration of the auxiliary gases ranged from 0.1 to 0.025 per cent. The seven most effective gases were found to be both irritating and toxic; listed in the order of decreasing effectiveness they were salicyl aldehyde, benzaldehyde, ethyl thiocyanate, allyl iso-thiocyanate, thiophenol, benzyl bromide, and perchloromethyl mercaptan. Salicyl aldehyde at 0.10 per cent concentration with HCN shortened the time of exposure necessary to give 100 per cent kill to 5 minutes, as did also the 0.05 per cent concentration. Even a concentration of 0.025 per cent reduced the exposure time to 10 minutes, in contrast to the 20 to 30 minute exposure necessary for HCN alone.[36]

**Gas Masks.** The use of carefully fitted gas masks should be insisted upon for all persons exposed to even moderate concentrations of hydrocyanic acid, chloropicrin, cyanogen chloride and other quick-acting fumigants. Masks should also be employed for higher concentrations or long exposures to nicotine fumes, ethylene oxide, methyl bromide, methyl formate, ethylene dichloride, carbon disulfide, carbon tetrachloride, and other organic fumigants.

### Carbon Disulfide ($CS_2$)

Carbon disulfide is a yellowish colored liquid which in the commercial form has a decidedly unpleasant odor, produces a yellowish stain, and leaves a visible precipitate after evaporating. The chemically pure liquid is almost colorless, has a sweetish odor, and leaves no visible precipitate. The specific gravity of the liquid is 1.263 at 20°C and the vapor is 2.63 times as heavy as air (vapor pressure 298 mm. at 20°C). The liquid is non-explosive but the vapor is highly explosive when mixed with air, and at 147°C (296.6°F) it ignites spontaneously. The boiling point is 46.2°C (115°F).[58] Its slight solubility in water makes it necessary to emulsify carbon disulfide with soap or a similar material when it is desired to dilute and apply it as a liquid. The vapor diffuses rapidly in the open and only by close confinement will a lethal concentration be obtained. The changes in time of exposure, necessary at varying temperatures to give 100 per cent kill with carbon disulfide, carbon tetrachloride, and chloropicrin are given in Table 38.[4] Contrary to the usual statement that because the vapor of carbon disulfide is much heavier than air it will penetrate rapidly to the bottom of a bin containing grain, it has been found that the vapor penetrates quite slowly a few inches into the grain. Also in a closed bin, after ample time for diffusion, the concentration of the gas is not greater at the bottom of the bin than at the top.[4]

Table 38. Minimun Time Required to Secure 100 Per Cent Kill of *Tribolium confusum*.
(Concentrations in pounds per 1000 cubic feet)

| Temp. | Chloropicrin | | | | | | Carbon Disulfide | | Carbon Tetrachloride | |
|---|---|---|---|---|---|---|---|---|---|---|
| (°C) | 1 lb. | | 2 lb. | | 3 lb. | | 15 lb. | | 20 lb. | |
| | hr. | min. | hr. | min. | hr. | min. | hr. | min. | hr. | min. |
| 35 | 1 | 15 | — | 31 | — | 15 | — | — | — | — |
| | | | | | | 21 | — | 30 | 1 | 30 |
| 30 | 1 | 45 | — | 35 | — | 25 | — | 45 | 3 | 15 |
| 25 | 2 | 15 | — | 50 | — | 30 | 1 | 00* | 7 | 00 |
| | | | | | | | 1 | 30 | — | — |
| 20 | 2 | 45 | 1 | 10 | — | 40 | 2 | 00 | 12 | 00? |
| 15 | 3 | 50 | 2 | 00 | 1 | 00 | 3 | 00 | — | — |
| 10 | 4 | 30 | 2 | 40 | 1 | 20 | 3 | 30 | — | — |

* In cases where 100 per cent kills were followed by percentages less than 100, both times when the first complete kills occurred were recorded.

**Carbon Disulfide as a Fumigant.** Carbon disulfide is widely used as a fumigant, especially for grain treatment. Fumigation should be at temperatures not lower than 15.5°C (60°F) and preferably 20°C and above.[59] It is easily applied by pouring the liquid evenly over the surface of the grain or absorbing it on sacking which is left in an exposed position. Exposure time is 12 to 24 hours. Fumigation should be conducted in isolated buildings because of the danger of fire and explosion. Carbon tetrachloride, in amounts ranging from 20 to 80 per cent, may be combined with carbon disulfide to reduce the hazard, but with a corresponding loss of efficiency. Dosages for carbon disulfide range from 5 pounds per 1000 cubic feet for treating tight vaults to 10 or 12 pounds per 1000 for more open construction.

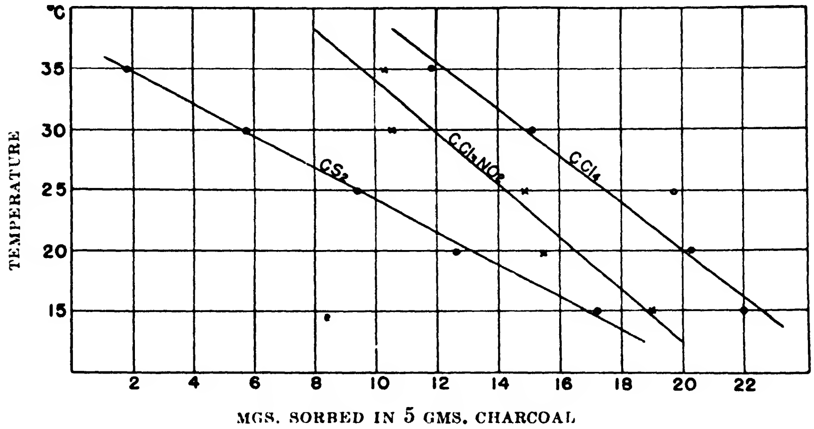


FIGURE 11. The relation of temperature to the sorption of carbon disulfide, chloropicrin, and carbon tetrachloride on active charcoal. Fumigant concentration 1 lb. to 1,000 cu. ft.

**Sorption of Carbon Disulfide by Foods.** Grain and seeds, unless moist, can be treated with practically no danger to germination. Dried fruit may be safely treated when followed by a period of aeration. Fresh berries, including blueberries, blackberries and raspberries, have been fumigated without injury.[30a] Fig. 11 shows the rate of sorption on charcoal at various temperatures.[4]

**Soil Fumigation.** The earliest use of carbon disulfide in soil work was by the French in combatting the root aphid, *Phylloxera vastatrix*.[60] Carbon disulfide has proved to be one of the most efficient chemicals for soil treatment.[62] It may be used at temperatures as low as 7.2°C (45°F); its sorption is low in the various soil types and on charcoal. Its stability reduces the possibility of chemical reaction in the soil. The lack of solubility in water retards its diffusion through wet soils, but favors the use of water seals to prevent loss of gas from treated areas. It should not be used in very dry soils, particularly the heavier types, as diffusion is too rapid. Soil moisture contents ranging from 5 to 15 per cent on the air-dry basis are commonly satisfactory for treatment.[63] Recommended dosages range from 0.5 to 1.0 pound per cubic yard of potting soil.[63, 65] Soil treatments are made with various types of injecting apparatus.[63]

Emulsions of carbon disulfide and water, with a variety of emulsifiers[64], are used in controlling the Japanese beetle, *Popillia japonica*, a number of soil-inhabiting insects, and the root-knot nematode, *Heterodera marioni.*[66] Stock emulsions are prepared containing about 50 per cent of carbon disulfide, and are diluted as required by the tolerance of plants of varying susceptibility. The field of usefulness for this material in treating living plants is thus greatly extended over what would be possible by using it undiluted. Formaldehyde may be added to the emulsion if greater fungicidal activity is desired.

A review of fumigants suitable for use in killing ground squirrels in their underground burrows resulted in selecting carbon disulfide as the most useful and economical material. The gas proved to be toxic to squirrels in 20-minute exposures at roughly 2 per cent concentration, which led to the recommendation of 1.5 to 2.0 ounces of the liquid applied in the burrow by means of a ball of fiber waste. On level ground or on slight inclines the gas flows to the lowest part of the burrow, but it does not flow over an elevation of 1 or 2 feet. These difficulties in diffusion have led to the use of vaporizing apparatus.[61]

**Carbon Disulfide as an Herbicide.** This material may be economically used to control perennial weeds, such as poverty weed, *Iva axillaris*, when they are not established over large areas. Dosages of 2 or 3 ounces of the liquid are poured into holes 12 to 15 inches deep and from 18 to 24 inches apart. Diffusion of the gas is rapid in dry, sandy soil; too rapid evaporation may be prevented by a water seal on the soil surface. Penetration in wet heavy soils is practically nil.[67, 68] The after-effects on following crops is generally beneficial.[69]

Sorption of the diffused vapor is influenced by the character of the soil, water content, density and temperature. Both sandy and heavy adobe soils sorbed large amounts of the gas, the rate of sorption of heavy soil being approximately double that of sandy soils. This is at variance with the sorptive rate of hydrocyanic acid gas, which shows almost no sorption in sandy soil.[31] The rate of diffusion of carbon disulfide vapor from decomposed potassium xanthate was as follows: In sandy subsoils, measurable amounts of carbon disulfide were recovered 6 to 18 inches (15–46 cm.) laterally and 5 inches (13 cm.) below the point where the xanthate was deposited. There was no recovery of carbon disulfide from undisturbed adobe below the decomposed xanthate.[70] In a study of vapor diffusion in various soil types, Hagan has shown that the partial pressure of the vapor increases by about 50 per cent with each 10°C rise in temperature. Further studies of the diffusion of the vapor through various soil types have shown the importance of the "plow sole" or "pan" in reducing the permeability of certain loam soils.[71]

### **Potassium Xanthates** ($KS_2COC_2H_5$)

These are water-soluble carbon disulfide compounds used in soil fumigation. The first use of this material was in the *Phylloxera* campaign in France from 1870 to 1885, [60] but it did not become general at that time because of its high cost. Later developments in chemical engineering have reduced the cost of xanthates to a point of economical treatment for the more profitable crops.[6]

Xanthates may either be drilled in at the depth desired or broadcast by hand and plowed under deeply, followed by irrigation to dissolve the compound and carry it downward into the soil. Since xanthates themselves decompose too slowly to yield lethal dosages of carbon disulfide, it is necessary to combine them with an acid salt or finely ground or precipitated sulfur which will oxidize readily to sulfuric acid, as liquid forms of acid are too difficult to handle in soil treatment. A practical formula for field treatment of soils is 200 to 400 pounds of potassium xanthates to an acre, with a similar amount of acid superphosphate ($CaHPO_4$) (the form used as a fertilizer) and 100 pounds of very finely divided sulfur. The smaller amount of chemicals is for very sandy soils and the larger amount for clay soils.[63a]

### **Sulfur Dioxide** ($SO_2$)

Sulfur dioxide is a non-flammable, colorless gas at room temperature with a specific gravity of 2.23, soluble in water to the extent of about 1 part by weight in 10 parts of water at room temperature. For commercial usage it is compressed into a volatile liquid boiling at −11.6°C (11°F). There are two grades of liquid $SO_2$, the more expensive form being used for refrigeration purposes; the cheaper grade, used for fumigation purposes, is usually marketed in steel cylinders containing 150 pounds of liquid. Drum pressure is 40.6 pounds per square inch at 20°C. This grade is sold as anhydrous, since it usually contains but 0.1 per cent of water.[79] Sulfur dioxide is readily absorbed by water, which takes up about 30 times its volume of the gas; for this reason allowance in dosages must be made in the treatment of ship's holds or other moist places.

The gas produced by evaporating liquid $SO_2$ is very heavy, since it is chilled by evaporation and expansion and unless agitated sinks to the lower levels of the fumigated space. When fumigating with 1 pound of $SO_2$

per 1000 cubic feet, but without agitation, rats placed near the ceiling of the room lived for 2 hours while those on the floor were killed within a few minutes. In the treatment of grapes in refrigerator cars as a preventive of mold[80] it has been found necessary to use an electric fan or other stirring device for uniform mixing of gas and air in fumigated spaces. Following the development of such improved mechanical means of agitation, it was found that the concentration of the gas (dosages ranging from 4 to 5 pounds per 1000 cubic feet) 60 minutes after delivery ranged from 3.8 per cent by weight at the top of the car to 0.8 per cent at the bottom. At the end of 3 hours the concentration at top, center, and bottom of the car would be similar and approximately 0.4 to 0.6 per cent by weight, owing to the tightness of the car.

Sulfur dioxide is readily produced by burning sulfur in metal containers; this method has frequently been used in the control of rats about harbors and in ships. The slowness of diffusion of the gas and the difficulty of obtaining uniform and toxic concentrations in every room and enclosure has led to general abandonment of this method of generation, and substitution of the liquefied form.[79]

The lethal concentration of gas for rats has been placed at 0.1 per cent by volume in 2- to 4-hour exposures; 0.2 per cent in 1 to 2 hours; and 1.3 per cent in 1 hour or less. These dosages are lower than for hydrocyanic acid gas, but the latter dissipates itself so quickly that little value exists after the actual period of fumigation. Sulfur dioxide, however, persists long after the application period, which makes possible much longer periods of exposure than is possible with the more volatile gas.[79]

Sulfur dioxide has been found to be a practical fumigant for refrigerator cars such as are used for shipping fresh fruit. Dosages of 4.8 to 6.4 pounds per 1000 cubic feet showed 100 per cent kills in all parts of the empty car, using the saw-toothed grain beetle, *Oryzaephilus surinamensis*, and the fig moth, *Ephestia cautella*, as indicators. Lethal concentrations of the gas both at the top and bottom of the car for 1-hour exposures ranged from 3.0 to 2.8 per cent by weight. Concentrations ranging from 2.6 to 0.8 per cent by weight with 2-hour exposures also proved lethal.

The use of sulfur dioxide as a volatile fungicide or fumigant has been attempted on a number of fresh fruits, including figs and cherries, but was of value only in the protection of grapes in transit and storage; this use has for years been a common commercial practice, especially in California. It has become so general that annual treatments run as high as 18,000 cars of grapes. A concentration of 2 per cent sulfur dioxide in refrigerator cars is commonly used. It combines readily with certain organic substances found in the grape, including the sugars. This combination of sulfur dioxide and sugar is fairly stable and doubtless constitutes a major part of the combined sulfur dioxide in the treated grapes. When grapes are treated with sulfur dioxide, a portion of the gas does not enter into combination; this so-called "free" sulfur dioxide is primarily responsible for retarding or preventing spoilage.[81] In sufficient concentration, it inhibits or stops the growth of various organisms causing spoilage, including the molds, *Aspergillus*, *Botrytis*, and *Monilia*, and certain yeasts and bacteria. In addition to this inhibiting action on the various organisms, the gas also slows the rate of respiration, thus tending to preserve the grape unchanged over a longer period of time, as shown in Table 39.

Table 39. Effect of Varying Amounts of Sulfur Dioxide on Keeping Quality, Appearance and Flavor of Grapes.

| Variety | Mg. of $SO_2$ per kg. added to the grapes | Color and texture of treated grapes | Days elapsing before spoiling | Effect of $SO_2$ on flavor |
|---|---|---|---|---|
| Black Prince | 0 (check) | — | 7 | |
| | 64 | Normal | 16 | Flavor normal |
| Cipro Nero | 0 (check) | — | 6 | |
| | 46 | Normal | 13 | Flavor normal |
| | 70 | Normal | 20 | Flavor normal |
| Malaga | 0 (check) | — | 8 | |
| | 35 | Normal | 14 | Flavor normal |
| | 92 | Normal | 16 | Flavor normal |
| | 201 | Normal | 20 | Stale after 20 days. Trace of $SO_2$ in taste |
| | 451 | Color lighter. Somewhat soft. | 25 | $SO_2$ taste pronounced |
| Hunisia | 0 (check) | — | 8 | |
| | 19 | Normal | 11 | Flavor normal |
| | 38 | Normal | 14 | Flavor normal |
| | 185 | Normal | 20 | Taste slightly injured |
| | 454 | Pale rose color. Somewhat soft | 25 | $SO_2$ taste pronounced |
| Ohanez | 0 (check) | — | 10 | |
| | 13 | Normal | 16 | Flavor normal |
| | 43 | Normal | 22 | Flavor normal |
| | 125 | Normal | 30 | Taste almost normal after 30 days |
| | 256 | Normal | 30 | Trace of $SO_2$ in taste |

Sodium bisulfite ($NaHSO_3$) has also been used as a source of sulfur dioxide for treating grapes. This method differs from regular fumigation in that the fruit is subjected to very much lower concentrations of gas, but for periods of months instead of hours.[82] Five to 10 grams of bisulfite are used per lug box of grapes (25 pounds). The chemical is either placed in pads in the box of fruit or mixed in the sawdust used as packing.

Swisher reports that a mixture of sulfur dioxide and acetone offers a simple method of utilizing sulfur dioxide as a house fumigant. This is believed to form an unstable compound, the vapor pressure of which permits confinement in tin cans, but which decomposes readily on exposure. Acetone itself is flammable and explosive in concentrations of 3 to 8.8 per cent by volume in air. A 1:1 by volume ratio of sulfur dioxide to acetone is easily handled and less flammable than hydrocyanic acid. A dosage of 1 pound per 1000 cubic feet of the 1:1 ratio gave a 100 per cent kill of bedbugs with a 15-hour exposure.[83]

## ALIPHATIC HALIDES

### Methyl Bromide ($CH_3Br$)

Methyl bromide is a colorless and practically odorless liquid, of boiling point 3.56°C, and specific gravity 1.732 at 0°C. The gas weighs 0.247 pound per cubic foot at room temperature. It is non-flammable at all concentrations at which it would be used as a fumigant. Vaporized methyl bromide is very stable under varying conditions of moisture, temperature and pressure.[38] It may be used at comparatively low temperatures and is remarkable for its penetrating qualities. The gas is only slightly soluble in water, thus reducing loss in fumigation and preventing contamination of foodstuffs with a high moisture content. There is, however, an appreciable loss of methyl bromide vapor by sorption on wooden containers and the paint coating of metal walls. This loss has been found to range from 20 to 36 per cent of the total volume of gas present.[36a] The lack of distinctive odor and irritating properties favors its use as a rodenticide, but these factors are objectionable from the standpoint of the operator. It is rated as safer to man than hydrocyanic acid, but prolonged exposures are dangerous to operators and the usual precautions during fumigation should be observed.

**Methyl Bromide as a Fumigant.** The first reported use of methyl bromide as a fumigant was in France in 1932.[37] Extensive experiments were made in quarantine work by the California Department of Agriculture, and by 1937 it was coming into general service (see Table 40).[39] The use of methyl bromide has expanded rapidly in food treatment, louse control[41a] and quarantine measures, until it has become one of the most widely used of all fumigants. Germination of fumigated seeds, as reported upon, has been affected to only a very slight extent,[40, 41] if at all.

Methyl bromide is distributed commercially in 1-pound cans and in cylinders of 10, 50 and 175 pounds net. The natural pressure of the gas is sufficient, at room temperature, to empty both cans and cylinders. The latter are usually supplied at slight increases of pressure.[10] Fumigation with this material in quarantine work includes treatments on nursery stock for the control of the Oriental fruit moth, *Grapholitha molesta;*[42] on alfalfa hay to control the weevil *Hypera* spp;[43] on orchids for various insects;[44] on papaya and tomato fruits;[45] on tomato fruits for control of pin worms, *Keiferia lycopersicella;*[46] on citrus fruits for various insects;[47] and on dried fruits for various insects.[30] Dosages in quarantine work range from 1 to 3 pounds of methyl bromide per 1000 cubic feet, depending on temperature, exposure time and the species of insect concerned. Experiments with it as a fumigant for the California red scale, *Aonidiella aurantii*, on Citrus trees have as yet not shown encouraging results.[48]

Table 40. Methyl Bromide as an Insecticide.

| Insect | Stage | Host | Temperature (°F) | Vacuum (inches) | Dosage (lbs. per M cu. ft.) | Exposure (min.) | Per cent control |
|---|---|---|---|---|---|---|---|
| *G. operculella* | Pupal | Potatoes | 75 | 27 | 2.5 | 90 | 100 |
| | Egg | Potatoes | 76 | 20 | 1.75 | 90 | 100 |
| | Larval | Potatoes | 88 | 20 | 2.5 | 90 | 100 |
| | Larval | Potatoes | 88 | 20 | 2.5 | 30 | 97 |
| | Larval | Potatoes | 89 | 20 | 1.75 | 90 | 100 |
| | Larval | Potatoes | 89 | 20 | 1.75 | 30 | 84 |
| *S. granarius* | Adult | Barley | 95 | 27 | 2.5 | 90 | 100 |
| *T. confusum* | Adult | Barley | 95 | 27 | 2.5 | 90 | 100 |
| *R. terrestris* | Adult | C. I. Palm | 88 | 27 | 2.5 | 90 | 100 |
| *C. aonidum* | Adult | Kentia Palm | 90 | 27 | 1.75 | 90 | 100 |
| *C. pomonella* | Larval | Lug boxes | 85 | 27 | 2.5 | 90 | 100 |
| | Pupal | Lug boxes | 85 | 27 | 2.5 | 90 | 100 |
| *G. lycopersicella* | Larval | Tomatoes | 97 | 20 | 2.5 | 90 | 100 |
| *P. ilicis* | Adult | Plane leaves | 76 | 20 | 2.5 | 90 | 100 |
| | Egg | Plane leaves | 76 | 20 | 2.5 | 90 | 100 |
| *A. lataniae* | 1st–3rd | Areca Palm | 80 | 20 | 2.5 | 90 | 100 |
| *C. aonidum* | 1st–3rd | Areca Palm | 80 | 20 | 2.5 | 90 | 100 |
| *D. boisduvalli* | 1st–3rd | Areca Palm | 80 | 20 | 2.5 | 90 | 100 |
| *A. cyanophylli* | 1st–3rd | Areca Palm | 80 | 20 | 2.5 | 90 | 100 |
| *L. gloverii* | Adult females gravid | Oranges | 53 | 20 | 2.5 | 90 | 70 |

G., *Gnorimoschema;* C., *Chrysomphalus;* S., *Sitophilus;* R., *Rhizoecus;* C., *Carpocapsa;* P., *Paratetranychus;* A., *Aspidiotus;* D., *Diaspis;* L., *Lepidosaphes.*

Greenhouse fumigation with this material has proved satisfactory on a large variety of plants in the control of cyclamen mite, *Tarsonemus pal-*

*lidus;* common red spider, *Tetranychus bimaculatus,* and the mealy bug, *Phenacoccus gossypii.* Successful dosages ranged from 1 to 1¼ pounds per 1000 cubic feet, at temperatures from 70 to 85°F. The best results were obtained in treating houses that had been thoroughly watered, this apparently acting as a seal to prevent soil absorption.[37]

**Sorption of Methyl Bromide by Foods.** Studies by Dudley and Neil have shown that methyl bromide is safe to use as a commercial fumigant for most types of foods. Small amounts of the gas are sorbed by fresh and dried fruits, fresh vegetables and whole grain, but this dissipates quickly.

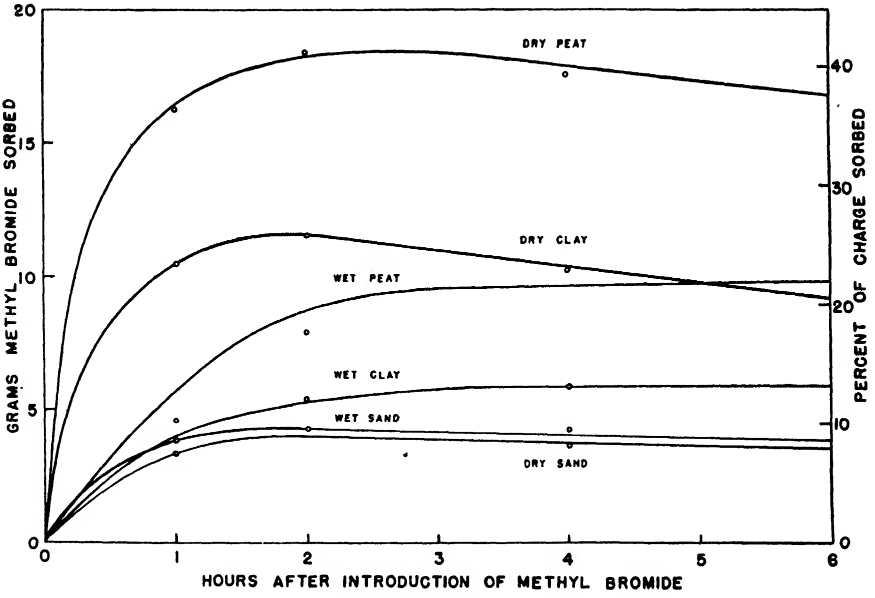


FIGURE 12. Methyl bromide sorbed by soils.

Cereals, cheese and nuts sorb larger amounts of the methyl bromide gas, and considerable amounts are retained after 24 hours. Dried dates fumigated for 24 hours did not show appreciable amounts of bromine residue, nor did the fumigant impart a disagreeable flavor.[47] The ripening of papaya fruits and tomatoes was delayed three to four days by fumigation with 2 pounds of methyl bromide per 1000 cubic feet. The treated papayas were found to be more susceptible to anthracnose injury than unfumigated fruit.[56] Similar injury to tomato fruit fumigated with methyl bromide was noted by Morris and Claypool. Increased tendency to decay was associated with fumigation temperatures of about 10°C (50°F).[57]

**Soil Fumigation with Methyl Bromide.** Control of the white-fringed beetles, *Pantomorus* spp., is reported by Livingstone and Swank[49] with dosages of 4.7 ml. of methyl bromide per square foot of land. Complete mortality of all stages of the beetle occurred in 3.75 days at temperatures between 16.5 and 39°C (62 to 89°F) and at an exposure of 6 days between temperatures of 7 and 16.5°C (45 and 62°F). Strongylid larvae, *Strongyloides*, and coccidia, a protozoan, have been killed with methyl bromide as the fumigant.[50] The snout beetle, *Brachyrhinus ligustici*, is reported controlled with an emulsion of equal parts of methyl bromide, dichloroethyl ether and water at a dosage of 450 ml. of the stock emulsion per 100 square feet of soil.[51] Sorption by soil in a fumigating chamber varied with the type of soil and moisture. The dosage used in the chamber was 2 pounds per 1000 cubic feet. Dry peat sorbed 41 per cent of the total charge, which was 4½ times the amount sorbed by sand. Dry clay sorbed 2¾ times as much as sand[52] (see Fig. 12).

Methyl bromide is a satisfactory fumigant for rodents, and is particularly useful in the control of ground squirrels and the insects harbored by them. It is used both in wet and dry soils and at temperatures as low as 10°C (50°F) and below.[53]

### Ethylene Dichloride ($C_2H_4Cl_2$) (1,2-dichloroethane)

Ethylene dichloride is a colorless liquid with chloroform-like odor, of boiling point 83.5°C and specific gravity of 1.256 at 20/20°C. Its flash point is 14°C; it is very slightly soluble in water, and resistant to oxidation and the action of acids and alkalies. Its vapor is more than 3 times as heavy as air. Its effect on animals is similar to that of chloroform. The odor of the vapors is self-warning, as is also the tendency to dizziness at moderate concentrations.[89] Exposure to high concentrations may produce unconsciousness before escape is possible. It is somewhat flammable and should be combined with a non-flammable chemical such as carbon tetrachloride or trichloroethylene.[10, 86a] Ethylene dichloride and carbon tetrachloride are miscible in all proportions; the mixture has physical properties intermediate between those of its ingredients and is free from corrosive action on metals and staining action on textiles.[90, 91]

**Ethylene Dichloride as a Fumigant.** It is an effective vault fumigant but should be used at a temperature of 20°C (68°F) and above. Three volumes of ethylene dichloride are commonly combined with one volume of carbon tetrachloride or trichloroethylene and used in buildings at the rate of 14 pounds per 1000 cubic feet of space. In air-tight vaults 6 pounds per 1000 is sufficient if the temperature is above 20°C. It is applied by pouring or forcing under pressure into the evaporating pan of the vault. Vaporization is hastened by the use of a fan blowing over the surface of the liquid. It may be used for treating grains and seeds with little danger to germination, but should not be used for foodstuffs with a high fat concentration as they will probably retain a disagreeable odor and taste after fumigation. Godfrey and Young have found ethylene dichloride effective in control of the nematode, *Heterodera marioni*, and the cotton root rot fungus, *Phymatotrichum ommivorum* at the dosages indicated in Table 42.[63]

Emulsions of ethylene dichloride at 15 and 20 per cent concentrations have been found effective in controlling the peach tree borer, *Sanninoidea exitosa*.[92, 93] A certain amount of injury has been reported, indicating variability in the action on trees owing to type of soil and condition.[94] The emulsion has also been found effective in controlling larvae of the Japanese beetle, *Popilia japonica*.[95]

### **Carbon Tetrachloride** ($CCl_4$)

Carbon tetrachloride has a boiling point of 77°C, and a specific gravity of 1.59 at 25°C. A non-flammable fumigant of rather low insecticidal value, it is used principally in combination with other, more toxic materials. It was recommended[92a] first as a substitute for carbon disulfide to avoid the flammability hazard of the latter. The dosage is 30 pounds or more per 1000 cubic feet for grain insects. Because of the high boiling point it should not be used at temperatures lower than 24°C (75°F). The combination of carbon tetrachloride with methyl bromide, methyl formate and ethylene dichloride tends to lower the toxicity below that of the three component fumigants when used alone.[119]

### **Tetrachloroethane** ($C_2H_2Cl_4$)

Tetrachloroethane has a boiling point of 147°C (297°F) and a vapor pressure of 5.1 mm. at 20°C. Limited use has been made of this material as a greenhouse fumigant. It has been found of some value as a fumigant for bedbugs, although decidedly less effective than hydrogen cyanide, chloropicrin, methyl bromide and certain of the nitriles. Tetrachloroethane is reported to be of value as a soil fumigant both as a fungicide and as a nematicide.[63] The low vapor pressure and high boiling point retard its elimination from the soil. Its use as an aerosol applicant for the housefly showed value for knockdown purposes but with small lethal value.

### **Hexachloroethane** ($C_2Cl_6$)

The boiling point of hexachloroethane is 185°C; it is a crystalline solid at room temperature and is made up for use as a fumigant in tablet form containing 10 per cent of starch. It has proved promising in experiments for the control of the corn ear worm, *Heliothis armigera*, the tablet being enclosed in the tip of the ear of corn and the opening closed with a wire clip.[96a]

**Propylene Dichloride** ($C_3H_6Cl_2$) (1,2-dichloropropane)

Propylene dichloride has a boiling point of 96°C, a freezing point of −70°C, and a specific gravity of 1.159 at 25/25°C; it is very slightly soluble in water. Its flammability is similar to that of ethylene dichloride.[106] Tested as a fumigant for the rice weevil it was found less toxic than epichlorohydrin and similar in action to trichloroethane.[105]

The value of propylene dichloride has been shown by Snapp in the treatment of peach-tree borers. Emulsions of 15 to 34 per cent concentration are used at one-half the dosage usually recommended for ethylene dichloride. Having a much lower boiling point than dichlorobenzene, it may be used at correspondingly lower soil temperatures.[106, 107]

A commercial blend known as "D-D", a mixture of propylene dichloride and 1,3-dichloropropene and their isomers, has been reported as a successful soil fumigant against nematodes and wire worms. It is stated to be comparatively easy to handle and does not require a soil cover, as does chloropicrin, for successful fumigation.[108, 108a]

**β-Methylallyl Chloride** ($CH{:}C(CH_2)\cdot CH_2Cl$) (3-chloro-2-methylpropene-1)

β-Methylallyl chloride has a boiling point of 72°C and a specific gravity at 20°/4° of 0.925. It forms a flammable mixture with air between 93 and 375 grams per cubic meter (5.8 and 23.41 pounds per 1000 cubic feet).[121] As a grain fumigant a mixture of 20 pounds of methyallyl chloride in carbon tetrachloride at a dosage of 2 gallons per 1000 bushels of shelled corn is suggested[121] for treating the rice weevil and the saw-toothed grain beetle. It was not as effective as 1,1-dichloronitroethane, ethylene dibromide and other fumigants against the cadelle beetle, *Tenebroides mauritanicus*.[99] It has been reported useful as a fumigant for bedbugs[78] and lice.[122]

**Ethylene Dibromide** ($CH_2BrCH_2Br$) (Ethylene bromide)

Ethylene dibromide has a boiling point of 131°C, a melting point of 10°C, and is very slightly soluble in water.[123] Experiments with ethylene dibromide as a fumigant for the Cadelle beetle, *Tenebroides mauritanicus*,[99] the Japanese beetle[123] and the wire worm, *Limonius californicus*, have uniformly shown a high degree of toxicity, with particular value indicated as a soil fumigant.[108a]

Ethylene dibromide is now being marketed in a form convenient for the gardener's use and without the difficulties of handling the concentrated chemical. It is diluted with an inert material such as naphtha and sold at concentrations from 10 to 42 per cent of the active ingredient. Trade names used included "Dowfume W-10 and W-40", also "Isobrom D", "Soilfume" and "Bromofume".[141]

Other halogenated compounds showing value as fumigants include benzol chloride,[96] methyl iodide, allyl iodide, allyl chloride, and methyl disulfide.[62]

### CHLOROHYDRINS

**Epichlorohydrin** ($C_3H_5ClO$)

Epichlorohydrin has a boiling point of 117°C and a specific gravity of 1.84 at 20°/4°C. It was the most toxic to the rice weevil of more than 100 compounds tested by Neifert *et al.* The dosage giving 100 per cent kill of the weevil was 0.23 pound per 1000 cubic feet in an empty jar. It was not rated a satisfactory fumigant for insects in grain, as it injures germination.[105] Epichlorohydrin has been reported as a successful soil fumigant for wire worms.[62]

"The comparative toxicity of the halogen-substituted alcohols is as follows:

Epichlorohydrin
Propylene chlorohydrin
Ethylene chlorohydrin
Ethylene bromohydrin
Trimethylene chlorohydrin
Trichloro-ter-butyl alcohol."[86a]

**Ethylene Chlorohydrin** ($C_2H_5OCl$)

Ethylene chlorohydrin has a boiling point of 128°C, a specific gravity of 1.213 at 20°C, and is water-soluble. Ginsburg reports this material as being very toxic to codling moth larvae even at 37° to 40°F (3–4.5°C).[109]

### NITROPARAFFINS

**Chloropicrin** ($CCl_3NO_2$) (Trichloronitromethane)

Chloropicrin is a colorless liquid with a boiling point of 112.4°C; its specific gravity at 0°/4°C is 1.692.[73] The specific gravity of air saturated with chloropicrin vapor is reported to be 1.1458 at 25°C and 760 mm. of mercury pressure.[74] It is used as a general fumigant for grains[73, 75, 77] and their products, and for dried and fresh fruit and seeds, although it is reported to injure the germination of alfalfa and radish seed. The lack of water solubility retards absorption of the vapor in moist food products. It is self-warning, of low fire and explosion hazard, not reactive with metals and fabrics, and is superior to many of the insecticidal fumigants in that it is fungicidal and bactericidal. It is a very effective fumigant for flour mills and is useful in rat control. A dosage of 5 pounds of chloropicrin per 1000 cubic feet of space is a common dosage and 2 pounds per 1000 in vaults and tanks. Because of the high boiling point the material should be applied under pressure in mill fumigation. It may also be sprinkled through the machines or soaked up on sacking spread on the floor. Blending one pound or more of chloropicrin in one gallon of carbon tetrachloride improves the volatilization and produces a very toxic gas. Chloropicrin is distributed in 100-pound cylinders for large operations[10] and 1-pound cans for house use. Richardson reports chloropicrin and methyl bromide to be the most effective of 26 chemicals, including hydrocyanic acid, against the bedbug.[78]

Godfrey and Young report the successful control of a number of soil-inhabiting fungi, besides certain species of nematodes and perennial weeds, by the use of a number of soil fumigants with varying physical properties and dosages as shown in Tables 42 and 43.[63]

Table 41. Physical Properties of Soil Fumigants.

| Chemicals | Sp. gr. of liquid | Weight per gals. (lbs.)* | Boiling point (°C) | Vapor pressure |  | Sp. gr. of gas |
|---|---|---|---|---|---|---|
|  |  |  |  | 20°C | 25°C. |  |
| Carbon disulfide | 1.256[1] | 10.18 | 46.2 | 297.5 | 361.0 | 2.8 |
| Chloropicrin | 1.67[1] | 14.00 | 112.0 | 18.2 | 24.0 | 5.7 |
| Ethylene dichloride | 1.257[1] | 10.53 | 83.5 | 60.4 | 77.1 | 3.5 |
| Methyl bromide | 1.732[2] | 14.47 | 4.5 | 1315.0 | 1821.0 | 3.3 |
| Pentachloroethane | 1.681[1] | 14.03 | 160.5 | 3.0 | 4.0 | 7.0 |
| Tetrachloroethane | 1.596[1] | 13.32 | 146.3 | 5.1 | 6.8 | 5.8 |

* 1 gallon of water weighs 8.34 pounds.

[1] at 20°C.

[2] At 0 C.

## 1,1-Dichloro-1-Nitroethane ($CH_3CCl_2NO_2$)

This compound has a boiling point of 124°C, a flash point of 136°F, and a specific gravity 1.415 at 20°C. The gas is self-warning both by odor and irritation of the eyes; it vaporizes rapidly at normal temperatures and penetrates flour and sealed packages readily.

O'Kane and Smith[97] state that the compound can be handled much like orthodichlorobenzene. They found that a dosage of 1.5 pounds per 1000 cubic feet at 26°C gave a 100 per cent kill in 1 hour of the larvae of the meal worm, *Tenebrio molitor*, and adults of the confused flour beetle and rice weevil. The same rate of kill was obtained with a dosage of 4 ounces and 8 hours' exposure. Burying the insects in grain required approximately twice the dosage. Practical use of dichloronitroethane, combined with carbon tetrachloride, is reported by Farrar and Flint[77] in bin fumigation of grain. It was reported as slightly less toxic than chloropicrin in this work. Good results are also mentioned by Richardson and Casanges[98] in the use of this compound as a fumigant for the confused flour beetle, and again by Richardson[99] in experiments with the Cadelle beetle, *Tenebroides mauritanicus*.

**1,1-Dichloro-1-Nitropropane** ($CH_3CH_2CCl_2NO_2$)

This compound is reported to be of similar value to dichloronitroethane as a fumigant for the confused flour beetle.[98]

Evaluation as fumigants of a number of the nitroparaffins have been made with the rice weevil and *Tribolium confusum* as test insects. Roark and Cotton[86a] found nitroethane more toxic than nitromethane. Later studies have shown a slight superiority of nitrobutane over the other nitroparaffins reported in Table 43.[99a] "The solubilities in water of nitromethane, nitroethane, and 1-nitropropane are about 10, 5, and 1.5 per cent, respectively, at 20°C. The flash point (Tag open cup) of nitromethane is 112°F, that of nitroethane 106°F, and that of 1-nitropropane 120°F. The vapor pressure of nitromethane at 20°C is 27.6 mm., which is close to that of chloropicrin (29.7 mm.) At the same temperature nitroethane has a vapor pressure of 16 mm., and this value is progressively lower as the homologous series is ascended."[99a]

Table 42. Dosages of Soil Fumigants.

| | Milliliters* per | | Pounds per | |
|---|---|---|---|---|
| Chemical | cubic foot | cubic yard | thousand square feet | acre foot |
| Chloropicrin | 2 | 54 | 7.4 | 320 |
| " | 2.5 | 67 | 9.2 | 400 |
| " | 3 | 81 | 11.0 | 480 |
| " | 4 | 108 | 14.7 | 640 |
| Carbon disulfide | 8.3 | 224 | 23.0 | 1000 |
| Ethylene dichloride | 11.6 | 313 | 32.0 | 1400 |
| Methyl bromide | 1 | 27 | 3.8 | 166 |
| Pentachloroethane | 12.4 | 335 | 46.0 | 2000 |
| Tetrachloroethane | 13 | 350 | 46.0 | 2000 |

* 1 milliliter (ml.) equals about 20 drops; 30 ml. equals 1 liquid ounce; 1 ml. equals 1 cubic centimeter (cc.). A teaspoon holds about 5 ml.

Table 43. Toxicity of Six Nitroparaffins and Carbon Disulfide as Fumigants against the Confused Flour Beetle after Exposure for 5 hours at 25°C.

| | Approximate Concentration to give | |
|---|---|---|
| Chemical | 50 per cent mortality (mg. per liter) | 95 per cent mortality (mg. per liter) |
| 1-Nitrobutane($CH_2NO_2CH_2CH_2CH_3$) | 8 | 10 |
| Nitroethane($CH_2NO_2CH_3$) | 9 | 14 |
| 1-Nitropropane($CH_2NO_2CH_2CH_3$) | 11 | 16 |
| 2-Nitrobutane($CH_3CHNO_2CH_2CH_3$) | 13 | 20 |
| 2-Nitropropane($CH_3CHNO_2CH_3$) | 19 | 35 |
| Nitromethane($CH_3NO_2$) | 37 | 55 |
| Carbon disulfide($CS_2$) | 56 | 100 |

## NITRILES

### **Acrylonitrile** ($CH_2$:CHCN)

Acrylonitrile has a boiling point of 77.3°C, a freezing point of −82°C, and a specific gravity of 0.801 at 25°C; its solubility in water is 7.0 per cent by weight and its flammability in air 3 to 17 per cent by volume. It is non-flammable in mixtures of equal volumes of carbon tetrachloride; its toxicity to warm-blooded animals is supposed to be due to the formation of hydrogen cyanide.

Dosages of acrylonitrile, giving 100 per cent kill, were 5 mg. per liter for the confused flour beetle and 1.6 mg. for the rice weevil. Dosage for 100 per cent kill of the confused flour beetle in wheat was estimated at 1.4 pounds per 1000 bushels and as 0.7 pound for the rice weevil. Adsorbed fumigant disappears quickly from wheat.[100] Richardson and Casanges reported a prolonged killing action for acrylonitrile for 5 hours, whereas hydrogen cyanide had no prolonged toxic action.[98]

Experiments with this material on bedbugs showed toxicity just inferior to hydrogen cyanide at 25°C in empty flasks. In filled metal cylinders chloropicrin and methyl bromide were slightly superior to an acrylonitrile-carbon tetrachloride mixture.[78] Equal volumes of acrylonitrile and carbon tetrachloride give a non-flammable mixture of greater efficiency as a fumigant than that of the former used alone.[78]

### **Monochloroacetonitrile** ($ClCH_2CN$)

Boiling at 127°C, this compound is reported as slightly more toxic than acrylonitrile to the confused flour beetle, but the high boiling point increases the difficulty of generating the gas[98] and of eliminating it after fumigating.

### **Trichloroacetonitrile** ($CCl_3CN$)

Trichloroacetonitrile has a boiling point of 85°C, a freezing point of −42°C, and a specific gravity of 1.44 at 35°C. The gas is non-flammable and decidedly irritating to the mucous membranes of nose and eyes.[100] The specific gravity of the gas is 4.95[48]. Its toxicity to warm-blooded animals is similar[102] to that of ethylene oxide and methylallyl chloride.

Cotton and Young suggest combining trichloroacetonitrile with carbon tetrachloride to reduce the extreme lachrymatory effect in fumigating practice.[100] Richardson found it slightly less toxic to bedbugs than acrylonitrile and chloroacetonitrile.[78] Glass reports a 50-50 mixture of acrylonitrile and trichloronitrile as a satisfactory house fumigant that penetrates well and is soon lost by ventilation.[101]

**Aromatic Nitriles.** Martin and Wain have shown in preliminary tests with a number of halogenated benzonitriles that the compounds were promising as fumigants but to a less degree as stomach poisons.[103]

### AMINES

Fumigation experiments in the control of the rice weevil showed varying degrees of toxicity with certain amines. Those showing the higher degrees of toxicity and with boiling points below 100°C included isoamylamine [$CH_3CH(CH_3)CH_2CH_2NH_2$], diethylamine $(C_2H_5)_2NH$, and triethylamine $(C_2H_5)_3N$.[86a]

Dahm and Kearns experimented with a limited group consisting of alkyl secondary amines, using adult house flies as the test insect. The quickest-acting compound, judging by the knockdown rate, was N,*n*-hexyl-*n*-heptylamine, $C_6H_{13}NHC_7H_{15}$. This is in the group of straight-, chain alkyl secondary amines. The branched-chain alkyl groups tested when substituted for the straight-chain alkyl group, resulted in a lowered toxicity.[104]

**Di-n-butylamine** ($C_8H_{19}N$). Boiling point 161°C; specific gravity 0.74 at 20°C. Reported as similar in toxicity to carbon disulfide, but because of its low rate of penetration it is not recommended as a fumigant for grain and its by-products.[104]

### ETHERS

**Dichloroethyl Ether** ($C_4H_8Cl_2O$); [bis-(β-chloroethyl) ether].

This compound has a boiling point of 178.5°C, a flash point of 85°C, a specific gravity of 1.22 at 20°/20°C, and a vapor pressure of 1.2 mm. at 20°C. It is oil-soluble and is about 1 per cent soluble in water at 20°C. It is one of the most effective fumigants for grain weevils of a group of over 300 organic compounds tested by Roark and Cotton.[86a] For soil treatments it is applied as an emulsion diluted with water. Snapp reported preliminary experiments against the plum curculio, *Conotrachelus nenuphar*, using two-thirds of a fluid ounce per gallon of water per square yard of soil.[110] Later data confirm the successful control of the plum curculio on peaches with an emulsion of 1.5 per cent on larvae and 4.5 per cent against pupae, using 1 gallon of the emulsion per 6 square yards of soil.[111] Control of the larval stage of the June beetle *Cotinis nitida* and the May beetle *Phyllophaga hirticula* is reported with dosages of 32 ml. of ether per gallon of water (37.8 ml. per gallon is a saturated solution at 20°C) and used at the rate of 1 gallon per square yard.[112] Dichloroethyl ether is used as a fumigant and repellent for wire worms[115, 116] and is a partial substitute for pyrethrins in the control of corn earworm, *Heliothis armigera*.[113, 114]

**Cyclopropyl Alkyl Ethers.** Three ethers were tested as fumigants of the confused flour beetle; clyclopropyl methyl ether, $C_3H_5OCH_3$; cyclopropyl ethyl ether, $C_3H_5OC_3H_7$; and cyclopropyl propyl ether, $C_3H_5OC_3H_7$. The ethyl form was slightly more toxic than carbon disulfide. The other two ethers were slightly less so.[117]

## ESTERS

### Methyl Formate ($CH_3CO_2H$)

Methyl formate has a boiling point of 32°C and a specific gravity of 0.973; it is water-soluble and flammable. Because of its high vapor pressure the fire hazard is not removed by combining it with carbon tetrachloride except at a decided loss of efficiency.[118] Smaller proportions of carbon dioxide-methyl formate, as shown in Table 44, reduce the fire hazard, although a slight excess over the amount indicated is safer.[86] Jefferson has shown a definite loss in toxicity or "antagonism" by combining methyl formate and carbon tetrachloride.[119]

Table 44. Lower and Upper Limits of Flammability of Fumigants in Air and Minimum Amount of Carbon Dioxide Necessary to Reduce These Limits to Nonflamability for All Ratios.

| Fumigant | Lower limit in air (%) | Upper limit in air (%) | $CO_2$ necessary to reduce limits of flamability By volume | By weight (pounds) |
|---|---|---|---|---|
| Carbon disulfide | 1.25 | 45.0 | 22.20 to 1 | 12.9 to 1 |
| Ethylene oxide | 3.00 | 80.0 | 7.15 to 1 | 7.2 to 1 |
| Methyl formate | 6.00 | 20.0 | 2.30 to 1 | 1.7 to 1 |
| Ethyl formate | 2.50 | 14.0 | 5.95 to 1 | 3.5 to 1 |
| Propylene oxide | 2.00 | 22.0 | 11.00 to 1 | 8.3 to 1 |
| Ethyl acetate | 2.00 | 9.0 | 6.25 to 1 | 3.1 to 1 |

Niefert *et al.* showed the value of this and other esters as a fumigant for grain weevils in comparison with carbon disulfide.[105] The methyl formate-carbon dioxide mixture has been recommended as a fumigant for empty warehouses and storage rooms at a dosage of 28 pounds per 1000 cubic feet and exposures of 12 to 24 hours. Higher dosages are required for occupied rooms. The gas mixture seems harmless to food and is of moderate toxicity to operators.[58]

### Ethyl Formate ($C_2H_5CO_2H$)

The boiling point of ethyl formate is 54.3°C. It is water-soluble, and its flammability hazard is high, but it may be used in combination with carbon dioxide. Attention has been called to the value of this substance as a fumigant by Neifert *et al.*[105] It has been recommended as a fumigant for dried fruit in the individual packed box.[120] The effect of the gas on the operator is similar to that of methyl formate. A dosage of 4 ml. of ethyl formate in hot weather and 7 ml. in cold weather is used for a 25-pound box of dried raisins (0.41 cubic feet). The fumigant is placed in the box just prior to packing and then sealed. Isopropyl formate (boiling point 71.2°C) may be used in a similar way.[120a]

The higher members of the alkyl formate series are combined with carbon tetrachloride, in the proportions shown in Table 45, with less fire hazard than is possible with ethyl and methyl formates.

### Methyl and Ethyl Acetate

These compounds are fumigants which have been suggested as substitutes for carbon disulfide.[105] Flammability hazard and a residual odor on wheat have restricted their use.

Table 45. Properties of Non-flammable Mixtures of Carbon Tetrachloride with Alkyl Formates.

| Alkyl Formate | Formate in Mixture by volume (%) | Formate in Mixture by weight (%) | Sp. gr. of mixture (20°/4°C) (Calc) | Weight of 1 gallon of mixture (Calc) |
|---|---|---|---|---|
| *n*-Propyl | 30 | 19.5 | 1.387 | 11.6 |
| Isopropyl | 25 | 15.6 | 1.417 | 11.8 |
| *n*-Butyl | 40 | 27.6 | 1.321 | 11.0 |
| *sec*-Butyl | 40 | 26.9 | 1.310 | 10.9 |
| Isobutyl | 40 | 26.8 | 1.310 | 10.8 |
| Isoamyl | 40 | 26.7 | 1.305 | 10.9 |

### Sulfur Compounds

In a study of grain fumigants a number of materials were found similar to or more effective than carbon disulfide; these included methyl and ethyl thiocyanates, allyl isothiocyanates, ethyl mercaptan and methyl and ethyl sulfides.[105] Further studies stressed the value of ethyl mercaptan, the thiocyanates and methyl sulfides.[86a] Lehman also found values as a wire worm fumigant for both allyl isothiocyanate and ethyl isothiocyanate.[62] Shepard and co-workers report on the value of methyl thiocyanate and ethyl thioacetate.[4a] See Table 46.

## MISCELLANEOUS FUMIGANTS

### Ethylene Oxide ($CH_2CH_2O$)

A colorless liquid boiling at 10.5°C, ethylene oxide has a specific gravity of 0.88 at 7°/4°C. It dissolves readily in water in all proportions and is soluble in the usual organic solvents. Flammability limits are 3 to 80 per cent by volume in air.[85] The usual commercial dosage of 2 pounds per 1000 cubic feet gives a calculated percentage by volume of ethylene oxide vapor of 1.8 per cent.[84] Its relative toxicity to animals is similar to ammonia.[85] A fan should be used for circulating the gas and mixtures of gases at 21°C and below.

The minimum lethal dosage of this material in a vault is 1 pound per 1000 cubic feet and 20 hours' exposure; this gives control of the common warehouse and household insects. Commercial fumigation is usually at the rate of 2 pounds per 1000 cubic feet. Ethylene oxide is similar in toxicity as a fumigant to carbon disulfide but much more effective than carbon tetrachloride.[86a] Penetration is good both into cereal packages and upholstered furniture. It is not active against metals, clothing and polished furniture. Foodstuffs, including nuts and dried fruits,[87] and certain fresh fruits, including raspberries and blackberries, are reported as being uninjured by fumigation at a dosage of 2 pounds per 1000 cubic feet. Blueberries following the same treatment were slightly less firm. Severe injury has occurred to bananas at this dosage.[30a] Injury to germination of wheat has also been noted.[87] Both ethylene oxide and its combinations with carbon dioxide may be used without danger to the milling qualities of grain or of objectionable odors.[86b]

Table 46. The relative toxicity of New Compounds as Fumigants; Temperature, 25°C. (Exposure Period, Five Hours).

| Compound | Boiling point (C°) | T. confusum Mg./liter to kill 50% | T. confusum Mg./liter to kill 99% | S. granarius Mg./liter to kill 50% | S. granarius Mg./liter to kill 99% |
|---|---|---|---|---|---|
| Propylene oxide | 35 | 32 | 52 | 25 | 41 |
| Acetyl chloride | 52 | 3.6 | 5.6 | — | — |
| Propionyl chloride | 80 | 4.1 | 8.3 | 5.0 | 14.0 |
| Thionyl chloride | 79 | 2.0 | 3.8 | 3.0 | 9.0 |
| α,β,-Dichloroethyl ether | 140 | 2.1 | 3.1 | 1.7 | 4.7 |
| β,β,-Dichloroethyl ether | 178 | 1.8 | 3.5 | 1.7 | 3.7 |
| Chloromethyl ether | 58–60* | 3.3 | 10.3 | — | — |
| sym.-Dichloromethyl ether | 100–108* | 10.2 | 14.2 | — | — |
| Methylene chloride | 40.5–42* | 82 | 182 | — | — |
| sym.-Dichloroethylene | 58–61* | 154 | 303 | — | — |
| Tetrachloroethylene | 119–121* | 55 | 99 | — | — |
| 1,1,2-Trichloroethane | 110–117* | 38.5 | 60.5 | — | — |
| Chloroform | 61 | 157 | 267 | 240 | 660 |
| Methyl thiocyanate | 130–131* | 1.6 | 2.6 | 3.5 | 5.7 |
| Ethyl thioacetate | 115–116* | 45 | 63 | 20 | 34 |

* Sample from the Eastman Kodak Co.: boiling point quoted from their price list.

Carbon dioxide is combined with ethylene oxide, to avoid flammability, in the proportion of 9 to 1.[10] More complete data on the ratio of carbon dioxide to various gases to produce non-flammable mixtures are given in Table 44[84] and are shown in Fig. 13. The combination of the two gases has also been found to decrease the necessary exposure time. Ethylene oxide at 3 pounds per 1000 cubic feet gave 100 per cent kill of the rice weevil and confused flour beetle in 3 hours; the addition of 14 pounds of carbon dioxide reduced the exposure time to 45 minutes.[88]

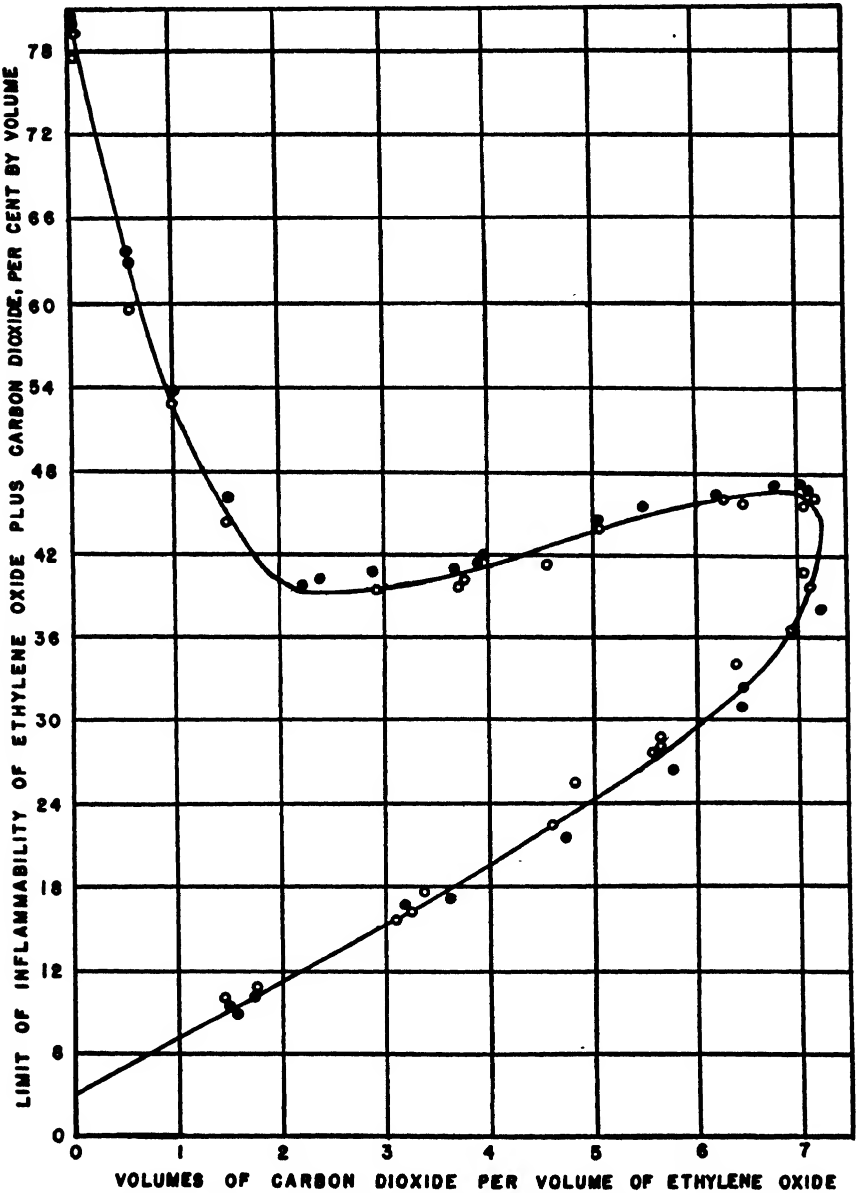


FIGURE 13. Extinction of ethylene oxide flames by carbon dioxide.

### Propylene Oxide ($C_3H_6O$)

Propylene oxide may be used as a fumigant in combination with carbon dioxide to reduce flammability, the proportions required being 11 parts by volume of carbon dioxide to 1 part of propylene oxide.[85, 86a] It is also used as a sterilizing agent for spices in which a preliminary heat treatment is followed by a vacuum fumigation with ethylene oxide or propylene oxide. This process is stated to kill heat-resisting bacteria. The method is also of value in killing insects and mold spores.[108b]

### Naphthalene ($C_{10}H_8$)

Naphthalene boils at 218°C and melts at 80°C. It is a commonly used household fumigant for fabric insects but is limited in its usefulness because of its low vapor pressure.

Crude flake naphthalene is sometimes used as a soil fumigant for wire worms.

Naphthalene vapor is less toxic than many other fumigants and requires a high minimum concentration; but even if a saturated atmosphere is obtained by rapid volatilization[127] or special means of dispersion[128] its field of usefulness is limited by the low toxicity of the vapor.

Combinations of naphthalene and more toxic fumigants have been found advantageous in certain instances. Experiments with the greenhouse whitefly, *Trialeurodes vaporariorum*, have shown increased efficiency over that of naphthalene at a lethal concentration of 0.56 mg. per liter (approximate saturation) by the addition of nicotine vapor at a concentration of 0.004 to 0.006 mg. per liter. The speed of paralysis was increased over that of either naphthalene or nicotine alone.[129] A solution of 30 grams of naphthalene dissolved in orthodichlorobenzene and made up to 100 ml. with the latter was sprayed onto a hot plate at about 375°C, using the American cockroach, *Periplaneta americana*, and the house fly, *Musca domestica*, as test insects. All flies were killed within 24 hours but the action was much slower with the cockroaches. Ninety-five per cent of the latter were dead in 3 days and 99 per cent plus after 10 days.[130]

The aerosol type of application of naphthalene has been shown to be effective on flies when the period of dispersal of the naphthalene particles was prolonged by the presence of smoke[131] The naphthalene was vaporized with a hot plate and, when not accompanied by the smoke of inert material, crystallized and precipitated in 15 to 20 minutes. In the presence of smoke crystallization is retarded and the naphthalene is distributed slowly and very uniformly giving a decidedly increased kill—more so in the covered than the uncovered cages.

Certain of the halogenated naphthalenes, including 3-chloroacenaphthene, 2-chlorofluorene, and 9-bromophenanthrene, have been found effective against houseflies when used as aerosol fumigants.[96]

**Paradichlorobenzene** ($C_6H_4Cl_2$)

Paradichlorobenzene has a boiling point of 172°C and a melting point of 53°C; it is insoluble in water and has a low vapor pressure. The gas shows only a slight hazard to man. It is used commonly as a control of the peach-tree borer, *Sanninoidea exitosa* (eastern species) and *Sanninoidea existosa graefi* (western species). Its value for treating peach trees was reported by Blakeslee in 1919[124] and greater details of treatment were developed by Snapp.[125] The dosages recommended are 0.75 to 1 ounce per tree depending on age. The crystals are placed in a shallow trench around the crown of the tree and are then covered with soil for a few weeks. Because of the high boiling point it must be used at soil temperatures of 54 to 75°F. Paradichlorobenzene is a standard fumigant for trunks and closets as a protection against fabric insects.

**Orthodichlorobenzene** ($C_6H_4Cl_2$)

Orthodichlorobenzene has a boiling point of 179°C, a melting point of $-17.6$°C, and is very slightly soluble in water. This compound, because of its greater hazard to plants, is not used in agricultural practice. Gibson recommends it in combination with Diesel oil for controlling bark beetles in pine trees.[126]

**Nicotine** ($C_{10}H_{14}N_2$)

Nicotine is one of the alkaloids derived from tobacco. Its boiling point is 246.7°C, its specific gravity 1.028 at 15°C, and it is readily soluble in water (see p. 188).

Nicotine volatilized from a water solution of the alkaloid or from a neutralized solution of nicotine sulfate[133] is generally recognized as having fumigating value, even though its vapor pressure is low. Richardson and Casanges in a series of experiments with a number of aphid species and codling moth found decided variation in the effect on various aphids and with varying ages of certain caterpillars.[134] Different methods of vaporizing nicotine in greenhouse experiments also showed an appreciable range of toxicity to various species.[135] Nicotine aerosols compared with the burning of bombs containing nicotine showed a more uniform kill of the aphid, *Myzus persicae*, throughout the greenhouse than resulted from the combustible mixture. Apparently the burning mixture either destroyed or did not evolve the nicotine present.[136]

A study by King and Frear of certain pyridine derivatives as fumigants has shown that the greatest toxicity occurred with the propyl or butyl derivatives. Normal side chains of alkyl pyridines were usually more effective than branched chains. The tests were conducted on the spider mite, *T. telarius*, the confused flour beetle, and the milkweed bug, *Oncopeltus fasciatus*.

## **Formaldehyde** (HCHO)

The boiling point of formaldehyde is −21°C, its specific gravity is 1.075 and it is water-soluble. The commercial mixture formalin usually contains 37 to 42 per cent by volume of formaldehyde.

It is used as a seed disinfectant,[138] either by being adsorbed upon an inert substance such as talc or bentonite or in aqueous solutions. The recommended dosage for treating damping-off fungi of seedlings is ½ fluid ounce of formaldehyde dissolved in water per square foot applied prior to planting.[140]

## **Nitrogen Trichloride** ($NCl_3$)

Nitrogen trichloride is handled in dilute form to avoid its explosive tendency. The gas is self-warning. Commercial use has been made of this material as a sterilizing fumigant for Citrus fruits. Dosages recommended are 5 to 15 mg. per cubic foot of air for a 3 to 5 hour treatment. Conidia of *Penicillium italicum*, *P. digitatum*, and the mycelium of *Phythophthora citrophthora* were killed at concentrations of 4 to 6 mg. of nitrogen trichloride per cubic foot.[139]

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# Chapter 8

## Plant Derivatives

The poisonous properties of certain naturally occurring compounds of various plants have been in use by man since the earliest times. The fish poisons of Australian aborigines and the poison-tipped arrow of other ancient tribes show how deeply such usage is buried in history. Modern chemistry has made available and standarized a few very valuable forms, including nicotine, pyrethrins, and rotenone. These organic forms are more specific in their fields of usefulness than are the inorganic compounds of the protoplasmic poison arsenic, which is destructive not only to insects but also to the higher and lower forms of plant life.

Plant-derived poisons are generally characterized by their greater safety for use on plant foliage than most inorganic compounds. The poisonous elements are due largely to structure, since the chemical elements of which they are made are largely nitrogen, oxygen, carbon, and hydrogen. The structure or form of the compounds is usually rather easily broken down into harmless bodies; nicotine fumes are readily oxidized[4], and rotenone, an extract of the tropical plant Derris, is quickly decomposed by alkalies. Attempts to synthesize the toxic plant compounds or their derivatives have not developed materials of commercial importance.[64, 159] Increased production by plant breeding, fertilization and other cultural practices has met with a certain degree of success. Progress has also been made in developing a variety of the tobacco plant *Nicotiana rustica* which will produce a higher content of nicotine than the tobacco plant of commerce; but the greatest development has occurred in marketing the compounds in new types of chemical carriers or of suitable solvents. Laboratory research in organic chemistry is now centered on the development of compounds quite different in structure from plant derivatives.

### **Nicotine** ($C_{10}H_{14}N_2$)

Nicotine, the principal alkaloid found in the tobacco plant of commerce, *Nicotiana tabacum* has a structure reported[63] as $\beta$-pyridyl-$\alpha$-N-methyl-pyrrolidine. The alkaloid nicotine is basic in its reaction, levorotatory, volatile and much more toxic in this form than when combined with acids (dextrorotatory) to form non-volatile or fixed compounds.[3] Racemic nicotine (*dl*-nicotine) is stated to be approximately one-half as toxic as natural nicotine (*l*-nicotine).[23, 64]

Nicotine of a high degree of purity is an oily, almost colorless and odorless liquid, of density 1.0093, and boiling point 246°C. It is readily soluble in water and to a less extent in mineral oil fractions. It is unstable as a vapor and in alkaline dust bases, probably due to oxidation.[4]

The alkaloid occurs in the leaves and stems of the tobacco plant, varying in amount from a fraction of 1 per cent to 4 or 5 per cent. Attempts made to increase the nicotine content by cultural processes have had but slight success.[2] One species, *Nicotiana rustica*, has been found to yield a higher nicotine content than *N. tabacum*. The annual production of nicotine in the United States ranges from 2,406,000 pounds (as nicotine sulfate solution of 40 per cent nicotine concentration) in 1941 to a maximum of 2,750,000 pounds.[66] Since this recovery includes almost all trimmings and waste products, there seems to be little possibility of large increases in the supply.

Table 47. United States Imports of Nicotine and Nicotine Sulfate (1933–42)*

| | U.S.S.R. | | Germany | | United Kingdom | | Total | |
|---|---|---|---|---|---|---|---|---|
| Year | Pounds | Value | Pounds | Value | Pounds | Value | Pounds | Value |
| 1933 | 89,270 | $29,043 | 35,678 | $12,206 | — | — | 124,948 | $41,249 |
| 1934 | 50,409 | 20,981 | — | — | — | — | 50,409 | 20,981 |
| 1935 | 164,389 | 70,667 | — | — | — | — | 164,389 | 70,667 |
| 1936 | 39,661 | 18,848 | — | — | 200 | $54 | 39,861 | 18,902 |
| 1937 | 2,910 | 1,862 | — | — | 255 | 91 | 3,165 | 1,953 |
| 1938 | 4,409 | 1,852 | — | — | — | — | 4,409 | 1,852 |
| 1939 | 28,659 | 8,620 | — | — | 120 | 35 | 28,779 | 8,655 |
| 1940 | 2,756 | 1,021 | — | — | — | — | 2,756 | 1,021 |
| 1941 | 35,549 | 12,503 | — | — | — | — | 35,549 | 12,503 |
| 1942[a] | | | | | | | 55,439 | 23,427 |

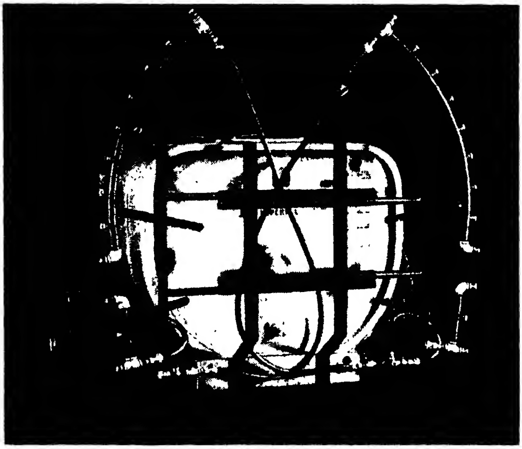
[a] For security reasons, only the total can be given.

* Source: Foreign Commerce and Navigation of the United States.

Exports of nicotine sulfate from 1933 to 1942 have averaged 425,000 pounds annually. These have been shipped principally to Australia, Canada, Japan, New Zealand, and the Union of South Africa. Imports of nicotine and nicotine sulfate from 1933 to 1942, inclusive, and the originating country are shown in Table 47.[65]

Finely ground tobacco dust may have a certain degree of toxicity, but since this varies with the natural nicotine content the results must be variable. The addition of 10 per cent of hydrated lime to the tobacco dust improves the physical qualities, but not the toxicity.[1] Nicotine extracts may be made from waste tobacco with either cold or hot water, but the efficacy of the solution will depend upon the original content of nicotine. If a known nicotine content is uniformly present, a degree of accuracy is possible if concentrations not higher than 0.04 to 0.07 per cent nicotine are desired.

Commercial production of nicotine is by steam distillation of tobacco in the presence of alkali. The alkaloid is commonly marketed as a nicotine sulfate. It forms a loose combination with sulfuric acid, usually with about 1 per cent of uncombined nicotine. The sulfate form is non-volatile and hence will not lose nicotine on exposure. As it is also less toxic than the alkaloid itself, it is somewhat safer to handle. Free or uncombined nicotine is also marketed in 40 and 80 to 85 per cent concentrations, the latter being sold only to manufacturers, as it is too hazardous for any but trained operators to handle, there being danger both from inhalation and absorption through the skin.



*(Courtesy The Hardie Manufacturing Co., Hudson, Mich.)*

FIGURE 14. Hardie multi-nozzle orchard sprayer.

Since nicotine sulfate is non-volatile and less toxic than free nicotine, it becomes necessary to neutralize all or the greater part of the sulfuric acid entering into the combination by the use of alkali. This is accomplished in part when alkaline water is used as a carrier for the nicotine, and also by the use of spreaders such as alkaline soap. The amounts of alkali in solution in waters varies greatly; it may be so slight, especially in "soft water", as to be of little value in neutralizing the acid present, in which case poor results in control may be expected. Moore found the tap water used in his experiments neutralized about one-half of the nicotine sulfate contained in the spray solution.[5] Other studies revealed that a tap water requiring 1.3 ml. of $N/50$ sulfuric acid to neutralize 100 ml., did not give the fullest possible toxicity even with the addition of soap.[3]

The correlation between the toxicity of nicotine solutions and their conversion from the combined form (nicotine sulfate) to the free alkaloid is shown in the data in Tables 48 and 49. The experiments include the determination of residual nicotine after application to foliage and correlated bio-assays, including both spraying and fumigating tests. The marked difference shown in Table 48 between the volatility rate in clear and rainy weather is due in part to the slower evaporation rate of water, which holds the nicotine longer in solution and hinders its volatilization. Nicotine may also volatilize or oxidize more rapidly from a dry film in low atmospheric humidity.

Table 48. Foliage Tests of the Volatility of Nicotine in Various Alkaline Solutions and Under Contrasting Meteorological Conditions

| No. | Type of Solution | Per cent of Nicotine Recovered Ser. (1) | Ser. (2) | Ser. (3) |
|---|---|---|---|---|
| | A* Clear weather | | | |
| 1 | Nicotine sulfate, no alkali | 48.5 | 29.9 | trace |
| 2 | Nicotine sulfate +0.25 ml. *N*/1 NaOH | 50.0 | 25.1 | 4.8 |
| 3 | Nicotine sulfate +0.5 ml. *N*/1 NaOH | 42.7 | 13.7 | trace |
| 4 | Nicotine sulfate in tap water | 51.5 | 15.7 | trace |
| 5 | Nicotine sulfate in tap water + soap equal to 4 lbs. per 100 gallons | 36.6 | 8.9 | 3.0 |
| 6 | Nicotine sulfate +0.75 ml. *N*/1 NaOH | 27.9 | trace | trace |
| 7 | Nicotine sulfate +1.0 ml. *N*/1 NaOH | 10.4 | trace | 0 |
| 8 | Free nicotine +0.013 gm. $Na_2SO_4$ | 14.1 | 0 | 0 |
| | B† Cloudy and rainy weather | | | |
| 1 | Descriptive matter as above | 82.6 | 46.1 | 13.4 |
| 2 | | 52.7 | 18.5 | 7.0 |
| 3 | | 26.9 | 7.7 | 6.0 |
| 4 | | 35.8 | 12.5 | 19.0 |
| 5 | | 33.2 | 7.4 | 0 |
| 6 | | 15.5 | trace | trace |
| 7 | | 17.9 | 0 | trace |
| 8 | | 41.9 | trace | 2.7 |

A* Laboratory Tests in clear weather.
B† Laboratory Tests in cloudy, rainy weather.
Series (1), Nicotine residue determined after 3 hours.
Series (2), Nicotine residue determined after 24 hours.
Series (3), Nicotine residue determined after 48 hours.

Nicotine solutions except No. 2 were made from pure nicotine combined with sulfuric acid. No. 1 is nicotine sulfate in distilled water. Nos. 2, 3, 6 and 8 were 4 gradations of the amount of neutralizing alkali added. No. 4 is the same as No. 1 except in the use of tap water. In No. 5 both tap water and an alkaline soap spreader were used.

It will be noted from Table 48 that the full amount of nicotine from a properly made spray is released in 24 hours and that from 85 to 90 per cent is available in the first three hours during clear weather, while the combined alkaloid may lack from 13 to 19 per cent of being completely volatilized after 48 hours of cloudy weather. Such long periods required for activation necessarily reduce the efficiency of a spray in two ways: the released nicotine may never attain a lethal concentration, or rain may wash off an application or dilute it to the point of inefficiency. The data in Table 49 show a close correlation between the effect of spraying and fumigation, further proof of the relation between volatility and toxicity.[3]

**Nicotine as an Insecticide.** Nicotine is used as an insecticide both in the volatile form and as a fixed or stable compound.[67] The first refers to sprays and dusts carrying free nicotine or nicotine sulfate, to which sufficient alkali is added to neutralize the combined acid. In such sprays and dusts the greater part of the nicotine is released or volatilized within 24 hours, the greatest concentration usually occurring within the first 4 hours after application. Fumigation with nicotine of course also requires a volatile form. The volatile nicotine sprays and dusts are used principally against soft-bodied insects, including aphids, thrips, psyllids, tingids, poultry lice, a very few of the beetles, and young lepidopterous larvae and sawflies. Nicotine sprays have a limited use in the more concentrated form as ovicides. Horticultural usage of nicotine has been generally extended to include dips for sheep scabies and other species of animal attacking mites as well as

Table 49. Toxicity to Aphids[1] from Spraying and Fumigating with Nicotine Sulfate in Solutions of Varying Alkalinity.

| No. | pH Value | Nature of Solution | % Aphids dead | |
|---|---|---|---|---|
| | | | Spraying | Fumigation[2] |
| 1 | 6.5 | Nicotine as sulfate, 1–1000, distilled water | 53.6 | 48.1 |
| 2 | 6.7 | Nicotine as sulfate, 1–1000 + 2.4 ml. $N/1$ NaOH, distilled water | 49.7 | 55.5 |
| 3 | 7.2 | Nicotine as sulfate, 1–1000 + 4.8 ml. $N/1$ NaOH, distilled water | 60.9 | 58.9 |
| 4 | 7.4 | Nicotine as sulfate, 1–1000, tap water | 51.0 | 62.9 |
| 5 | 7.6 | Nicotine as sulfate, 1–1000, tap water + soap at the rate of 4 lbs. per 100 gals. | 65.3 | 66.6 |
| 6 | 7.8 | Nicotine as sulfate, 1–1000 + 7.2 ml. $N/1$ NaOH, distilled water | 65.4 | 88.4 |
| 7 | 7.9 | Nicotine (free) 1–1000, + an amount of sodium sulfate equivalent to that formed in No. 6, in distilled water | 74.6 | 82.9 |
| 8 | 8.2 | Nicotine as sulfate, 1–1000 + 9.6 ml. $N/1$ NaOH, in distilled water | 76.5 | 75.7 |
| Check | | Untreated aphids | 7.7 | 22.3 |

[1] Ivy aphid (*Aphis hederae* Kalt). Green peach aphid (*Rhopalosiphum persicae* Sulzer).

[2] Concentration of nicotine in the spraying and fumigating experiments 1 to 1000. In the fumigating experiments 5 ml. of the respective solutions were placed at the bottom of a glass cylinder 6 inches high. Leaves infested with aphids were placed in the upper end of the cylinder, which was then closed with a cork.

lice.[20] The customary concentration of nicotine sulfate (40 per cent) in spray solutions is 0.03 to 0.05 per cent of actual nicotine. It is also stated in the dilution range of 1 to 500 to 1 to 1200 of nicotine sulfate in water. Spreaders, including soap or certain organic compounds, are commonly added to the spray solution. Moore reports on the value of nicotine oleate in the control of greenhouse insects.[68] Hansberry and Norton found a high rate of toxicity for nicotine laurate, oleate, linoleate, stearate, and naphthenate. A second group with inferior wetting properties included nicotine alginate, caseinate and humate. Insoluble compounds, including nicotine silicotungstate and nicotine peat, showed little toxicity to aphids.[69]

*(Courtesy The Hardie Manufacturing Co., Hudson, Mich.)*

FIGURE 15. Hardie multi-nozzle orchard sprayer in action.

Nicotine dusts for orchard use were first made in California in 1917, using equal parts of ground tobacco and sulfur. Varying contents of nicotine in the available dusts quickly led to the use of standardized concentrates of nicotine sulfate. Kaolin was substituted for the sulfur base, but was found to be too absorptive. Calcium carbonate and hydrated lime gave a high initial concentration of nicotine with a correspondingly higher kill of aphids, *Chromaphis juglandicola*, than occurred with a prolonged release at a lower concentration.[6] Since a light, uniform mixture of the nicotine and dust base is essential, power mixers were used from the first, both in the factory and in the orchard.[7] Further studies[8,-12] have developed a number of modifications of the dust base and the concentration of the nicotine to meet the needs of eastern and western conditions. Hydrated lime continues to be one of the principal ingredients of the base because of its availability and fineness of division. Carbonates generally give a quicker release of nicotine from the sulfate form than do the hydroxides. Dolomite,

$CaMg(CO_3)_2$, when finely powdered, has been found satisfactory in certain formulas. The use of free nicotine, instead of the sulfate form, led to greater flexibility in the choice of dust bases, particularly where sulfur was desired in the formula.

Manufactured nicotine dusts are marketed with nicotine contents varying from 1 to 4 per cent of actual nicotine. A common formula is one containing 10 pounds of nicotine sulfate, but because of loss of nicotine[13] on standing and to conform to guarantees the content is usually stated as 3.6 per cent of nicotine. Dating of the package is customary, and those unsold at the expiration of a certain time are returned to the manufacturer. Packaging is usually in multi-wall paper bags, with an impervious inner layer, or in light-weight steel drums, the latter being used for longer shipments.

**Oil Carriers of Nicotine.** Nicotine solutions in water carriers of spray mixtures require the addition of a wetting or spreading agent. One or more pounds of soap are frequently added to 100 gallons of spray, which may be sufficient for a wetting effect on certain of the aphids and thrips larvae. For insects with heavier wax coatings, such as the mealy bug (*Pseudococcus*), wooly aphid of the apple (*Eriosoma lanigerum*) and the scale insects (*Coccidae*), oils are commonly used as carriers (see p. 137).

Free nicotine of 95 per cent concentration rather than nicotine sulfate should be used for combining with oils. Very high concentrations of nicotine in oil may be obtained by dissolving it first in pine-tar oil and then combining with the desired petroleum fraction.[12]

Oil-nicotine combinations in very volatile petroleum are applied as a mist to plants at the rate of 5 to 9 gallons per acre but without first emulsifying, as is customary with heavier oils.[14] Foliage injury may result from high dosages of nicotine.

**Nicotine Fumigation.** The high toxicity of nicotine to insects and its tolerance by plants has led to many efforts to use it as a fumigant, particularly in greenhouses. Painting it on heaters and burning nicotine-saturated papers have been tried with some degree of success. All efforts have failed to maintain toxic concentrations longer than an hour.[78] Laboratory concentration of nicotine as low as 0 003 to 0.25 mg. per liter were fatal in 30 minutes or less to 13 species of aphids and thrips. Practical applications of similar methods of releasing nicotine have not been developed.[79]

**Non-volatile Carriers of Nicotine.** Fixed or stable nicotine compounds are of permanent or residual type that is effective over a period of many days. They may be ingested by feeding on coated leaves or act as a repellent to prevent feeding and induce migration. Non-volatile compounds have been used principally against codling moth (*Carpocapsa pomonella*)[17, 19, 72], grapeberry moth, (*Polychrosis viteana*), pistol casebearer (*Coleophora malivorella*)[66], and citrus thrips.[73] Increased attention has been given to the use of nicotine for codling moth control because of the difficulty of removing poisonous residues on fruit after the use of lead or calcium arsenate and fluorine compounds. One of the first compounds tested for this purpose was nicotine tannate. A tank mixture of 2 pounds of tannic acid and 1 pint of free nicotine (50 per cent nicotine) to 100 gallons was used and 2 pounds of a nicotine tannate powder (20 per cent nicotine) plus skim milk spreader and 5 pounds of colloidal sulfur as a fungicide. Similar control was obtained with both nicotine tannate and lead arsenate. No foliage injury resulted from the nicotine applications. Sixty to 70 per cent of the nicotine tannate was lost from the foliage within 10 days.[17]

The absorption of nicotine on certain clays and other inert substances, as a means of giving prolonged action, is used in making certain "nicotine pills" for removing internal parasites from poultry[21], and in nicotine-bentonite compounds. The latter form was developed by Steiner and Sazama as a tank mixture, using a Wyoming bentonite which absorbs a large amount of the nicotine present. Five pounds of bentonite, 1 pint of nicotine sulfate, 1 quart of soybean oil and a spreader are used in 100 gallons of spray. The residue at harvest time is largely bentonite, with little nicotine present, and is removed by washing or brushing.[19] Smith has shown that the reaction between nicotine and bentonite is principally one of base exchange; the exchange is due to chemical equivalency of the organic base and the bentonite.[18, 74] Fahey's study of a large number of bentonites revealed striking differences in their ability to remove nicotine from water solution and to form an insoluble compound. Flocculating substances, naturally present in some bentonites, may be removed by treatment with dilute mineral acids, thus aiding suspension. Satisfactory bentonites for tank mix purposes should swell to at least 4 times the original volume when wet with water, flocculate on the addition of nicotine sulfate, and remove at least 90 per cent of the dissolved nicotine.[75] The process has been found effective in the middle west, but it is unsatisfactory because of the heavy residue. Further investigations have shown the value of certain Mississippi bentonites which in the natural state have been equally effective for codling moth control, but without leaving objectionable residues.[76] The nicotine-bentonite tank mix had not been generally accepted up to 1942 as a satisfactory substitute for lead arsenate for codling moth control, except in light infestations.[71]

The compatibility of nicotine-bentonite mixtures with copper fungicides varies with the alkalinity of the latter and the resulting pH reaction in the spray tank. The residual value of the nicotine-bentonite mixture is broken down by the addition of an alkali; the nicotine becomes water-soluble and is washed off or volatilized. Untreated bentonite, in a nicotine combination, tends to reduce the soluble copper content of the fungicide compound.[77]

**Nicotine Humate.** This non-volatile material is produced by combining nicotine with peat. "The liquid separated from nicotine peat also contains nicotine, not as the free base, but in combination with humic acid derived from the peat. This aqueous solution can be treated with alkali and the nicotine recovered by distillation; but since the compound in solution, nicotine humate, may have a usefulness of its own, it has been recovered unchanged by evaporating the water. Nicotine peat and nicotine humate are thus companion products formed in a single reaction. Nicotine humate is a black product, soluble in water, forming what is undoubtedly a colloidal solution."[15] The amount of nicotine humate produced depends on the type of peat used, its preliminary treatment and the ratio of peat to nicotine.[15] "Two types of peat have been used in the production of the material, New Jersey peat and German moss peat. New Jersey peat is screened for the removal of impurities, dried to a moisture content of 10 per cent, soaked in 2 per cent hydrochloric acid, washed free of soluble matter, and then treated with nicotine in the presence of water. The mixture is dried and ground to a fine powder. German moss peat is treated directly with nicotine. The nicotine content is about 10 per cent, and the nicotine insolubility is 88 per cent of the total for the New Jersey product and 68 per cent for the German product."[16]

Hansberry, in a comprehensive study of nicotine compounds for codling moth control, showed the value of combinations with fatty acids as contact sprays, but without residual value. Among the fixed nicotine compounds those giving the most promise were fine powders, resistant to wetting and forming adhesive deposits. Nicotine cupro-cyanide at the rate of 0.5 pound to 100 gallons was superior to lead arsenate.[70]

**Compatibility of Nicotine Compounds.** Nicotine sulfate and the alkaloid nicotine are compatible both as sprays and dusts with Bordeaux mixture, lime-sulfur solution, cryolite, foliage oil sprays, sulfur dust, soap, arsenates, Paris Green and zinc arsenite. Nicotine has been used with pyrethrum and rotenone, but the latter should not be added to alkaline-base dusts. Nicotine dusts should not be combined with dinitro-*o*-cyclohexylphenol.

The fixed or stable nicotines should not be combined with alkaline-base dusts, lime-sulfur solution, Bordeaux mixture, lime or dinitro-*o*-cyclohexylphenol.

## Anabasine ($C_{10}H_{14}N_2$)

Anabasine is also known as neonicotine; it is an alkaloid having the same empirical structure as nicotine, of which it is considered to be an isomer. Anabasine is soluble in water in all proportions and in many organic solvents. It has a specific gravity of 1.0481 (20/20), a boiling point of 280.9°C, is basic in reaction, and, being less volatile than nicotine, it is with difficulty distilled in steam.[85] It has been shown by Smith[80] that the alkaloid β-pyridyl-α-piperidine, which he synthesized, is the same as the natural alkaloid anabasine. The latter, however, is levorotatory while neonicotine is optically inactive. The commercial form of anabasine sulfate is derived from one of the chenopodiaceae, *Anabasis aphylla*, indigenous to portions of northern Africa, Russian Turkestan and Transcaucasia. The product as marketed is said to analyze 40 per cent alkaloids, the predominating one being anabasine.[81]

In a study of the comparative toxicity of anabasine, nicotine and rotenone to goldfish it was found that the two alkaloids are 6 or more times as toxic as rotenone. Anabasine was considered slightly less toxic than nicotine under the conditions of the test.[24] Anabasine sulfate is similar in toxicity to nicotine sulfate in the control of the aphid, *Aphis fabae*, but the former showed inferior results in controlling chewing insects.[22, 23]

### **Nornicotine** ($C_9H_{12}N_2$)

The structural formula of nornicotine is β-pyridyl-α-pyrrolidine; it is soluble in water and organic solvents, and but slightly volatile with steam. It has a specific gravity of 1.072, a boiling point of 270°C and is basic in reaction.[86] The alpha and beta forms correspond to the respective forms of nicotine. They were synthesized in 1934 by Craig.[83] Smith reported finding the alkaloid *l*-nornicotine in *Nicotiana sylvestris*. The isomeric form *l*-β-nornicotine is the common one of tobacco.[82]

Alkaloids other than nicotine present in tobacco were reported by Pictet and Rotschy[87], but owing to the low volatility and difficulty of recovery by steam distillation, the insecticidal value of nornicotine was not recognized for many years. *l*-Nornicotine was reported by Smith in 1937 in *Nicotiana sylvestris*. The total alkaloidal yield was 1.4 per cent, of which 43 per cent was nornicotine and 57 per cent nicotine.[88] Markwood found a high percentage of nornicotine in *N. tabacum*, recoveries ranging as high as 95 per cent.[89] The two forms *d* and *dl* nornicotine have been recovered from the Australian plant, *Duboisia hopwoodii*.[90] Analytical methods of distinguishing between the alkaloids nicotine and nornicotine in commercial products have revealed the presence of the latter in proportions as high as 12 per cent of the total alkaloid.[84] A method of classifying tobaccos according to their nicotine and nornicotine content has been developed using the melting points of the picrates as the indicator. The nicotine and nornicotine are steam-distilled and combined with picric acid. The melting point of the resulting crystals is then determined and classified according to the data in Table 50.[92] Experiments to date using the aphid, *Aphis fabae*, as the test insect indicate superiority of nornicotine over nicotine[23, 84, 91] as an insecticide.

## Pyrethrum

The value of insect powder, prepared from certain species of Pyrethrum as a control for fleas, has been recognized in eastern Europe and parts of Asia for over a century. Reference is made in 1851 to *Pyrethrum roseum* and *P. carneum* as the source of insect powder. The original source of the Dalmatian insect powder was apparently first the species *Pyrethrum cinerariaefolium*. The group *Pyrethrum* is a section of the genus *Chrysanthemum* which belongs to the compositae. Commercial production both for use as a powder and for extraction purposes is predominantly that of the species *P. cinerariaefolium*, although the three species are legally recognized in the United States as ingredients of "insect powder".[25]

The United States is the largest consuming country of Pyrethrum and its derivatives, and since production in this country is hampered by the high cost of harvesting, large amounts are imported annually. Variations in the amounts of imports and the source is shown in Table 51.[93] Prior to World War I the principal source of supply was the Dalmatian coast.[94] Production having been checked, Japan became a large exporter until the opening of World War II. The Kenya district of British East Africa was early recognized (1930) as producing a superior grade of flowers, which has led to the present large expansion of the industry. Increasing amounts are being grown in Brazil, Ecuador and other South American countries. Other districts in Africa are also making large-scale trials in production, particularly the Belgian Congo. Exports of pyrethrum products from the United States consist principally of the baled flower and the extracts, although powder shipments are quite large.[93]

Table 50. Melting-point Spread of Picrates of Known Mixtures of Nicotine and nornicotine.

| Nicotine (%) | Nornicotine (%) | M.P. Spread (°C.) | Nicotine (%) | Nornicotine (%) | M.P. Spread (°C.) |
|---|---|---|---|---|---|
| 0 | 100 | 186.9–189.6 | 45.3 | 54.7 | 175.5–204.1 |
| 5.2 | 94.8 | 167.8–180.4 | 52.5 | 47.5 | 180.0–206.2 |
| 10.6 | 89.4 | 180.3–184.1 | 62.4 | 37.6 | 192.0–208.3 |
| 13.7 | 86.3 | 177.8–184.6 | 68.9 | 31.1 | 194.5–211.7 |
| 15.7 | 84.3 | 175.3–183.1 | 81.6 | 18.4 | 204.9–217.5 |
| 20.8 | 79.2 | 178.4–182.6 | 89.9 | 10.1 | 213.0–219.9 |
| 30.0 | 70.0 | 178.4–182.5 | 100 | 0 | 218.7–224.8 |
| 35.6 | 64.4 | 177.4–199.9 | | | |

Increases in the pyrethrin content of the flower through selection and cultural practices have been made in cultivation experiments in England[26, 27, 28] and in parts of Colorado[29], but not to an extent that overcomes the high cost of labor in hand-picking the flowers.

Harvesting the pyrethrum flower is largely a matter of hand labor, preference being given to those about three-fourths blown, as this stage is found to yield the highest pyrethrin content. The flowers are dried both in the open and in dehydrators, and are then pressed into bales of 448 pounds each, which is the export package.[32, 95] The total pyrethrin content of good quality pyrethrum flowers usually ranges from 0.5 to 1.5 per cent, the commercial basis for pricing being a 1.3 per cent pyrethrin content, with fluctuations in price as the quality rises or falls below the standard. Slight losses of pyrethrins occur when the flowers are dried in the open or at dehydrator temperatures of 52°C (126°F) to 60°C (140°F).[30]

Table 51. United States Imports (in pounds) of Crude Pyrethrum from Certain Countries.

| Country | 1937 | 1938 | 1939 | 1940 | 1941 |
|---|---|---|---|---|---|
| Japan | 17,849,611 | 10,895,604 | 7,485,587 | 2,030,746 | 762,400 |
| Yugoslavia | 519,099 | 218,368 | 388,166 | 66,142 | — |
| Italy | 276,807 | 28,474 | 78,409 | 10,853 | — |
| East Africa British | 1,422,803 | 2,864,205 | 5,524,120 | 10,386,974 | 10,068,438 |
| Brazil | 661 | 497,166 | 79,755 | 78,408 | 10,983 |
| Total* | 20,091,596 | 14,537,417 | 13,569,300 | 12,591,210 | 11,020.506 |

| Country | 1942 | 1943 | 1944 | 1945 |
|---|---|---|---|---|
| Japan | — | — | — | — |
| Yugoslavia | — | — | — | — |
| Italy | — | — | — | — |
| British East Africa | 8,829,997 | 5,984,807 | 7,685,064 | 12,597,000 |
| Brazil | 397,325 | 593,317 | 2,202,540 | 2,592,000 |
| Total* | 9,452,350 | 6,777,845 | 10,658,009 | 18,270,000 |

* Includes additional amounts besides those listed by country.

Pyrethrum flowers, when ground, show a constant loss of pyrethrin content over a period of months or even years, the rate varying with the fineness of grinding and the exposure to air and sunlight. Thin films of dust or liquid spray residues, exposed to sunlight and air, lose their insecticidal value in a matter of hours, the loss being confirmed by both analytical and biological testing. Such losses occur in atmospheres both of nitrogen and oxygen, but a little more slowly in the former. Heat and ultraviolet light may also affect the loss of pyrethrins. The rate of loss from the whole flower is slower than for the ground powder, but is influenced by the same factors. Concentrated extracts of pyrethrum exposed in thin layers to air and sunlight also show deterioration. The loss of activity in pyrethrum dusts may be retarded by the addition of such antioxidants, as tannic acid, hydroquinone, and resorcinol.[31, 33, 34, 96]

Excessive dosages of pyrethrins, as used in vineyard applications of the "fog" type, have shown no injury to sheep or lambs compelled to feed on the treated foliage over a period of 48 to 81 days. Similar experiments with rabbits have given no harmful results from such enforced feeding and with normal gains in weight.[43]

The active principle in pyrethrum was stated in 1920 by McDonnell and co-workers[25] to be two closely related esters (pyrethrin-1 and pyrethrin-2), but not until 1924 was there a method developed for determining the pyrethrins separately.[35] This method resulted in the formation of chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid, which by further treatment yielded pyrethrin-1 and pyrethrin-2, respectively.[35] Further contributions to the standardization of methods of determining the two esters were made by Staudinger and Harder[35]; Tattersfield, Hobson, and Gimingham[38]; Gnadinger and Corl[40]; Seil[39]; Haller and Acree[37]; and Wilcoxon.[42] Martin in 1938 reviewed the various proposed methods of analysis and the variation in results between the Wilcoxon and Seil methods, and suggested that the method of analysis should always be given in an evaluation of pyrethrins.[41]

Pyrethrin-1 is generally considered more active as an insecticide than pyrethrin-2[37, 38] and for that reason much attention has been given to methods for determining each separately rather than as a total.

The pyrethrins are non-volatile, very slightly soluble in water and generally incompatible with alkalies. They should not be combined with Bordeaux mixture, calcium arsenate, hydrated lime, lime-sulfur, or soaps. They can be combined with the fluosilicates and fluoaluminates, lead arsenate, mineral oil; rotenone and sulfur.

Solvents used for extracting pyrethrins were first petrolic ether and alcohol[41], but because of the common use of such extracts for household sprays the hazard of low flash point solvents must be avoided. A kerosene type of solvent with a flash point of 125°F is frequently used. Carbon tetrachloride, ethylene dichloride, nitromethane and other organic solvents are also used. The kerosene extract may be added directly to the inert dust base, or certain organic solvents may be used to extract the total oleoresins. The solvent may be recovered and the residue diluted as desired and either used as a liquid or combined with a dust base.

The general use of pyrethrins in aerosol bombs has led to the preparation of highly concentrated extracts from commercial preparations of the oleoresin, free from precipitated materials which might clog the nozzle. During the investigation evidences were found of the polymerization of pyrethrins and the formation of insoluble products. Nitromethane was found to be a very satisfactory solvent.[99] Further studies of pyrethrin concentrates showed that the solubility in dichlorodifluoromethane of the precipitates formed was a guide to the degree of deterioration in toxicity. The addition of 0.1 per cent of hydroquinone retarded the formation of precipitates, with accompanying loss of toxicity. Storage of the concentrate in the dark at 2°C prevented loss of toxicity, and dilution with deodorized kerosene also inhibited deterioration.[100]

**Pyrthrum as an Insecticide.** Ground pyrethrum flowers, diluted with an inert base such as talc, bentonite, ground walnut shell and sulfur, has had extensive use, originally as a household insecticide and later for limited agricultural purposes. For the former, it is frequently combined with sodium fluoride for controlling ants, fleas, cockroaches and bedbugs. In the garden it was used at 15 to 50 per cent of pyrethrum powder to control leaf hoppers, aphids, cucumber beetles, *Diabrotica* spp., and cabbage worms. Large areas were dusted at rates of 5 to 25 pounds per acre. The pure dust has been used at the rate of 3 to 5 pounds per 100 gallons of water for the young stage of canker worms. Variation in the content of the active principles and the general recognition that grinding does not release the full value led to the general practice of extraction and to the commercially prepared concentrate. Development of methods of analysis was of great assistance in establishing accurate standards, just as in the preparation of nicotine sprays. The new standards were adopted for legal classification, and guarantees are now required to be expressed in percentages of pyrethrins.

The commercial concentrate usually contains the extract of 20 pounds of pyrethrum flowers to a gallon of solvent, the pyrethrin content varying from 0.5 to 5.0 per cent pyrethrins. This is diluted from 0.05 to 0.25 per cent pyrethrins for fly sprays. Since the action of the pyrethrins tends toward paralysis rather than outright killing, they are frequently supplemented with rotenone or organic compounds such as thiocyanates. A limited use has been developed of a low pyrethrin content (0.03 per cent) light mineral oil spray as a "fog" in the control of vineyard leafhoppers. The liquid is applied without dilution at high pressure at the rate of 5 to 8 gallons per acre. The extract is also used as a standard garden spray for aphids, thrips, Mexican bean beetle, and Japanese beetle. It is a common ingredient of the dairy type of fly spray, and the oil-pyrethrum extract is emulsified and used for treating water pools in controlling mosquitoes.[101]

The scarcity of pyrethrum during World War II stimulated search for methods of extending available stocks, and much progress has been made in developing activators or "synergists," as they are usually termed. By the addition of such materials (which in themselves might have little or no value as insecticides) the efficiency of the pyrethrins is increased materially. Certain components of pine oil and its derivatives were reported to be of value in fly sprays, particularly ethylene glycol ether of pinene.[102]

Similar increases in toxicity over pyrethrins alone was shown in the use of mosquito larvicides.[103] N-Isobutyl undecyleneamide has been found to increase the normal toxicity of pyrethrins to houseflies.[104] The combined action of pyrethrum oleoresins and the activator has been shown to have a distinctly different effect on the nervous system of the adult housefly from that of the pyrethrum alone.[105] This synergist has also been shown greatly to increase the toxicity of pyrethrins to the body louse, *Pediculus humanus corporis.*[106] A group containing three related compounds gave similar synergistic reactions as fly sprays; the group included N-isobutyl piperonylamide, N-butyl piperonylamide and N,N-diethyl piperonylamide.[107] The latter is reported by Weigel and Gertler to be an effective synergist of pyrethrum marc, the extracted pyrethrum powder in which small quantities of pyrethrins remain. It has but little toxic value in itself without a synergist, but is used as a diluent for powders of high pyrethrin content.[108] Eagleson[110] reported the value of sesame oil as a synergist for pyrethrins, and Haller and co-workers identified the active principle as sesamin ($C_{20}H_{18}O_6$). The alkaloid piperine, derived from black pepper, is stated by Bishopp to be a synergist of pyrethrum. He calls attention to the presence of 3,4-methylene-dioxyphenyl in the piperine compounds sesamin, isosesamin, asarinin and substituted piperonyl cyclohexenone.[111] The aerosol type of application has been found satisfactory for the combination of pyrethrins and sesame oil, with dichlorodifluoromethane as the solvent, in the control of mosquitoes in airplanes.[112]

## Rotenone and Rotenoids*

Of the recognized fish-poison plants of the world only a few are known to be sources of important insecticides. These are found largely in tropical countries, although a few species of *Tephrosia,* indigenous to the United States, offer promising possibilities. Hamlyn-Harris reports *Derris uliginosa, D. koolgibberah* and *Tephrosia rosea* in Central Australia and adjoining islands.[50]

Derris grows principally in the far East. Eighty or more species are known but only two, *Derris elliptica* and *D. malaccensis,* are cultivated.[114] It grows in the form of a shrub, but in cultivation is staked or trained on trellises to facilitate harvesting of the roots, which are the principal source of rotenone and the total ether extractives. The roots are dug when the plant is about two years old and at a time of year when the rotenone content is thought to be at its highest. The yield is from 800 pounds to a ton per

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* Organic compounds structurally related to rotenone which occur naturally in certain fish-poison plants of the family *Fabaceae* (*Leguminosae*). The more important of these tropical or semi-tropical plants are *Derris* (*Dequelia*), *Lonchocarpus*, and *Tephrosia* (*Cracca*).[113, 114]

acre. Selection of stem cuttings from high-yielding varieties and proper care in planting will raise the value of the crop.

The rotenone content of Derris grown in the Philippines averages 4 to 5 per cent, but this may be raised by selection. Derris growing in Ceylon, Polynesia and Brazil is generally of an inferior quality.[114] Yields of improved strains of Derris have ranged as high as 10 per cent rotenone, and even higher.

Table 52. United States Imports (in pounds) of Cube, Timbo or Barbasco Root (Crude).

| Country of origin | 1937 | 1938 | 1939 | 1940 |
|---|---|---|---|---|
| Brazil | 197,892 | 58,979 | 146,365 | 387,413 |
| Peru | 378,259 | 476,760 | 1,730,023 | 2,225,347 |
| Venezuela | — | 55,115 | 170,230 | 74,163 |
| Total | 576,151 | 590,854 | 2,046,618 | 2,686,923 |

| Country of origin | 1941 | 1942 | 1943 | 1944 |
|---|---|---|---|---|
| Brazil | 615,135 | 91,066 | 310,120 | 91,790 |
| Colombia | — | — | 5,012 | 124,642 |
| Ecuador | — | — | 16,756 | 24,244 |
| Peru | 2,485,658 | 2,356,515 | 1,913,849 | 5,340,208 |
| Trinidad | — | — | — | 12,974 |
| Venezuela | 60,796 | — | — | 151,703 |
| Total | 3,161,589 | 2,447,581 | 2,245,737 | 5,745,561 |

| Country of origin | 1945 | 1946 |
|---|---|---|
| Brazil | 61,029 | 348,919 |
| Peru | 4,490,766 | 10,644,026 |
| Trinidad | 6,600 | — |
| Venezuela | 41,124 | 5,267 |
| Total | 4,599,519 | 10,998,212 |

The genus *Lonchocarpus*, found principally in South America and Central America, is the chief source of rotenone for the United States at present, as noted in Table 52, although imports of Derris, prior to World War II were principally from the far East (Table 53).[116] Roark lists a large number of species of this genus,[53] but only a very few are cultivated and of commercial importance. *L. nicou* is cultivated in Peru where it is spoken of as "cube" or "barbasco," although the latter is a common Spanish name applied generally to all plants used as fish poisons. Brazil is growing an increased amount of one or more species of *Lonchocarpus*, which is marketed under the name of "timbo."[52] Rotenone content of cube and timbo varies from 5 to 15 per cent. World production is shown in Table 54.

**Tephrosia** (also known as *Cracca*). About 150 species are known, these being widely distributed in Africa, Asia, Australia, North America and South America.[55] A number of species are herbs but many are shrubs attaining a height of 8 to 10 feet. Cultural experiments in Texas of the species *T. virginiana* have shown a rotenone content as high as 5 per cent.[114] Further information on the development of improved strains of this species

Table 53. United States Imports (in pounds) of Derris or Tuba Root (Crude).

| Country of origin | 1937 | 1938 | 1939 | 1940 |
|---|---|---|---|---|
| Br. E. Africa | — | — | — | 8,664 |
| Br. Malaya | 401,975 | 583,035 | 2,325,492 | 1,842,087 |
| Fr. Indochina | — | — | 33,069 | 143,911 |
| Neth. E. Indies | 57,524 | 136,235 | 262,445 | 996,845 |
| Other Br. W. Indies | 314 | — | — | — |
| Panama | 54 | — | — | — |
| Philippine Is. | 110,528 | 23,391 | 228,632 | 229,465 |
| United Kingdom | 2,257 | — | — | — |
| Total | 572,652 | 742,661 | 2,849,638 | 3,220,972 |

| Country of origin | 1941 | 1942 | 1943 | 1944 |
|---|---|---|---|---|
| Br. E. Africa | 15,008 | — | — | — |
| Br. Malaya | 1,930,257 | 652,494 | — | — |
| Fr. Indochina | 77,822 | — | — | — |
| Haiti | — | — | 60 | — |
| Neth. E. Indies | 1,699,781 | 429,525 | — | — |
| Mexico | — | 8 | — | — |
| Panama | — | — | — | — |
| Philippine Is. | 377,167 | 19,362 | — | — |
| Total | 4,100,035 | 1,101,389 | 60 | — |

| Country of origin | 1945 | 1946 |
|---|---|---|
| Belgian Congo | 45,446 | 16,096 |
| Guatemala | — | 9,961 |
| Honduras | 2,963 | — |
| Leeward Islands | — | 1,633 |
| Liberia | — | 300 |
| Fr. Indochina | — | 331 |
| Philippine Is. | 1,800 | — |
| Trinidad | — | 1,443 |
| Total | 50,209 | 29,764 |

show rotenone concentrations ranging from 3.69 to 6.13 per cent. Clay types of soil are apparently superior to sandy soils for increasing the rotenone content.[118] A second species, common in parts of Florida, is also being studied as to possibilities of commercial development.[47] Species of *Tephrosia* found in New Jersey showed almost no rotenone present. The leaves of *T. vogelii*, widely distributed in Africa, have been found of value in controlling aphids and thrips,[48, 54] while the roots of both *T. toxicaria* from British Guiana and *T. candida* from the West Indies have insecticidal value.[54] Because of the rather low rotenone content (0.1 to 0.5 per cent) found in certain of the species it has been assumed that other substances present contribute to the insecticidal value.[46]

Rotenone has also been found in 1 per cent concentration in the roots of *Spatholobus roxburghii* from Burma. There being a number of species of *Spatholobus* in the Malay Peninsula, the Philippine Islands and India, this may lead to a new source of rotenone.[56]

Table 54. Estimated World Production of Rotenone-Bearing Roots (Derris, Cube, Timbo).*

| Country | 1938 | 1939 | 1940 | 1941 | 1942 | 1943 |
|---|---|---|---|---|---|---|
| | | | Thousands of pounds | | | |
| Brazil | 2,500 | 1,500 | 1,000 | 1,250 | 1,000 | 1,500 |
| Peru | 1,500 | 2,500 | 3,000 | 3,000 | 3,600 | 3,200 |
| Venezuela | [1] | 200 | 100 | 75 | [1] | [1] |
| Br. Malaya | 2,000 | 3,500 | 3,000 | 2,500 | [1] | [1] |
| Fr. Indochina | [1] | 300 | 150 | 125 | [1] | [1] |
| Japan | 100 | 650 | [2]2,000 | [1] | [1] | [1] |
| Netherlands, E. Indies | 250 | 1,500 | 1,750 | 2,800 | [2]2,700 | [1] |
| Philippine Is. | 200 | 650 | 900 | 450 | [1] | [1] |

[1] Not available.

[2] Anticipated production as reported from that area.

* Source: Consular reports, export statistics, etc.

In addition to the above Roark lists the following groups as sources of rotenone *Mundulea suberosa*, *Ormocarpum* and *Millettia*.[44] The insecticidal value of the latter has recently been noted, but without identification of the active principle.[120]

Rotenone-bearing roots are dried in the sun or dehydrators, a 12 per cent maximum moisture content being acceptable in commercial practice. The dried roots are packed in bales of about 100 pounds. Chopped roots and the ground powder are shipped in heavy paper bags or drums; the rotenone content varies from almost nothing to a maximum of 13 per cent, the commercial standard being set at 5 per cent. The standard practice for evaluation is as a crude rotenone in the form of a carbon tetrachloride solvate.[45] The insecticidal value also includes the total ether extract, which may range as high as 30 per cent for derris and 16 per cent for cube and timbo.[116] The roots are ground both in high-speed hammer mills and in roller mills; to avoid losses through oxidation grinding may be done in a carbon dioxide atmosphere. Two grades of powder are made: a coarse form for extraction and a finer one for dusting purposes. The latter is ground to a standard of 90 per cent passing a 200-mesh sieve. The particle size of commercial derris and cube powders, as determined by the air-permeation apparatus,[116, 122] has been found to be about 6 microns.[123]

### Chemical Properties of the Derivatives from Derris and Related Plants.

*Rotenone* ($C_{23}H_{22}O_6$) is a white crystalline derivative of *Derris*, *Lonchocarpus* and *Tephrosia*, the structure of which was described by La Forge, Haller and Smith.[127] Its melting point is 163°C, and it is levorotatory. Crystalline rotenone is stable, but in certain organic solvents it breaks down after varying lengths of time, particularly on exposure to sunlight and ultraviolet radiation and probably by oxidation.[44, 60, 62, 124] Pyridine solutions are among the first to decompose, followed by chloroform and ethylene dichloride. Acetone and dichlorobenzene (mixture of ortho and para) solutions are more stable, and benzene increasingly so. Solutions in kerosene proved quite stable.[62] The use of antioxidant materials such as hydroquinone to retard decomposition is suggested by Gunther.[124, 136, 137, 138] Stability is affected by alkalies. Rotenone is insoluble in water and but slightly soluble in kerosene.[44] Jones and Smith list a number of organic solvents in the order of efficiency including chloroform, ethylene dichloride, trichloroethylene, benzene, acetone, alcohol and toluene.[125] Crystalline solvates (solids containing solvent of crystallization) of rotenone are also listed by Jones[57]; acetic acid forms a crystalline compound containing one molecule of acetic acid to two of rotenone. Solvates containing one molecule of rotenone to one of solvent were formed with carbon tetrachloride, benzene and chloroform. Crystalline solvates were not formed with acetone, ethyl acetate and ethyl alcohol.

The extractives of Derris and related plants include, in addition to rotenone, varying amounts of resin from which additional toxic substances have been isolated and identified. Deguelin, $C_{23}H_{22}O_6$, described by Clark in 1931,[126] is generally recognized as an active insecticide. Toxicarol, $C_{23}H_{22}O_7$, also described by Clark[128] is toxic to goldfish but only slightly active as an insecticide.[129, 132] Sumatrol has been isolated by Cahn and Boam[130] and its insecticidal value established by Tattersfield and Martin.[131] Tephrosin is now considered to be an oxidation product of deguelin, instead of being present in the root in this form.[46, 114] Roark[114] lists the additional compounds elliptone and malaccol as derivatives of derris root. Certain derivatives of rotenone have been tested by Gersdorff[133] using goldfish as the test animal; and although dihydrorotenone was rated as 1.4 times the toxicity of rotenone, none of the materials has been used as an insecticide.

Chemical determination of rotenone may be made by extracting the ground root with chloroform and converting this into the solvate form with carbon tetrachloride.[135]

**Rotenone and Related Compounds as Insecticides.** These substances act both as contact and stomach insecticides, but not as fumigants. Their value as residual toxicants is limited by their instability in the presence of sunlight and oxygen. This is particularly noticeable in the semi-arid areas where the lack of moisture and airborne suspended particles gives a greater exposure to actinic rays, usually resulting also in higher temperatures. Such instability under field conditions, however, is also a valuable attribute in that applications to food crops, including leafy vegetables and berries, break down into harmless ingredients.

Applications are made as dusts, sprays, dips, baits and as aerosols. Dust mixtures are compounded with an inert base and may include a fungicide such as sulfur. Liquids may be suspensions of the powdered root; diluted aqueous extracts; concentrated solute diluted with water or other liquid; concentrated solute suspended in water as a colloid or in particle form.

Rotenone and rotenoids are used to supplement the limited supply of nicotine; in combination with pyrethrins to give higher mortalities; as partial substitutes for the arsenicals and cryolite, particularly in treating food crops; and in new fields of insect control such as the cattle grub, *Hypoderma bovis* and *H. lineatum*, and the pea weevil, *Bruchus pisorum*.

One of the first recorded insecticidal uses of a derris extractive is that of Campbell.[139] McIndoo, Sievers and Abbott[49] report on a large series of experiments with various solvents and on large number of insects. Specific mention was made of the control of fleas, lice, flies, aphids, and a number of insect larvae. The superiority of rotenone as an aphidicide was shown by Davidson,[58] its value in combination with pyrethrum as a fly spray by Campbell and co-workers,[61] and the increased toxicity over lead arsenate by Shepard and Campbell. Rapid expansion of insecticidal uses,[141, 142] came, as with the plant derivatives generally, only after the development of analytical methods made possible standardized measurements of both powders and extractives.

**Formulation of Dusts and Sprays.** The commercial standard for derris and cube roots, as indicated above,[116] is 5 per cent of rotenone. During processing the powdered root is set at this standard for distribution. In field practice the concentration is usually reduced to from 1.0 to 0.5 per cent. Dosages vary from 10 to 25 pounds per acre, but may range as high as 30 pounds per acre for the more resistant insects.[143] Higher concentrations are required for treating the cattle grub, but by the use of selected types of dust bases the concentration may be reduced from 2½ per cent of rotenone to 1.66.

Studies by Wilson and Jones[144] on the influence of the type of diluent have shown that the clays used were not compatible with rotenone and that but few deposits of talc are satisfactory, the toxicity of the insecticide varying with the degree of compatibility. Superiority in the diluent was shown by an increase in the efficiency of a lower concentration of rotenone. This resulted in lowering the rotenone concentration from 0.75 or 1.0 per cent to 0.5 or even 0.25. The electrostatic charge on the applied dust particles could also be varied with different bases. Further studies by Wilson[145] have shown the effect of the hardness or abrasive qualities of a material in relation to its value as a rotenone diluent. Quartz dust, the hardest of the series tested, consistently gave the best control of the pea aphid, *Macrosiphum pisi.* Turner[146] confirmed the findings of Wilson that clay and certain talcs were not the most efficient carriers for rotenone, but found that with pyrophyllite (a hydrosilicate of aluminum) as the diluent it was possible to reduce the rotenone concentration to as low as 0.25 per cent. Diatomaceous earths are similar to pyrophyllite in their use as diluents.[147] Alkaline earths should not be used in dust mixtures for storage.

Suspensions of finely powdered (90 per cent through a 200-mesh screen) derris or cube root at 5 per concentration of rotenone are commonly used at 2 pounds per 100 gallons of water. Concentrated extracts made with organic solvents are used commonly as spray; if the solvent is water-soluble the rotenone will remain in solution in the spray tank, but with an immiscible solvent a suspension or colloidal solution results. The addition of a rotenone solution to a mineral oil may be accomplished by the aid of a mutual solvent such as acetone. Cressman and Broadbent,[115] in experiments in the control of the California red scale, *Aonidiella aurantii,* used concentrations of 1.1 to 1.2 per cent by weight of the cube or derris resins with oil concentrations of 1.67 to 2 per cent. Dibutylphthalate and trichloroethylene proved equally satisfactory as solvents. Rotenone concentrations in sprays may fall as low as 0.01 to 0.004 per cent, usually when accompanied by other extractives.

Rotenone solutions in combination with other insecticides are in use in aerosol form, with liquefied gases as the distributor.

**Compatibility of Rotenone.** Nicotine dusts should not contain rotenone unless the diluent is non-alkaline. Hydrated lime, carbonates and alkaline forms of talc should not be used as dust bases. Neutral dusts such as pyrophyllite, walnut shell flour, diatomaceous earth and sulfur are preferable for dilution. Lead arsenate has frequently been combined with rotenone; calcium arsenate is combined with it in cotton dusting but may cause decomposition on storage. Neither lime-sulfur solution, Bordeaux mixture nor tartar emetic should be combined with this substance.

## Miscellaneous Plant Derivatives

**Sabadilla.** The common name of a plant of the family *Liliaceae,* including about 20 species distributed principally in Mexico, Central America, part of South America and to a limited extent in the United States. One species, *Schoenocaulon officinale,* is found throughout much of Central America, Peru and Venezuela. Sabadilla seed is gathered in quantities from the natural growing stands of the plant. The toxic principles are apparently a mixture of alkaloids grouped under the name of veratrine, including cevadine, veratridine, sabadilline and sabadine, of which the first two are the most important. Kerosene extracts of ground sabadilla seed at room temperature are much less effective than when the extraction is at temperatures ranging from 25 to 150°C. Preheating the powder for 1 hour at a temperature of 150°C compared favorably with hot extraction.[149] Mixing the powdered seed with an alkali, such as hydrated lime, prior to extraction or as a dust base, also increases the toxicity. Freshly ground seed was non-toxic but the application of heat, hot extraction or blending with an alkali developed toxicity. Aging the powder increased toxicity to a varying degree. Kerosene extracts in amber-colored bottles were found to be stable up to 22 months, but quickly deteriorated when exposed to light.[149]

**Sabadilla as an Insecticide.** Powdered sabadilla seed 1 part to 10 parts of wettable sulfur was reported in 1943 as a successful substitute for rotenone dust in controlling the cattle louse, *Bovicola bovis.*[150] Control of the Mexican bean beetle, *Epilachna varivestis,* and the harlequin bug, *Murgantia histrionica,* with the Allen formula of sabadilla seed and an alkali, is reported by Fisher and Stanley.[151] Allen and co-workers have shown the value of heated and alkali-treated seed for flysprays.[152] The alkaloid cevadine was found to be the most toxic of all the sabadilla extracts to the milkweed bug, *Oncopeltus fasciatus,* and the red-legged grasshopper, *Melanoplus femur-rubrum.*[153] Sabadilla has been found to be relatively free from injury to foliage and particularly useful on crops where residues would be dangerous. It is being recommended for the control of harlequin cabbage bug, *Murgantia histrionica,* and other plant bugs.

**Strychnine** ($C_{21}H_{22}N_2O_2$) is one of the alkaloids, strychnine and brucine, found in the dried ripe seed of *Strychnos Nux-vomica.* The total alkaloidal content is from 2 to 2.7 per cent. This is a small tree native to India, Ceylon, French Indo-China and Northern Australia. A large proportion of the world's supply comes from India, as shown in Table 55. Nux vomica is used principally as a medicine, the industrial use being confined largely to rodent baits.[148] It is marketed both as an uncombined alkaloid and in the sulfate form known as strychnine sulfate. One part of the alkaloid is equivalent to 1.28 parts of strychnine sulfate in the alkaloidal content.

The control of ground squirrels, *Citellus beecheyi* and *C. Richardsoni,* on the Pacific Coast, both as an economic measure in protecting grain and range land and as an indirect protection against bubonic plague, has been accomplished largely by strychnine baits. A common formula is 1 ounce of strychnine sulfate to 18 pounds of whole barley. The strychnine is dissolved in hot water to which is added a thin starch solution containing a small amount of corn sirup and saccharine; the mixture is then stirred over the grain.[154] Similar formulas, but with different bases, are used in baits for rats and mice. Alternating types of baits for such rodents include thallium sulfate, zinc phosphide, red squill and certain new types of organic compounds.

Decided variation in susceptibility to strychnine is shown by different animals. The rat has been found to be 5 to 6 times as resistant to the substance administered subcutaneously as is the domesticated rabbit.[156] The California quail, *Lophortyx Californica* has been found quite resistant to strychnine.[155]

Table 55. United States Imports of Nux Vomica, 1938–44.

| Country of origin | 1938 pounds | 1939 pounds | 1940 pounds | 1941 pounds | 1942 pounds | 1943 pounds | 1944 pounds |
|---|---|---|---|---|---|---|---|
| British India | 1,017,128 | 1,089,448 | 2,288,224 | 2,102,003 | 4,033,425 | 1,065,506 | 1,137,618 |
| French Indo-China | 66,202 | 1,368,599 | 1,179,605 | 44,990 | — | — | — |
| Ceylon | — | — | — | — | 56,056 | — | — |

**Quassia** is the extract from the bark and wood of a small tree, *Quassia amara*, native to Surinam, Brazil, Guiana, Colombia, Panama and the West Indies. An extract is made from the woody chips which apparently consists of several closely related compounds. A similar extract is obtained from the Jamaican plant *Aeschrion excelsa*, native to Jamaica and the Caribbean Islands. The extract from *Quassia amara*, generally mentioned in the literature as "quassin," is considered to be a mixture of related compounds.[158] Clark has investigated these and isolated two compounds, quassin and neoquassin[159]; the formula for both is $C_{22}H_{30}O_6$.

The insecticidal properties of quassia have been studied by McIndoo and Sievers who report its value, as tested on aphids, as less than nicotine, though it is similar in cost.[157]

**Hellebore.** The insecticide sold under this name is derived from the liliaceous plant, *Veratrum irride*, native to North America. This material has had considerable use in the control of the currant and gooseberry worms, *Nematus* spp., and also in thrips control, *Thrips tabaci*.[160] Lack of methods of chemical standardization, however, has hindered extensive use of the product.

Chemical studies of the plant have shown two predominating alkaloids, jervine and pseudojervine, the former being present in considerable excess of the latter. Both alkaloids were found to be non-toxic to the American cockroach, *Periplaneta americana.* The crude alkaloidal fractions were found to be very toxic.[160]

**Red Squill** is the dried powdered bulk of the perennial plant, *Urginea maritima*, (*U. silla*), native to the coast of Southern Italy, Sicily, Sardinia and Northern Africa, which is used as a rodenticide, primarily for the rat. Two commercial varieties are commonly marketed, white squill used in medicine and red squill used only as a rodenticide; in both instances the large fleshy bulb is the only portion of the plant used.

Chemical studies of squill made by George[161] revealed a red glucoside derived from the African squill, *Urginea burkei.* He states that the active principle has not been isolated and identified, but lists certain glucosides as having been derived from the species of squill.

Squill is especially valuable for rat control as there is less danger to human beings and domestic animals from its use than is the case with many other rodenticides. The bait is either refused or promptly vomited if taken by dogs or cats. Chickens and pigeons have a high resistance to squill. Prairie dogs and gophers refused squill baits but mice took them readily in results reported by Silver and Munch.[162, 163]

Variable results from squill baits during the war years led to the development of a method of "fortification" and standardization of baits, with resulting uniformity. The dried bulb is ground to a 40-mesh powder and extracted with 80 per cent ethyl alcohol. The extract is concentrated by removing the alcohol under pressure; the sirup is dissolved in water and blended as necessary with raw red squill powder to produce a toxic concentrate. The usual rate of concentration is the extraction of 75 parts of squill powder to add to the remaining 25 parts. Fortified powders are dried at a temperature of 80°C and ground to a 20-mesh powder. The proportions vary with different lots of squill. The fortified product is not considered more dangerous to use than the original form.[164]

A bio-assay is made of the fortified powders, which are required to kill male rats at dosages of 200 to 400 mg. per kilo of rat weight. The fortified powders are used at 10 per concentration in different types of foods.[164]

**Castor Bean Derivatives.** Reports of insecticidal values attributed to the castor bean plant, *Ricinus communis*, or its seeds have led to attempts to isolate and identify any active principles present. Ricin, a toxic protein, and the alkaloid ricinin both occur in the seeds and other parts of the plant.[165] The former has been found to be non-toxic to cod ing moth larvae, but the latter highly toxic. In addition to natural ricinin, the synthetic form, 1,2-dihydro-4-methoxy-1-methyl-2-oxonicotinonitrile, and a related compound, 1,2-dihydro-1,4,6-trimethyl-2-oxonicotinonitrile, were found to be effective toxicants.[166]

**Ryania.** Derivatives of the tropical plant, *Ryania speciosa*, have been found effective in the control of the European corn borer, *Pyrausta nubilalis*, when applied as a dust at concentrations of 30 to 50 per cent, which it is stated will compete in cost with a 1 per cent rotenone dust.[167] Spray applications of the Ryania preparation at 2 to 4 pounds per 100 gallons of water gave excellent control of the borer with 3 and 4 applications. Sprays of 6 pound concentration per 100 gallons had value in controlling codling moth on apples. Less value was found when it was used as a dust on a number of truck crop insects.[111]

**Phellodendron Derivatives.** Insecticidal values have been found for extracts from the fruit of the Amur cork or velvet tree. *Phellodendron* spp. grows on the Sakhalin Island and other coasts adjoining the Japanese Sea. Comparative values have been found to that of rotenone for the control of mosquito larvae and to that of Derris for housefly control.[168] Commercial types of fly sprays made with the extracts were of little value. Chemical fractionation of the extract developed compounds of greater value than the original form.[169]

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# Chapter 9

# SYNTHETIC ORGANIC COMPOUNDS*

The earlier history of insecticides, with the exception of certain plant derivatives and petroleum fractions, deals largely with inorganic compounds, particularly the elements lead, mercury, arsenic and copper. The latter are cumulative in their systemic action, with slow elimination. These elements are toxic in variable degree to all living organisms, but are not specific in their action to a narrowly defined group of insects or plant diseases. Arsenic in particular is a protoplasmic poison of the living cell, whether of plants or animals.

Increasing consideration, both for the welfare of the consumer of treated fruits and vegetables and the operator in the factory and farm, has led to safety devices in factories and strict regulations of tolerated spray residues on fruits and vegetables following treatment. This movement is one of the principal incentives to the search for organic chemicals useful as insecticides.

In addition to safety requirements there is the urgent necessity of greater efficiency in the control of injurious insects and organisms causing plant diseases, but with a minimum of hazard to the host plant or animal. Few of the older insecticides and fungicides gave satisfactory pest control and too frequently there was the necessity of balancing uncontrolled pest damage against possible host plant injury. Besides improvements in established pest control, new fields have been established, notably, seed disinfectants, insect repellents and insecticides for use on animals.

Many thousands of organic compounds have been tested as insecticides during the last few years; it is estimated that at least 5,000 are tested annually, of which only a very few are equal or superior to current usage. An investigation of the limited field of mosquito larvicides covered 6,000 compounds of which only 175 showed a mortality above 50 per cent in 58 hours at a concentration of 1 ppm. At 0.1 ppm. 22 compounds gave mortalities of 50 per cent or above. Only three, including benzene hexachloride, were superior as larvicides.[24]

The attention given to organic compounds must not, however, lead to the conclusion that older remedies, particularly inorganic compounds, are being supplanted. Rather it should be considered that the two groups complement each other. The current market condition illustrates the

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* Includes also a few naturally occurring substances such as creosote and acetic acid,

strong situation which the older insecticides occupy, with the demand for nicotine exceeding the supply, heavy importations of arsenic supplementing local production, and a "tight" market on certain zinc and copper compounds.

Organic compounds may be classified into three large groups, aliphatic, aromatic and heterocyclic compounds, with important insecticides in each group. Examples of the first class are methyl bromide, ethylene dichloride and trichloroacetonitrile; benzene hexachloride and dichlorobenzene are well known aromatic compounds; and nicotine and rotenone have heterocyclic structures. For convenience of discussion a second grouping is made of organic sulfur compounds. The latter is an arbitrary classification, as examples from all the three divisions may be found in it; but it serves to emphasize the importance of the sulfur compounds as insecticides. Confusion has been manifest in the nomenclature of current articles on organic insecticides, but this is being overcome through the efforts of both chemists and interested biologists.

**Acetic acid** (1-trichloromethyl-2,2′-methylene-bis-[4,6-dichlorophenyl] diester) is one of the three most effective mosquito larvicides selected from a group of 6,000 organic compounds. At a concentration of 0.1 ppm all larvae were killed in a test period of 48 hours.[24]

**Amines.** A recommended formula for treating livestock to kill infesting screw-worms and to prevent reinfestation contains diphenylamine, $(C_6H_5)_2$-NH. Three and one-half parts are dissolved in an equal amount of benzol, to which is added 1 part of Turkey red oil and lamp black to give a satisfactory consistency for treating wounds.[31,162] Tattersfield and Gimingham determined the insecticidal value of certain aliphatic and a large number of aromatic amines, using the bean aphid, *Aphis fabae*, as the test insect. The aliphatic amines were found to have a higher insecticidal value than the aromatic groups.[32]

*p-Aminoacetanilide* has been found effective as a control for the Mexican bean beetle, *Epilachma varivestis*, without foliage injury in the tests reported.[25]

*Aminoazobenzene hydrochloride*, $C_{12}H_{11}N_3HCl$, in preliminary field and laboratory tests has been found equal in effectiveness to Derris against the melon worm, *Diaphania hyalinata*, the cross-striped cabbage worm, *Evergestis rimosalis*, and certain other defoliators. It was not found toxic to the American cockroach, *Periplaneta americana*, or the cowpea weevil, *Calosobruchus maculatus*.[34] Further investigations have shown decided value for this product against the hornworms, *Protoparce sexta* and *P. quinquemaculata*.[28]

[*Ammonium nitro compounds* are discussed under Dinitro compounds (p. 238); *Anthracene oil* is discussed under Creosote (p. 221)].

**Azo Compounds.** Azobenzene, $C_{12}H_{10}N_2$, has shown moderate value in field tests as a control of the European corn borer, *Pyrausta nubilalis*, with only slight foliage injury.[33] In a whiting or bentonite dust base at a 20 per cent concentration it is now being used commercially as a control for the spider mite, *Tetranychus bimaculatus*, and the Mexican bean beetle, *Epilachna varivestis*.[47] Its greatest reported value is as a greenhouse fumigant. A mixture of 70 per cent azobenzene to 30 per cent dust base, painted on the steam pipes, has given kills of 90 to 99.75 per cent of the spider mite, including the egg stage.[35]

*Azoxybenzene* ($C_{12}H_{10}N_2O$). This material proved superior to a large series of azo compounds as a control for the larvae of the screwworm fly, *Cochliomyia americana*.[36] As a control for the European corn borer, it has proved to be one of the most effective of a large series of organics, but is inferior to Derris.[38] Moderate effectiveness has also been found for it as a control for the body louse, *Pediculus humanus corporis*.[37]

**Benzaldehyde** ($C_6H_5 \cdot CHO$). A number of derivatives of this group, including halogens and sulfonic acid, have been patented in England and Germany as mothproofing compounds.[26]

**Benzene hexachloride** ($C_6H_6Cl_6$). This compound is also known as 1,2,3,4,5,6-hexachlorocyclohexane; a common name for it is "666". The insecticidal value of this compound was discovered about the same time in France and England during the war period and in 1945 experiments were also begun in this country.[45]

A persistent musty odor has restricted the use of benzene hexachloride on fruit, but this objection is being overcome. The lack of satisfactory methods of chemical standardization is hindering commercial development and utilization.

Benzene hexachloride, commonly known also as hexachlorocyclohexane, is an addition product of benzene chlorine. The reaction, which may be either an additive one or a displacement process, is influenced by light, heat and the type of catalyst used. In the presence of iron, iodine and ferric chloride mono- or dichlorobenzene may be formed and with the displacement of all the hydrogens, hexachlorobenzene ($C_6Cl_6$) is formed. Benzene hexachloride, by contrast, is an additive formation. Since the chlorine atoms may attach to the benzene structure in a number of ways, at least five different or isomeric benzene hexachlorides may form. The gamma isomer of the compound is generally recognized as being the active insecticide. Its content may vary from 10 to 40 per cent of commercial benzene hexachloride. The remainder of the product is largely that of the other four isomers. Federal regulations on official ingredient statements require that the percentage of gamma isomer of benzene and of other isomers of benzene hexachloride [41] be stated on the label.

The melting point of the pure isomers is as follows:[45]

| Isomer | Melting point (C°) |
|---|---|
| Alpha | 157.5–158 |
| Beta | 309. |
| Gamma | 112.5 |
| Delta | 138–139 |
| "Epsilon" | 218.5–219.3 |

Benzene hexachloride is more volatile than DDT, resulting in a shorter residual action; both compounds release hydrogen chloride in the presence of alcoholic alkali.

A wide range of values has been developed, as shown by Bishopp,[43,44] including the control of the grain weevil, *Sitophilus granarius*, house fly, anophelian mosquitoes, human lice, and chiggers, *Eutrombicula alfreddugesi*. In agricultural fields, the list includes certain species of aphids, grasshoppers, cotton boll weevil,[49] certain of the Lygus bugs, and the spider mite on cotton. Edy and Carson found benzene hexachloride to be of outstanding value as an ovicide.[47] This material has been found to be much more toxic to the larva of the housefly than DDT, thiourea and borax. The benzene chloride was dissolved in acetone, the solution poured over crushed oats and the acetone evaporated. Cultures of fly larvae were added and the results determined by the number of adult flies emerging.

**Benzenesulfonic acid,** including both the *p*-chlorophenyl and the phenyl esters, was found in laboratory tests to be more toxic than lead arsenate against the codling moth. The *o*-tolyl and *o*-chlorophenyl esters were also found promising.[43]

**Benzil** ($C_6H_5CO \cdot CO \cdot C_6H_5$) also known as dibenzoyl, is used for impregnating clothing as a preventive of the attachment of chiggers. Much use of this material has been made by the Chemical Warfare Service as a protection against certain species of mites found in the South Pacific.[50]

**Benzoic Acid** (2,4-dinitro-6-cyclohexylphenyl ester) is one of a very few compounds that caused 100 per cent mortality at 1.0 ppm. concentration with an exposure of 48 hours[24] when used as a mosquito larvicide. A number of derivatives of benzoic acid have been found effective in preventing attacks by chiggers, but they are not as yet in commercial use.[50] Another derivative, methyl (*p*-amino) benzoate, is a promising ovicide against the human body louse.[40]

**Benzyl benzoate** ($C_6H_5 \cdot COOCH_2C_6H_5$) is also known as benzoic acid, and benzyl ester. It has come into general use as a protection against chigger attachments. Treated clothing is effective after two washings and partially so after the third washing.[50] Availability, ease of handling and cost favor the use of this material. In addition to benzoic acid benzyl ester, a number of other related esters have been found experimentally to be effective against chiggers, but have not yet entered commercial use;

they include benzoic acid, phenyl ester (phenyl benzoate); benzoic acid, 3,5-dimethylphenyl ester; 1,2,5,6-tetrahydro-*o*-methyl benzoic acid, 1,2,5,6-tetrahydro-*o*-methylbenzyl ester; benzoic acid, α-methylbenzyl ester; benzoic acid, phenylethyl ester; and benzoic acid, 2-chlorophenyl ester.[50]

2-Benzylpyridine is listed as one of ten compounds that were most effective and durable against the body louse.[47]

**Bis(5-chloro-2-hydroxyphenyl)methane** [$C_6H_3Cl(OH)_2CH_2$] is one of the most effective compounds selected from a large number of organics tested against the European corn borer, *Pyrausta nubilalis*. Good results were obtained at concentrations ranging from 1 to 4 pounds per 100 gallons of water.[29]

A number of bromine compounds have been found promising in a large series of organic insecticides that have been investigated. The more efficient materials tested against mosquito larvae include 4-(*p*-bromophenylazo)-resorcinol; 4-(*p*-bromophenylazo)-*o*-cresol; *p*-(*p*-bromophenylazo)-phenol; 4-(*p*-bromophenylazo)-*m* cresol.[27]

*p*-Bromohydrazobenzene has shown a high rate of efficiency when used at a dilution of 4 pounds per 100 gallons of water in control of the European corn borer.[38]

Tertiary butyl valone has been shown to be a very effective ovicide against the human body louse, *Pediculus humanus corporis*, at concentrations as low as 1 per cent and through a series of regulated humidities.[37] 3-Butoxy 2-cyclohexene-1-one is reported to be one of the most effective and durable compounds used against this insect.[47]

*o*-Chlorobenzylchloride, a condensation product of *o*-chlorobenzyl chloride and *p*-chlorophenol has been patented in Germany as a mothproofing compound.[26]

**Chlordane** ($C_{10}H_6Cl_8$) is also known as "Velsicol 1068" and "Octo-Klor." A recently discovered insecticide, it appears valuable both in horticultural and sanitary fields. It is a colorless, odorless liquid with a boiling point of 175°C at 2 mm. pressure. It is soluble in many organic solvents, but insoluble in water. Miscible in deodorized kerosene, it decomposes in the presence of weak alkalies. Its volatility is intermediate between DDT and benzene hexachloride. It is used as an insecticide in oil emulsions, dusts or dispersible liquids.

It is variable in its effect on aphids and effective against the squash bug, *Anasa tristis*, similar to DDT as a mosquito larvicide, it is active against the house fly and roaches.[52,53,66]

**Chloromethyl-4-chlorophenyl sulfone** ($ClC_6H_4SO_2CH_2Cl$). This is one of eight compounds, selected from a large number of organics over a period of years, that gave the highest control of the larvae of the European corn borer, *Pyrausta nubilalis.* In the experiments reported, it gave 100 per cent control at a dilution of 1 pound to 100 gallons of water, without feeding injury to the host plant.[29]

2-Chlorofluorene (crude) ($C_{13}H_9Cl$) was included in an earlier report[38] of materials tested against the European corn borer as a promising material, but was not included among the effective compounds in the later report.[29]

Chloromethylphenyl sulfone ($C_6H_5SO_2CH_2Cl$) and 1-cinnamoyl-2-phenylhydrazine ($C_6H_5NHNHCOCH{=}CHC_6H_5$) are also listed among the more effective compounds tested against the European corn borer.[29] The former compound has been found to be a very effective and durable control of the body louse, *Pediclus humanus corporis*, as has also chloromethyl-*p*-chlorophenyl sulfone.[47]

**Creosote and Related Compounds.** Creosote is the most extensively used material for protecting wood products against the attack of wood-destroying fungi, termites[55,57] and borers. The magnitude of this industry is shown in a report by Helphenstine of data compiled by the Forest Service of the United States Department of Agriculture.[54] The total volume of creosote, solutions of creosote and coal tar, refined water-gas tar and solutions of mixtures of creosote and petroleum consumed in the United States treating plants in 1942 totaled 286,600,000 gallons. Lumber treated by creosote exceeds the combined volume of all other methods of treatment.

During the manufacture of coke and illuminating gas from coal the vapors from the heated coal are condensed to form coal tar. The latter product is distilled, with creosote oil being recovered below 270°C and anthracene oil above 270°C.[56] Lumber treatment with creosote is usually by immersion, preferably by pressure, in large tanks. Brush application of creosote is not considered to give permanent protection, but anthracene oil or carbolineums are usually applied by non-pressure processes.

Wood creosotes are produced in the refining of wood tar; when properly standardized and carefully applied these are highly effective as wood preservatives. They are used largely in non-pressure processes.[58]

Certain tar distillates have been used quite generally as dormant sprays for fruit trees as ovicides, particularly against aphids,[59,60,62] but they have been largely displaced by the dinitro compounds. The distillates used for this purpose are redistilled from creosote oil at temperature ranges from 200 to 360°C. This eliminates much of the acids, which come off as a very light distillate, and utilizes the neutral or basic portions. Concentrations of the tar distillates in the spray mixture vary from 2.5 to 7.5 per cent, depending on the insect concerned.

**Dichloro-diphenyl-trichloroethane** (or more correctly 2,2 bis-(*p*-chlorophenyl)-1,1,1-trichloroethane),[98c] popularly called DDT, is prepared from

Table 56. Toxicity of DDT Isomers to Adult Houseflies and the Mosquito *Anopheles Quadrimaculatus*.

| DDT isomer[1] | Houseflies Knockdown in 10 min. (%) | Knockdown in 30 min. (%) | Kill in 24 hours (%) | Mosquitoes Knockdown in 10 min. (%) | Knockdown in 30 min. (%) | Kill in 24 hours (%) |
|---|---|---|---|---|---|---|
| *o,o'* | 0 | 0 | 1 | 5 | 6 | 15 |
| *p,p'* | 0 | 14 | 50 | 20 | 69 | 89 |
| *o,p'* | 0 | 0 | 0 | 6 | 8 | 20 |

[1] One ml. of a 1 per cent solution of each of the isomers in refined kerosene was sprayed into a 100 cubic foot chamber containing approximately 300 insects.

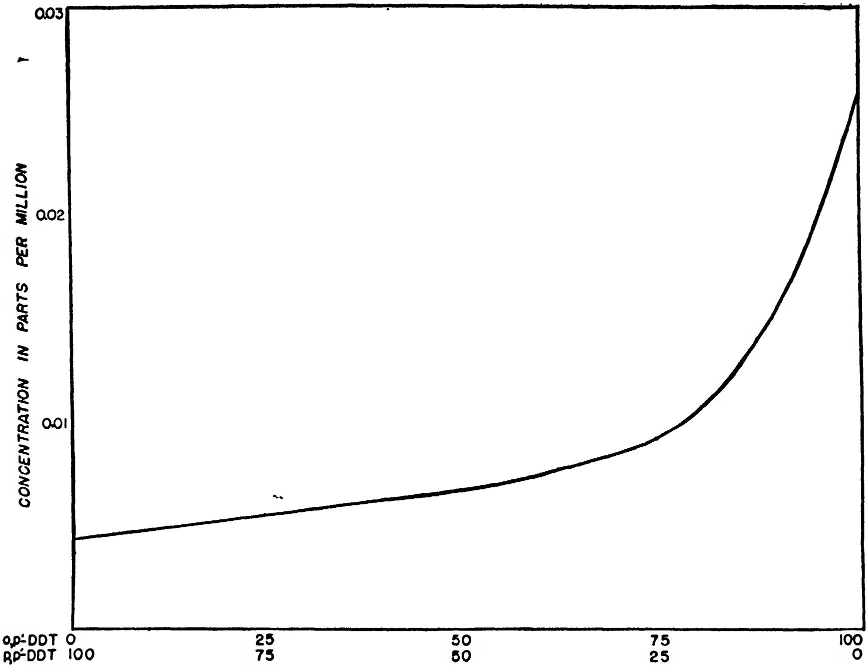


Figure 16. Concentration of *o,p*-DDT and *p,p*-DDT, and of several mixtures of these materials, required to give 50 per cent kill in 48 hours of fourth-instar larvae of the mosquito *Anopheles quadrimaculatus**.

1 molecule of chloral (chloral hydrate) and 2 molecules of monochlorobenzene in the presence of sulfuric acid. The setting point is about 88°C. and the melting point about 109°C. Three isomers have been identified in the reaction: (1) *p,p'*-DDT [1-trichloro-2,2-bis(*p*-chlorophenyl)

---

* "The concentration required to give 50 per cent mortality of *Anopheles quadrimaculatus* larvae in 48 hours has been plotted against the proportions of *p,p'*-DDT and *o,p'*-DDT in the materials tested. From this graph it is possible to determine for any mixture of the two pure materials the concentration that will give 50 per cent mortality in 48 hours."[60]

ethane], which usually makes up from 70 to 77 per cent[63] of the commercial material; (2) the principal impurity is *o,p'*-DDT(1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane); and (3) *o,o'*-DDT[1-trichloro-2,2-bis(*o*-chlorophenyl)ethane]. Variations in toxicity of the three isomers will be seen in Table 56[65] and Fig. 16.[69] It is non-volatile and active as a residual toxicant. The material is stable under many conditions but splits off hydrochloric acid in the presence of ferric oxide and iron and aluminum oxides[64] (see page 234).

The methoxy analog of DDT [1-trichloro-2,2-bis(*p*-methoxyphenyl) ethane] is reported to be ineffective in the control of body lice and mosquitoes. Greater promise is shown in agricultural fields, including the control of the Mexican bean beetle, stored grain pests and the white fringed beetle. It is believed to be less toxic to higher animals than DDT.[43,66] Diaryl trichloroethanes in which bromine is substituted for chlorine in the benzene ring $(C_6H_4Br)_2CHCCl_3$), was found less effective than DDT against the codling moth.[67]

Another relative of DDT [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] known as "Rothane" and also as "TDE," was found to be more toxic than DDT as a mosquito larvicide. It gave a good kill on house-flies and shows promise in certain agricultural fields.[43]

Di(4-chlorophenoxy)methane$(C_{13}H_{10}O_2Cl_2)$ has had limited use against the citrus red mite, *Paratetranychus citri*, and as a mosquito larvicide. Concentrations used are 1 pound per 100 gallons of water and at 4 per cent in dust bases.[61]

DDT is slightly soluble in various petroleum fractions, practically insoluble in water, and readily soluble in certain organic compounds: (see Table 57). Because of the flammability and explosive hazard of a number of these compounds they are emulsified in water when applied.

The permanence of DDT residual deposits is affected by light and temperature. Light reactions include both the radiation from ultra-violet lamps and sunlight. Solution deposits are broken down more quickly than solid deposits (suspensions and dusts). Auxiliary solvents used with kerosene in residual sprays should have a boiling range similar to kerosene. Those of low flash point are to be avoided.[70] The effect of combinations of temperatures and light is particularly noticeable in semi-arid regions between applications in early spring and those of midsummer. The effect of the higher temperatures of summer are supplemented by the lack of screening layers of moisture in the air, resulting in a much more rapid loss of efficiency. An application of DDT (1 pound per 100 gallons of water) against onion thrips, *Thrips tabaci*, under Pacific Coast conditions is effective for 3 to 4 weeks in April and from 5 to 9 days in July. A 5 per cent solution of DDT in kerosene, as a residual spray for flies in buildings, is effective for 10 days to two weeks; the same type of application in the middle of September would be active, but with a slower killing action, as long as flies were present, in the latter part of November. These findings on flies have been confirmed by Brett and Fenton in operations in Oklahoma.[71] A quicker "knockdown" and higher mortality of houseflies was noted at 70° than 95°F, using 5 per cent solutions of DDT in kerosene.[72]

Table 57. Solubility of DDT* in Organic Solvents

| | Grams per 100 ml. |
|---|---|
| Cyclohexanone | 116 |
| Benzene | 78 |
| Isophorone | 74 |
| Trichloroethylene | 64 |
| Tetrahydronaphthalene | 61 |
| *o*-Dichlorobenzene | 59 |
| Acetone | 58 |
| Xylene (10-degree) | 53 |
| Carbon tetrachloride | 45 |
| Benzyl benzoate | 42 |
| Dimethyl phthalate | 34 |
| Cottonseed oil | 11 |
| Ethyl alcohol (95 per cent) | approximately 2 |
| Mineral oils: | |
| Stoddard solvent | 9 |
| Kerosene, crude | 8–10 |
| Kerosene, refined, odorless | 4 |
| Fuel oil No. 1 | 8–11 |
| Fuel oil No. 2 | 7–10 |
| Coal-tar light-oil distillate fractions: | |
| Hi-Flash Solvent | 48 |
| Heavy Solvent | 58 |
| K-327 (chiefly methylnaphthalenes) | 67 |
| Aromatic petroleum fractions: | |
| Velsicol AR-50 (chiefly mono- and dimethylnaphthalenes) | 55 |
| Solvesso No. 3 (aromatic fraction, medium boiling range) | 33 |
| APS-202 (refined high-boiling fraction of S/V Culicide Oil B | 45 |

* Recrystallized DDT (m.p. 107.5 to 108°C. Temperature of solutions from 27 to 30°C.[96]

The correlation between the permanence of the residual deposit of DDT and the prevention of settling and development of the "crawler" stage of the California red scale, *Aonidiella aurantii*, has been investigated by Gunther and associates.[73] The formulas used, including two different solvents and the addition of aluminum stearate, are given in Table 58 and the amounts of residual DDT, as shown by chemical assays, in Table 59. The applications gave poor control of the adult scale, but all were uniformly effective against the young stage for three weeks, after which a gradual decrease in value was shown. The higher dosage, 8 gm. per 100 milliliters of kerosene, gave a longer control period than one-half this dosage. A minimum of 12 micrograms of DDT per square centimeter gave complete protection against settling and development; less than 7 micrograms per square centimeter was ineffective upon either settling or development. These experiments were made on Citrus trees in Southern California during the highest temperatures of the year and good exposure to sunshine.

Table 58. Spray Treatments* Applied to Citrus Trees to Determine Rates of Decomposition of DDT (see Table 59).

| Treatment No. | Grams of DDT Tech. | Grams of DDT C.P. | Milliliters of Kerosene | Milliliters of "Tetralin" | Milliliters of "Velsicol AR 60" | Grams of Aluminum Stearate |
|---|---|---|---|---|---|---|
| 1 | 4 | — | 100 | — | — | — |
| 2 | 4 | — | 100 | — | — | 1 |
| 3 | 8 | — | 90 | 10 | — | — |
| 4 | 8 | — | 90 | 10 | — | 1 |
| 5 | 8 | — | 90 | — | 10 | — |
| 6 | 8 | — | 90 | — | 10 | 1 |
| 7 | — | 4 | 100 | — | — | — |
| 8 | — | 4 | 100 | — | — | 1 |
| 9 | — | 8 | 90 | 10 | — | — |
| 10 | — | 8 | 90 | 10 | — | 1 |
| 11 | — | 8 | 90 | — | 10 | — |
| 12 | — | 8 | 90 | — | 10 | 1 |

* All sprays were of a 3 per cent concentration of kerosene emulsion and in addition contained 4 ounces of blood albumin spreader. Alternating series carry the auxiliary solvents "Tetralin" and "Velsicol AR 60." Aluminum stearate is used to retard penetration of the kerosene into the leaf with a resulting higher deposit of DDT on the surface.

Table 59. Rates of Decomposition of 12 Spray Mixtures Containing DDT. (See Table 58 for composition of these spray mixtures)

| Treatment No. | Micrograms of DDT/cm² of leaf surface after 0 day | 1 day | 2 days | 5 days | 13 days | 21 days | 42 days | 86 days | Overall % Decrease in DDT deposit |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12.3 | 17.1 | 17.0 | 17.2 | 14.3 | 15.3 | 12.2 | 2.4 | 81.5 |
| 2 | 17.3 | 18.1 | 17.8 | 16.3 | 15.8 | 13.5 | 10.7 | 0.8 | 95.4 |
| 3 | 21.1 | 26.7 | 22.9 | 23.5 | 20.3 | 17.9 | 15.6 | 2.5 | 88.2 |
| 4 | 25.5 | 25.5 | 25.1 | 25.2 | 22.2 | 17.1 | 12.9 | 1.6 | 93.7 |
| 5 | 29.4 | 25.5 | 26.0 | 26.0 | 20.9 | 18.5 | 11.8 | 3.6 | 87.7 |
| 6 | 30.1 | 23.2 | 24.5 | 21.5 | 18.7 | 15.7 | 13.3 | 1.8 | 94.0 |
| 7 | 16.0 | 18.5 | 20.2 | 18.2 | 14.5 | 13.1 | 12.4 | 1.2 | 92.5 |
| 8 | 20.1 | 21.7 | 22.7 | 20.5 | 15.5 | 15.4 | 13.7 | 2.1 | 89.5 |
| 9 | 26.8 | 28.9 | 29.2 | 30.2 | 25.8 | 20.8 | 18.7 | 4.0 | 85.0 |
| 10 | 35.8 | 30.8 | 31.4 | 31.0 | 27.9 | 27.8 | 20.1 | 7.4 | 79.3 |
| 11 | 31.2 | 28.3 | 29.2 | 26.9 | 27.3 | 19.5 | 17.1 | 4.7 | 85.0 |
| 12 | 37.2 | 34.7 | 37.3 | 33.9 | 31.1 | 24.7 | 19.8 | 5.2 | 86.0 |

**Insecticidal Preparations.** The waxy nature of DDT makes it difficult to grind to the very small size desirable for the greatest effectiveness. Micronized samples of a particle size of 2.5 to 4 microns have been available for research work, but commercial dusts are ranging from 4 to 40 microns in diameter. Shipments have been made largely in 50 per cent concentration of DDT, including both those for dust and spray applications. Much higher concentrations are possible, but if very finely ground they may cake, particularly if exposed to the sun's rays. Diluents include talc, pyrophyllite, sulfur, bentonite and other materials. For water suspensions a wetting agent is incorporated in the mixture or may be added at the time of preparing the spray. For agricultural work sprays containing 1 pound of actual DDT per 100 gallons of water and a suitable wetting agent are commonly used. Colloidal suspensions of DDT have been prepared using a 10 per cent concentration of DDT in a suitable solvent, such as "Cellosolve," and 10 per cent of a surface-active agent such as "Nopco 1216" or "Triton X-100." These mixtures are very active as mosquito larvicides but are limited in use as they may kill fish.[74] Dust applications are commonly made at concentrations of 2 to 6 per cent of DDT.

Wetting and sticking agents include: soap powder at 1 per cent of the DDT; fish glue, 1 ounce dissolved in 1 pint of water, per pound of DDT; soybean flour, ½ pound per pound of DDT; and a number of proprietory compounds. The summer type oil emulsion in combination with fish glue makes a satisfactory spreader for many types of water. It is used at the rate of 1 quart of emulsion, 1 pint of fish-glue solution (1 pound of the paste fish glue per gallon of water) to 1 pound of actual DDT in 100 gallons of water.[75]

Dusts for use as mosquito larvicides have been prepared by combining DDT with stearic acid and metallic stearates. The former produces a solid solution with DDT which may be ground or dissolved in a mutual solvent and sprayed.

Solutions of DDT up to 5 per cent concentration may be made with refined kerosene, or to 7 and 8 per cent by using unrefined fractions. Much higher concentrations are possible with certain organic solvents. Cyclohexanone is frequently included in the formula in amounts necessary to secure the desired concentration. Emulsions may be made from concentrated solutions and diluted as desired for spraying. A xylene-DDT emulsion is recommended by Jones and Fluno for use as an all-purpose emulsion concentrate on insects attacking man.[76] A number of satisfactory organic emulsifiers are listed, as well as those giving varying degrees of stability in different types of water. Such an emulsion must be satisfactorily stable when diluted from 0.1 to 10 per cent concentrations in soft, hard and sea water, and must contain a high concentration of DDT

Xylene is available in quantity, and is an active solvent (53 gm per 100 ml.)[63]; it evaporates rapidly from clothing treatment and is effective both in larvicidal and residual spray applications for mosquitoes. The recommended formula contains 25 per cent of DDT, 10 per cent of emulsifier ("Triton X-100"), and 65 per cent of xylene.[79]

Aerosol generators of DDT solution include those producing pressure both by liquefied gas and by heat.[78] The formulas vary with the type of insect being combatted, space (enclosed room),[80] and field crop applications.[82] Cyclohexanone is commonly used as the solvent; oils, either vegetable or mineral, are added as additional solvents;[81, 88] synergists are included for their physical properties, particularly their influence on particle size; and DDT, either alone or in combination with pyrethrins. The propelling liquid is usually dichlorodifluoromethane ("Freon-12"); for field work methyl chloride may be substituted, as it is a more active solvent and less expensive. Another ingredient used in the field crop formula is an organic solvent such as acetone boiling between 20 and 100°C. This displaces part of the liquefied gas and increases the particle size of the aerosol, thus permitting it to drift near the ground without dissipating.[79]

**DDT as an Insecticide.** This material is renowned not only as a very successful insecticide in itself but because of the encouragement it has given the entire field of research in organic insecticides. It was first synthesized by Zeidler in 1874, but no use was made of it until about 1940 when its value as an insecticide was established by the researches of Paul Müller. The earliest patents were issued in Switzerland and England, and one covering the use of diluents or carriers as U. S. Patent No. 2,329,074 was issued to Müller in September, 1943.[87] The rapid rise in the popularity of this material is shown by the number of publications; in 1943 a few scattered notes were published,[89] but in 1944 it was the predominating subject in both technical and popular entomological publications and still maintains its lead as the most publicized insecticide.

The original investigation of DDT in United States was of the products known as "Gesarol Spray" and the "Gesarol Dust Insecticide", samples of which were tested in November, 1942, against the body louse. The value of the product was also established against houseflies, bedbugs, mosquitoes and fleas.[83] This little group of commercial products has been expanded to include some of the most important control measures of insects attacking livestock such as horn flies, stable flies, house flies, lice, ticks and others of minor importance. Insects controlled in the horticultural field include injurious forms of both the biting and sucking types. In the former group the codling moth is very important, and so favorable has been the reaction that certain of our larger manufacturers of lead arsenate are now changing their recommendations for this insect almost exclusively to

DDT. Both in the East and the West very satisfactory control of this insect is obtained with a minimum of plant hazard. If these results are maintained it will be a great contribution to this field, in which control by arsenicals has met with only partial success attended by persistent plant hazard.[42] The residual problem also is less than with the arsenicals, as the present (1947) tolerance for DDT on fresh fruit is 7 ppm whereas that of metallic arsenic is 2.7 ppm.[93]

Defoliating insects on truck crops have shown a high degree of control with both spray and dust applications of DDT; but because of the danger of residues, its use is limited to the earlier stage of the crop and to those such as dry onions and potatoes, where no possibility of harmful residue exists. Plant mites or spider mites have shown more resistance to the material than do many insects. Certain of the leaf hoppers, thrips, a few species of scale insects, and aphids show rather high susceptibility to DDT at some stage of development. Control of aphids is, however, frequently correlated with the effect of DDT on predatory and parastic insects. Many of the latter are quite susceptible, and it becomes a matter of adjusting the possible benefit of aphid control against loss of efficiency from the predators. Consumption of DDT is increasing rapidly, and with lowered prices due to volume production, it will no doubt continue to expand.

Greater tolerance is being shown by toxicologists studying the public health problem, as indicated by the action of the U. S. Food and Drug Administration in placing the residue DDT tolerance on fruit at almost three times that of metallic arsenic. Much more information remains to be assembled on the possible danger of residues on leafy vegetables, soft fruits and in animal tissues, as a guide to the entire problem of the toxicology of DDT. It is definitely known that solutions of DDT in kerosene, when used as sprays on animals, may on repeated applications show the presence of DDT in the kidney fat. Yet such test animals were apparently in good physical condition and gaining flesh normally. Instances are also known of sufficient DDT being ingested to show in the milk secretion; yet this does not prove that dangerous amounts of DDT would be ingested by animals grazing in fields treated with this material. Dairy cows and sheep showed no unfavorable results after feeding for 4 to 5 months on pea vine silage treated with 1 pound of DDT per ton of fresh vines prior to placing in the silo. Calves and lambs feeding on milk containing 15 ppm of DDT also showed no ill effect.[97]

Satisfactory control of the pea aphid, *Macrosiphum pisi*, was obtained with DDT dusts at 3 and 5 per cent concentration applied at the rate of 35 to 40 pounds per acre. Residual DDT on foliage just after application ranged from 2 to 3 ppm. DDT from silage in December ranged from 0 to 3.6 ppm, where fields received from 35 to 50 pounds per acre.' No DDT was found on peas shelled by hand or in the viner.[100] It is generally agreed that there is little danger to the operator from continued exposure to field spraying operations or to the use of DDT aerosols in closed rooms, if in the latter case the usual precautions are taken. However, there is the possibility of food contamination that might lead to dangerous reactions, and undue exposure of the body to oil solutions of DDT might prove hazardous.[96]

(*Courtesy Bridgeport Brass Co., Bridgeport, Conn.*)

Figure 17. Aerosol bomb. Formula used 3 per cent DDT and 2 per cent pyrethrum in compressed Freon gas. Kills flies, mosquitoes, moths and similar insects. Non-flammable and with a mild characteristic odor which quickly dissappears.

The killing of birds and fishes has been reported from the heavier applications of DDT to forests and streams, but apparently satisfactory control of destructive insects is possible with dosages which will be tolerated by wildlife in general.[94]

The literature on DDT, which is already voluminous, has been reviewed to date by Roark [89–92], from which a few papers on typical subjects have been selected.

**Mosquito Control.** Ground applications of DDT aerosols have proved very efficient in the control of adult mosquitoes and as larvicides. Careful regulation of the particle size is necessary, as those of larger diameter than 10 microns will not penetrate dense foliage nor be carried as far by air currents. Particles 0.4 to 1 micron in diameter are not effective insecticides. The particle size of larvicides should be somewhat larger than that for adult mosquitoes and varied according to the wind speed as follows:[83]

| Wind Speed | Particle Diameter |
|---|---|
| 1 to 3 mph | 16 microns |
| 3 to 6 " | 24 " |
| 6 to 10 " | 32 " |

DDT, as prepared and distributed by aerosol, gave a kill of 50 per cent adult mosquitoes. *Aedes* spp., at the rate of 0.002 pound per acre. Deposition of 0.001 pound of DDT per acre controlled from 95 to 100 per cent of the larvae of *Anopheles quadrimaculatus.* There is no residual value at these dosages to mosquitoes migrating into treated areas; hence the treatment must be repeated as necessary.

The dosage commonly used was 15 gallons per 1000 feet of front for the control of adults. The formula was 50 parts of lubricating oil to 50 parts of water in emulsion form containing dissolved DDT in amount equal to 10 per cent of the weight of oil. Xylene was used as the solvent and three-fourths pound of an organic type of emulsifier. The xylene, being very volatile, quickly evaporates but afterwards the particles remain constant in size.[83]

A combination "knockdown" and lethal fly and mosquito aerosol formula is 3 per cent of DDT, 5 per cent of cyclohexanone, 5 per cent of lubricating oil and 0.3 per cent of pyrethrins. This is commonly used in the small aerosol "bomb".[84,85]

Atomized spray applications were made against adult mosquitoes, *Aedes* spp., using 5 per cent solutions of DDT in fish oil and 10 to 20 per cent solutions of DDT in an organic solvent, applying with a paint sprayer, a capillary tube sprayer, and a pressure sprayer. The first two sprayers make air-floated particles of 10 to 18 microns in diameter, but the pressure sprayer gave particles with an average diameter of 136 microns. The capillary tube sprayer gave the most effective results, using 30 ml. per acre of a 20 per cent solution of DDT. Concentrations greater than 10 per cent of DDT were found impractical in the paint sprayer. Part of the effectiveness of the oil solutions used was from the petroleum fraction.[100]

A laboratory experiment of the comparative value of various mosquito larvicides, *Aedes* spp., using suspensions, solutions and emulsions of DDT in petroleum fractions, various organic compounds, pyrethrins and Paris Green has shown the superiority of DDT to all other materials tested. Complete kills were obtained at dosages of 0.02 pound of DDT per acre, compared with 2 pounds of Paris Green and from 2.5 to 10 gallons per acre of petroleum fractions alone and in pyrethrum-oil emulsion.[101]

Residual sprays of DDT applied as water emulsions, water suspensions and kerosene solutions to walls of buildings were found effective against adult mosquitoes, *Anopheles quadrimaculatus*, for periods ranging from 70 days to 32 weeks. Dosages used ranged from 56 to 400 mg. per square foot. Treatments were effective on unpainted surfaces and on those with two coats of a cold water-casein paint, but they were less effective on recent applications of oil paint.[102,103,104]

**House Flies.** Five per cent solutions of DDT in kerosene applied to walls of houses and barns as a residual spray gave control of house flies ranging upward to 200 days.[72] The spray should be applied in coarse drops rather than a fine mist. Muslin strips treated with a solution or suspension of DDT and hung where flies congregate were effective for months. Water suspensions of DDT gave longer protection than solutions, but since they give a visible coating they should be used in barns rather than residences.[105]

Spraying the entire surface of walls and ceilings is unnecessary; rather, favored localities where flies congregate should be treated as frequently as necessary to prevent the fly population from building up. (See aerosol type of spraying for use of DDT in "knockdown" sprays for mosquitoes and flies).

**Horn Flies.** Treatment of cattle against horn flies under Florida conditions where heavy rains occur was accomplished by spraying with water suspensions and emulsions of DDT. One per cent concentrations of DDT in the former were active for two weeks and maintained a low fly population for a month. Long periods of protection from emulsions required at least a concentration of 2.5 per cent DDT.[106]

A comparison of dipping and spraying cattle under Kansas conditions with a water suspension of DDT at 0.1 per cent concentration in the dip and 0.2 per cent concentration in the spray as a protection against horn flies showed equal effectiveness for four dippings and four sprayings. Dipping, however, required about 3 times the amount of DDT. An average gain of 30 pounds per head was found between treated and untreated animals. Supplementary treating of barns with residual sprays gave control of both the stable fly, *Stomoxys calcitrans*, and the house fly.[107] Suspensions and emulsions of DDT have also given control of cattle lice and reduced the population of the screw worm fly and the Gulf Coast tick, *Amblyomma maculatum*.[108]

**Lice Attacking Humans.** Two methods of using DDT against lice have been developed—local applications of dusts or liquids and impregnation of clothing. Ten per cent concentrations of DDT in talc or pyrophyllite is a practical treatment for the body louse, *Pediculus humanus corporis*. The head louse, *P. humanus humanus*, may also be treated with the 10 per cent powder, although a liquid is preferred. The formula consists of benzyl benzoate 68 per cent, DDT 6 per cent, benzoraine (ovicide) 12 per cent, and an organic emulsifier ("Tween 80"). Dilute with 1 to 5 parts of water before applying. This formula will also control the crab louse, *Phthirus pubis*.[109]

Impregnation of clothing, as a protection against lice, is the most satisfactory method of treatment. The formula commonly used contains 25 per cent of DDT, 10 per cent of organic emulsifier ("Triton X-100"), and 65 per cent of xylene. The emulsion is diluted with water to contain 1 to 2 per cent of DDT and the clothing dipped in this and wrung out dry. The treatment will resist laundering up to 6 or 8 times.[109, 110]

**Fleas and Bedbugs.** Dusts and sprays of DDT as recommended for body lice may be used against fleas on the person, in clothing, or on floors. Spraying floors with a 5 per cent solution or emulsion of DDT at the rate of a gallon per 1000 square feet of surface is recommended.[109]

Bedbugs are easily controlled with a 5 per cent solution or emulsion of DDT sprayed thoroughly on the entire bed and adjoining walls and floor, leaving a deposit of at least 100 mg of DDT per square foot.[112]

**Cockroaches and Ants.** Good control of the American cockroach, *Periplanata americana*, and the oriental roach, *Blatta orientalis*, is reported with 10 per cent DDT powders, but greater difficulty has been experienced in the control of the German roach, *Blatta germanica*, and the brown banded roach, *Supella supellectilium*. DDT in powder form affords a short period of protection against the common species of house ants, but sprays have given protection for about a month.[113]

**Moth-Proofing.** Fabric treatments are recommended with solutions of DDT sufficiently concentrated to leave a residue of 2 per cent or more of DDT based on the dry weight of the fabric. Such treatments will resist a number of washings. A DDT aerosol treatment for clothes moths in a large wool warehouse killed all adult moths with some residual action on emerging adults and larvae. The particle size is an important factor in penetration and distribution.[114] Solutions or emulsions of DDT are of value for treating the hiding places of the carpet beetle.[113]

**Stored Product Insects.** DDT in solution, emulsions or suspension at 5 per cent concentration is of value in destroying moths, beetles and weevils present in warehouses and granaries.[113]

Seed grain may be protected against insects by adding dusts containing DDT at concentrations of 2.5 to 20 per cent, at the rate of 1 ounce per bushel of seed. No effect was noted on germination with a 20 per cent concentration of the dust.[115]

**Orchard and Garden Insects.** Codling moth control throughout many of the apple-growing districts has shown DDT to be superior to the arsenicals for this insect, with a minimum of foliage injury. The usual dosage is 1 pound of actual DDT per 100 gallons of spray, at least for the earlier applications, and 0.75 pound per 100 gallons for later sprays. No difficulty is anticipated in meeting the residual tolerance of 7 ppm on fresh fruits. Infestations of the plant mites, in DDT-sprayed orchards, are less frequently noted in eastern apple districts than in the semi-arid west.[116,117,118]

Driggers shows, in 3 years of experiments on peaches, that a high degree of control of the Oriental fruit moth, *Grapholitha molesta*, can be obtained with a single application of DDT at a concentration of 1 pound of DDT per 100 gallons of water. No injury resulted on either peach or apple trees.[119] Similar values for DDT were found against the plant bug, *Lygus oblineatus*, which attacks peaches. A concentration of 5 per cent DDT in dusts or 1 to 2 pounds in 100 gallons of sprays was sufficient.[120]

Effective control of the Japanese beetle, *Popilia japonica*, on peach, apple, plum and cherry is reported by Langford and Cory with applications of both suspensions and emulsions of DDT, the former method proving more effective. The protective period ranged from 7 to 20 days. Dust-coated foliage was also found repellent. Compatibility of DDT exists with sulfur, lime-sulfur and Bordeaux mixture.[123]

Limited applications of DDT have been made on Citrus trees; they were confined largely to the control of citrus thrips, *Scirtothrips citri*, citricola scale, *Coccus pseudomagnoliarum*, and California red scale, Anodiella aurantii.[93]

The pea aphid, *Macrosiphum pisi*, is controlled with DDT dusts at 35 to 40 pounds per acre. If the pea vines are to be converted into silage a safer formula is a 2 per cent concentration of DDT and 0.25 per cent of rotenone.[93,97] Potato insects controlled by DDT applications include the Colorado potato beetle, *Leptinotarsa decemlineata*, the flea beetle, *Epitrix cucumeris*, the leaf hopper, *Emposaca fabae*, and the aphids, *Aphis abbreviata*, *Myzus persicae*, *M. pseudosolani*, and *Macrosiphum solanifolii*. Both dust and spray types of applications were used. DDT is also very effective against leafhoppers in growing potatoes for seed purposes, under western conditions. The control of these insects, which are carriers of certain virus diseases, is very important to the industry. Successful use of

DDT as dusts and sprays has been made against defoliators on cauliflower, including *Pieris rapae*, *Autographa brassicae*, and *Plutella maculipennis*. The squash vine borer, *Melittia satyriniformis*, was controlled with a 3 per cent concentration of DDT on the Hubbard and the Acorn squash, but was injurious to the latter variety, and to a less extent to cantaloupe.

**Compatibility of DDT.** DDT is stable in itself but may decompose in the presence of certain catalysts, forming hydrochloric acid and 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene. The latter is inferior to DDT as an insecticide.

No catalytic action on DDT was noted in the presence of commercial grades of sodium fluoride, sodium fluosilicate, cryolite, Paris Green, calcium arsenate, lead arsenate, pyrethrum or rotenone. Pure nicotine caused decomposition of DDT; this reaction was apparently of the type caused by alcoholic caustics. Commercial lime-sulfur solution and 2,3-dichloro-1,4-naphthoquinone showed no reaction with DDT.

Accessory materials used as diluents for DDT varied in their catalytic action, which probably indicated the presence of small amounts of active catalysts distributed through the powder. This action might result from the presence of known catalysts such as ferric oxides, chromium and anhydrous ferric, aluminum and chromic chlorides. DDT in contact with the metals may form ferric and chromic chlorides.

Catalytic action is slow in diluted dusts except at temperatures above the melting point of DDT. Solutions of DDT are quite stable with many of the solvents commonly used except the nitro and chlorobenzenes.[124]

**Dichlorobenzene** ($C_6H_4Cl_2$) (also known as PDB). The para form of this compound is a white crystalline substance, insoluble in water but soluble in alcohol, ether, and certain petroleum fractions. Its boiling point is 172°C and it vaporizes slowly at room temperature. Its use as a fumigant is preferably at temperatures above 15°C; this use is usually against the peach tree borer, *Sanninoidea exitosa*.[57] The borer girdles the crown of the tree in a band 4 to 6 inches above the soil surface and downward to a depth of 6 to 10 inches. The *p*-dichlorobenzene is placed in a shallow trench around the tree trunk and about 2 inches distant, then is covered with loose soil 4 to 6 inches deep and high enough to cover infested portions of the trunk. The dosage is 1 ounce per tree of 5 years or older and 0.75 ounce for trees 2 to 4 years old. Very young trees should not be treated. Prolonged exposure in wet soils or at temperatures below 65°F may result in injury to the tree.

Housefly larvae were killed by mixing *p*-dichlorobenzene with garbage, the median lethal concentration being 430.5 mg per 100 grams of food, the toxic action being apparently both as a fumigant and stomach poison.[127] McDuffie and co-workers found the material useful in treating pit latrine both as ovicides and larvicides for the house fly.[134]

*o*-**Paradichlorobenzene** is a liquid at room temperatures, and has a boiling point of 172°C. It is insoluble in water but is soluble in alcohol and certain petroleum fractions. Though an active fumigant, it is too dangerous to plants. It has limited use in treating logs and poles for borers. It is effective as a larvicide for houseflies, in treating pit latrines and to destroy flesh fly larvae on cadavers. For the latter purpose it may be diluted 1 to 4 with fuel oil and sprayed over the carcass and the larvae-infested soil beneath it.[134]

**Di(4-chlorophenoxy)methane** ($C_{13}H_{10}O_2Cl_2$) is giving promising results in the control of the citrus red mite, *Paratetranychus citri*, at a concentration of 1 pound per 100 gallons of spray. The residual toxicity is very marked, particularly under winter conditions. The material is chemically stable, slightly soluble in water and dissolves up to 4 per cent in kerosene.[125,126]

**2,3-Dichloro-4-naphthoquinone,** also known as Phygon, is soluble in acetone, benzene, *o*-dichlorobenzene, and vegetable and animal oils. It is used as a seed disinfectant and as a fungicide in foliage spraying and textile treatment.[135,136] Nagel reported excellent control of late blight on potatoes with this material.[137]

**Difluorodiphenyl disulfide** is one of the most effective and durable insecticides against the body louse, *Pediculus humanus corporis*, as reported by Eddy and Carson in testing about 7500 compounds for this purpose.[47]

**2,4-Dichlorophenoxyacetic acid,** also known as 2,4-D, was first developed for stimulating plant growth when used in minute proportions. At higher concentrations it has proved to be one of the most effective herbicides. It was first reported in 1944 by Mitchell and Hamner[128] and also by Hamner and Tukey.[129] The earliest patents[130] stressed its value as a growth stimulant, while a later one[131] developed its use as an herbicide.[132] It is now available commercially in the acid form, as a sodium salt and as an ester. The molecular weights and comparative percentages of this acid in various forms are given in Table 60.[133] 2,4-D is most effective against broad-leaved plants, such as dandelion and wild mustard, and has but little effect on most grasses. After absorption by the leaf it may be carried downward into the roots, thus killing deep-rooted perennial plants such as wild morning glory, *Convolvulus arvensis*. It also acts as a soil sterilizer, persisting over a period of 30 days to 6 months, depending on the type of soil, concentration, temperature and moisture conditions; hence it may act as a selective herbicide for grain field and lawns.[141]

Dosages for annual weeds in grain fields is $\frac{1}{2}$ to $\frac{3}{4}$ pounds of acid per 100 gallons; for lawns and pastures $1\frac{1}{2}$ pounds per 100 gallons; on perennials $1\frac{1}{2}$ to 3 pounds of acid per 100 gallons.[132]

Care is necessary in applying sprays of 2,4-D to avoid drift onto valuable plants and to wash and clean thoroughly all tanks and apparatus before applying other materials.[141] The ester form of the compound is reported difficult to remove even with strong alkalies and acetone. Volatile products from tanks containing 2,4-D ester solution have been found injurious to delicate plants in closed rooms or greenhouses.[142]

**2,4-Dinitroanilines.** Certain N-substituted derivatives of this compound were tested against codling moth larvae. One substance, 2,4,4′-trinitrodiphenylamine, was found to be slightly more toxic than lead arsenate, but the others were of very little value.[138]

**2,4-Dinitroanisole,** $CH_3OC_6H_3(NO)_2$. This compound has been found quite effective as a mothproofing agent and against the furniture carpet beetle, *Anthrenus vorax*,[145,49] and also against the cockroach.[139] Its greatest value is apparently that of a control of the human body louse. Hansens[37] lists it as one of the most effective ovicides of a large number of compounds tested against this insect. Later it formed one of the ingredients of the officially recommended formula for use against the body louse.[130]

Table 60. 2,4-D Equivalents.[131]

| Substance | Molecular weight | 2,4-D acid (%) | Grams required to contain 100 grams of 2,4-D acid |
|---|---|---|---|
| 2,4-D acid | 220 | 100 | 100 |
| 2,4-D ammonium salt | 237 | 93 | 108 |
| 2,4-D sodium salt (anhydrous) | 242 | 91 | 110 |
| 2,4-D sodium salt monohydrate | 260 | 85 | 119 |
| 2,4-D diethanolamine salt | 305 | 72 | 139 |
| 2,4-D triethanolamine salt | 339 | 65 | 154 |
| 2,4-D methyl ester | 234 | 94 | 106 |
| 2,4-D ethyl ester | 248 | 89 | 112 |
| 2,4-D propyl esters (2 with same weight) | 262 | 84 | 119 |
| 2,4-D butyl esters (4 with same weight) | 276 | 80 | 125 |
| 2,4-D amyl esters (about 15 with same weight) | 290 | 76 | 132 |

**Dinitro-o-secondary butyl phenol** and its ammonium salt are reported as promising lethal dust barriers for the chinch bug, *Blissus levicopterus*, at 2 and 4 per cent concentrations.[143]

**4,6-Dinitro-o-cresol,** $C_7H_6N_2O_5$. In European literature this chemical is known as 3,5-dinitro-*o*-cresol. During an investigation[10] of certain benzene derivatives it was found that the nitro-derivatives of phenols and cresols are more toxic to aphids than the parent substances, and that the dinitro-compounds were better ovicides than either the mono or trinitro compounds. Dinitro-*o*-cresol and its salts were found very toxic to both aphids and the eggs and more effective than dinitrophenol. Their injury to foliage, however, restricts their use to dormant applications only. The sodium salt is active as a fungicide against wood-infesting fungi of the dry-rot type.[145] Monochloronitrobenzene is similar in toxicity to nitrobenzene, while 1-chloro-2,4-dinitrobenzene is less toxic than *m*-dinitrobenzene.[144] Dinitro-*o*-cresol and its sodium salt were similar in toxicity to the eggs of the moth, *Selenia tetralunaria*, at concentrations ranging from 0.1 to 0.025 per cent. These applications also removed algae and lichens from the tree.[145]

Dormant applications of a proprietary mixture containing 20 per cent concentration of sodium dinitro-*o*-cresolate, used at the rate of 3 pints per 100 gallons of water, gave satisfactory control of the mealy plum aphid, *Hyalopterus pruni*, in the egg stage. The material was injurious to the cover crop.[146]

Laboratory experiments with dinitro-*o*-cresol against the European corn borer, *Pyrausta nubilalis*, have shown a high degree of efficiency, but with so much foliage injury as to make its use impractical.[38] A high degree of efficiency against this insect was obtained with 4,6-dinitro-*o*-cresol ethyl ether, $(NO_2)_2(CH_3)C_6H_2OC_2H_5$.[33]

An emulsion of 4 pounds of dinitro-*o*-cresol dissolved in 10 gallons of stove oil and containing a penetrant of 1.5 gallons each of ethylene glycol monobutyl ether and trichloroethylene to 100 gallons of spray has been used successfully against the hibernating larvae of the codling moth. An application of 3 to 5 gallons of the spray per tree is made during the dormant season only to the trunk and scaffold branches.[149] The deposit persists for months as indicated by the deep yellow color, and has been found to kill larvae over a year after application.[150] The penetrants used in the above formula being unavailable during the war period, a substitute of 3 pounds of diatomaceous earth per 100 gallons of spray has been developed which is giving promising results.[151] Gahan has shown the value of this compound against the American cockroach, *Periplaneta americana*, at a concentration of 5 per cent in either talc or redwood bark flour. Tendency to stain floors and danger to pets limits its field of usefulness.[152] Eddy and Carson[47] have shown it to be a very effective insecticide for the body louse.

**2,4-Dinitro-6-cyclohexyl phenol.** Also known as 2,4-dinitro-*o*-cyclohexyl phenol, this material, used at the concentration of 8 ounces in 2 gallons of petroleum oil per 100 gallons of spray, increased the ovicidal action against the European red mite.[153]

Dinitro-*o*-cyclohexylphenol (DNOCHP) and its dicyclohexylamine salt has come into general use as a control for the citrus red mite, *Paratetranychus citri*, as it is not hazardous to foliage, as are dinitrophenol and dinitrocresol.[154] Dust mixtures of the parent phenol compound are made with talc or walnut shell flour and are marketed as DN dusts with a concentration of 1 per cent dinitro-6-cyclohexyl phenol. Effective control of the spider mite, *Tetranychus telarius*, on hops has been reported with concentrations of less than 1 per cent.[155] The salt is quite insoluble in water but is soluble in acetone, ethyl alcohol and benzene. Its low vapor pressure gives it a prolonged residual effect. Dust preparations may be made by incorporating a solution of 1.7 per cent concentration in an inert base. This equals a concentration of 1 per cent of dinitro-6-cyclohexyl phenol.[9]

This compound, its sodium salt, and the dicyclohexylamine salt have been found of moderate effectiveness in barrier dusts for chinch bugs but are safer to foliage than the more active dinitro-*o*-secondary butyl phenol and dinitro-*o*-cresol.[143] It is also effective against the wood ticks, *Dermacentor andersoni* and *D. variabilis*, the principal carriers of Rocky Mountain spotted fever, when applied as a spray.[156]

A combination of equal parts of a 1 per cent DN dust and sulfur has proved very effective against the potato leafhopper, *Empoasca fabae*, and without injury to the foliage of potato, bean and alfalfa.[157]

Sodium dinitro-*o*-cresylate is marketed as a very effective herbicide under the name of "Sinox." It is used against broad-leaved annuals in grain fields, onions, on roadsides and in pastures. It is marketed both as a water suspension and an oil-soluble powder.[147]

Crafts and Reiber have compared the value as herbicides of the sodium and ammonium salts of dinitro phenol, dinitro-*o*-cresol, dinitro-*o*-phenyl phenol, and dinitro-*o*-cyclohexyl phenol; in every instance they found the ammonium salt more toxic than the sodium salt. They also discovered that sodium dinitro-*o*-cresylate ("Sinox") spray could be activated by adding one pound of ammonium sulfate per gallon of "Sinox" and then acidifying the solution until a slight precipitate occurs. Sodium bisulfate is suggested for acidification in preference to sulfuric acid.[148]

**Dinitronaphththalene** $C_{10}H_6(NO_2)_2$. Experimental work in the Canal Zone has shown the value of this material as a repellent for termites at a 5 per cent concentration in petroleum fractions. Test stakes, absorbing the material at a rate of 14.3 pounds per cubic foot, were in good condition after 10 years' exposure.[57]

**2,4-Dinitrophenyl ester of acetic acid** $CH_3CO_2C_6H_3(NO_2)_2$. This compound has been found superior to standard chemicals used against the clothes moth, *Tineola bisselliella*, and the furniture carpet beetle, *Anthrenus vorax*, in the protection of fabrics.[134]

**Diphenyl** $(C_6H_5 \cdot C_6H_5)$. The vapors from this chemical showed an active fungistatic action against a number of destructive fungi including *Aspergillus*, *Botrytis*, *Diplodia*, *Dothiorella* and *Phomopsis*. Vegetative growth and sporulation were both checked without fungicidal action. The use of diphenyl wraps for treating fruits is discouraged because of the disagreeable odor.[158] Loucks and Hopkins tested diphenyl-impregnated wraps for oranges but found them ineffective against the fruit rot fungus, *Diplodia*.[159]

A quick-acting residual effect as a louse powder for poultry was noted from a concentration of 5 per cent diphenyl and 30 per cent micronized sulfur in a dust base.[160]

**Diphenylamine arsenious oxide** is used successfully against the marine pile borer, *Limnoria lignorum*, at a concentration of 1 to 100,000.[161] Diphenyl arsenious oxide has given protection against termite attack for more than 16 years in tests being conducted by official agencies.[57]

**Diphenylene oxide** is an effective wound protectant against the screwworm, *Cochliomyia americana*, attacking livestock. The material is less effective than diphenylamine but is recommended because of its low cost and lack of caking at high field temperatures.[162]

**1,10-Dipiperidinodecane** and dodecylmorphaline have both been found very effective and persistent in their action against the body louse. These compounds are two of a list of ten chemicals selected from about 7500 synthetic compounds tested against the body louse.[47]

**Glyoxalidine Derivatives.** Three compounds out of a series of glyoxalidine derivatives have been selected as active fungicides.[163,164] The following derivatives have given satisfactory results in field tests in addition to those of the laboratory:

(1) 1-Hydroxyethyl-2-heptadecylglyoxalidine
(2) 2-Heptadecylglyoxalidine
(3) 1-Aminoethyl-2-heptadecylglyoxalidine.

Compared with Bordeaux mixture against black spot of rose, *Diplocarpon rosae*, Number 2 at a concentration of 3 pounds per 100 gallons of spray showed control equivalent to Bordeaux and without a conspicuous deposit. Number 1 was inferior in control and somewhat injurious to foliage.

Tested on the McIntosh and Stayman apples in Pennsylvania, Numbers 1 and 2 at 1 pound per 100 gallons and Number 3 at 3 pounds per 100 gallons gave control of apple scab, *Venturia inaequalis*, equivalent to that obtained from standard lime-sulfur solution and better than "Fermate" at 3 pounds per 100 gallons. Number 1 caused foliage injury at 3 pounds per 100 gallons. Number 2 at 1 pound per 100 gallons produced a better-appearing foliage with heavier growth than did lime-sulfur solution. It also showed a decided residual effect on scab control.

**Hydroxypentamethylflavan** (2′-hydroxy-2,4,4,4′,7-pentamethylflavan). This insecticide has been found of value principally in horticultural fields. A 10 per cent dust gave protection against the corn ear worm, *Heliothis armigera*. At a concentration of 4 pounds of 25 per cent wettable powder it was effective against the two-spotted spider mite, *Tetranychus bimaculatus*. Dosages of 2 to 8 pounds per acre gave protections against chiggers.[66]

**2-Isobutyryl-1-phenylhydrazine** $C_6H_5NHNHCOCH(CH_3)_2$. A series of hydrazine derivatives tested as larvicides against the European corn borer, *Pyrausta nubilalis*, have developed a number of toxic compounds. Besides the isobutyryl form two others of similar toxicity are included, 1-Phenyl-2-phenylhydrazine ($C_6H_5NHNHSO_2C_6H_5$) and 1-isocaproyl-2-phenylhydrazine, $C_6H_5NHNHCO(CH_2)_2CH(CH_3)_2$.[29]

**1-Isovaleryl-2-phenylhydrazine** $C_6H_5(NH)_2COCH_2CH(CH_3)_2$. This compound was the only one giving slightly better control of codling moth larvae than was obtained with standard lead arsenate. It is also very effective against the European corn borer.[29] A large series of hydrazines were included in the test and all compounds used at concentrations of 4 pounds per 100 gallons of the carrier. The latter, for laboratory use, consisted of 80 gallons of water and 20 gallons of 95 per cent ethanol.

The compounds were prepared by the interaction of phenylhydrazine with an acid or acid chloride. They were principally phenylhydrazides of aliphatic acids and in addition certain aromatic and sulfonic acids.

**Mercury Compounds-(Organic).** This class of compounds is used principally as seed disinfectants,[166] their function being that of sterilization and protection against parasitic soil organisms. The composition of the compound, rather than the mercury content, is considered the vital factor. A series of halogenated compounds including ethyl, methyl and phenyl iodides, chlorides, phosphates and nitrates were investigated by Weston and Booer in England. The conclusion of these exploratory studies was that the methyl mercury series, at recommended dosages, did not injure germination.[165] Ethyl mercury compounds have predominated in American practice for several years; these include ethyl mercury phosphate ("New Improved Ceresan"), ethyl mercuric chloride ("Ceresan"), sodium ethyl mercurithiosalicylate ("Merthiolate"), and ethyl mercury *p*-toluene sulfonanilide ("DuBay 1452-C").[174] Ethyl mercury phosphate in light applications of 20 to 25 pounds per acre gives effective control of the bottom rot of lettuce caused by the fungus *Rhizoctonia solani*.[174] Phenyl derivatives are a later development; they include hydroxymercurichlorophenol ("Semesan"),[169] phenyl mercury urea ("Leytosan"),[168] and phenyl mercury cyanamide, the latter being used principally on seed corn.[170] Phenyl mercuritriethanolammonium lactate ("Improved Puratized N5E") has been reported as very effective against *Colletotrichum lilic* in lily bulbs. Concentrations of the compound at 1 to 1000 and 1 to 2000 reduced the percentage of diseased bulbs effectively.[171] This chemical has also proved effective against the Diplodia stem-end-rot of citrus fruits[172] and in checking "copper spot" (caused by the fungus *Gloeocercospora Sorghi*).[173]

The organic mercurial seed disinfectants are usually applied in dust form, thus eliminating the need of drying after the use of hot water and other liquid methods. Dust treatment of large volumes of seed, however, necessarily requires precautions against inhalation of the dust by the operator.

**2-Methyl-4-chlorophenoxyacetic acid** (also known as "Methoxon") is an herbicide developed and used generally in England for many of the resistant weeds, including yellow and white charlock, Buttercup and Pennycress.[167]

**Naphthalene Derivatives.** In a study of a number of derivatives including nitro, dinitro, cyanogen, hydrogenated and chlorinated naphthalene, the most toxic to the bean aphid, *Aphis fabae rumicis*, was α-chloronaphthalene. At a concentration of 0.35 per cent it killed 99 to 100 per cent of the insects.[144] α-Naphthylamine has also been found to be quite toxic to this aphid.[32] Certain of the chlorinated naphthalenes are being used as protectants against termites and wood decay fungi. Halogenated naphthalenes and naphthalenesulfonic acid form the basis for a number of German patents for mothproofing compounds, as do also naphthol derivatives.[26]

**β-Naphthol** ($C_{10}H_7OH$). This compound has had general use as a wood preservative against both termites and wood decay fungi. It is used at a 5 per cent concentration in mineral oil fractions in the open-tank method of treatment.[57] It is the standard chemical for impregnating tree bands for codling moth control. One pound of β-naphthol is dissolved in light lubricating oil; rolls of corrugated paper are dipped in the hot solution and then allowed to drain.[6,7]

**α-Naphthylthiourea** ("Antu"), also known as α-naphthylthiocarbamide, is one of the war-developed compounds which has come into general use as a rodenticide and is considered safe for the inexperienced operator to handle. It is a specific for the Norway rat (common gray form) and is more effective against adults than young rats. It is less effective against the black or Alexandrian rat and against ground squirrels. It is toxic to dogs and most carnivorous animals and in varying degree to the herbivorous ones. Tolerance is developed by rats surviving sublethal doses. Concentration in baits is commonly 1 per cent with a dosage for Norway rats of 6 to 8 mg. per kg. "Antu" is mixed with ground baits, dusted over pieces of fruit, vegetables or meat and blown into runways.[175]

**Nitro Compounds.** With few exceptions the mono nitro compounds are of moderate toxicity as compared with dinitro forms, which it will be noted cover a wide field of usefulness. *o*-Nitrodiphenyl at 10 per cent concentration is reported as a quick-acting toxicant but without residual value when used against the poultry lice, *Eomenacanthus stramineus*, *Menopon gallinae*, and *Goinocotes holgaster*.[166] Other nitro compounds that have been found of some value against the larva of the European corn borer include 6 nitro-2,4-bis(trichloromethyl)-1,3-benzodioxane; *p*-nitrobenzoic acid ethyl ester; *p*-nitrobenzoic acid propyl ester, and 3-nitrobenzanilide.[29]

**Pentachlorophenol** is a commonly used wood preservative to protect against decay fungi and termites. Two forms are commercially available, the flake or crystal and concentrated solutions to be diluted with fuel oil at 2 to 10 or more parts per solvent. Light-colored concentrates are used for treating finished lumber and darker grades for framing timbers and posts. For the latter purpose the length of the protective period has not been determined, but for a number of woods it is at least 10 years. Solutions of this material are particularly useful in the cold-soaking method, as good penetration is secured within 48 hours.[176] Favorable results have also been obtained in protecting fiberboards against termites.[57] The compound has been included as one of the 10 most effective compounds against the body louse, *Pediculus humanus corporis*, being very effective as well as long-lasting.[47]

The value of pentachlorophenol as an herbicide is shown by Steiner, using a concentrate of 1 pound per quart dissolved in a carrier. Two quarts of this solution were combined with 2 gallons of oil in 100 gallons of spray. Top growth of all weeds was killed and recovery required from 3 to 5 weeks.[177]

Sodium pentachlorophenate shows promise as a control for brown rot, *Sclerotinia fructicola*, on deciduous trees as a dormant spray.[12] Solutions of this compound, when activated by one of the acid salts, have been found much more active than when used alone.[148] A 2 per cent concentration of this compound, when added to glue size used in treating plasterboard, prevented the growth of molds.[184] It is also used in industry against growths of slime and algae in water pipes. It is stable in alkaline solution and non-volatile during aeration processes.

**2-Phenylcyclohexanone.** See Repellents (p. 250).

**Phthalonitrile** $C_6H_4(CN)_2$ also known as orthodicyanobenzene, is a general type of insecticide which, in comparison with Derris and lead arsenate, proved superior in the control of the melonworm, *Diaphania hyalinata*; Hawaiian beet webworm, *Hymenia recurvalis*, and the Southern beet webworm, *Pachyzancla bipunctalis*. It was also effective at a concentration of 1 to 3000 as a soil treatment in the control of termites.[30]

This substance has also been found similar in effectiveness to diphenylamine against the screwworm larvae, *Cochliomyia americana*,[39] and similar to thiourea against the larvae of the housefly.[179]

**Pyridine Derivatives.** A series of N-heterocyclic compounds tested against the spider mite, *Tetranychus telarius*, showed increased value by the addition of an amino group in the $\alpha$-position. Condensing the pyridine nucleus with a benzene ring to form quinoline increased the toxicity, and to a greater extent by adding two benzene rings to form acridine.[180]

**Semicarbazones** are condensation products of semicarbazide with aldehydes and ketones. Some of these compounds have been found of value against the codling moth.[181] Further studies showed promising values for the following semicarbazones: *p*-chloroacetophenone, 2-heptanone, cyclopentanone, 2-octanone, and 2-furaldehyde. Decided foliage tolerance was also indicated.[182] Experiments with a number of other insects, including defoliators, cockroaches and termites further confirmed the value of the following: *p*-chloroacetophenone, cyclohexanone, and cyclopentanone semicarbazones.[25] A 1 per cent suspension of 2-methylcyclohexanone semicarbazone killed all larvae of the cross-striped cabbage worm, *Evergestis rimosalis*, and 97 per cent of the Southern army worm, *Prodenia eridania.*[184] The findings to date have been reviewed by Gertler,[183] who states that 21 out of 33 semicarbazones have definite insecticidal value. Four patents covering the use of such materials are listed.[185]

**Tetrachloro-p-benzoquinone,** also known as "Spergon," is a disinfectant for peas, cotton and sorghum seed. It is a yellow powder of extreme fineness that adheres readily to seed.[168,186] It is also used as a dip for seed sweet potatoes to prevent decay.[187]

**Tetrachlorophenate.** (See pentachlorophenate,[57] p. 242).

**2,4,5-Trichlorophenate** as a zinc salt has been found effective as a seed disinfectant for cotton and peas. It is heat-stable and only slightly soluble in water and organic solvents. This form was more effective than 2,4,6-trichlorophenol.[188]

**Sodium ethyl mercurithiosalicylate.** (See Mercury compounds, p. 240).

**Sodium pentachlorophenate.** (See Pentachlorophenate, p. 242).

**Sodium phenylphenate** is used at concentrations of 1.25 to 2 per cent as a control of decay in citrus fruits. It may be applied with other solutions and wax emulsions.[189]

**Xanthene.** This compound and xanthydrol have been found to be among the most effective of a large number of organic compounds tested against screwworm larvae.[39]

**Xanthone.** ($C_6H_4COC_6H_4O$) ("Genicide"). This substance has proved effective in commercial applications in the control of codling moth. Its greatest value, in comparison with lead arsenate-mineral oil or nicotine, is as an ovicide. The effect as a larvicide is similar to that of lead arsenate. Xanthone is also effective against the spider mites, *Paratetranychus pilosus* and *Tetranychus bimaculatus.*[190,191,192]

Hoskins has shown a moderate degree of efficiency with xanthone against the larvae of the flesh fly, *Lucilia sericata.*[193]

**Zinc 2,4,5-trichlorophenate.** (See Trichlorophenol p. 243).

## Organic Sulfur Compounds

**Benzothiazole, 1-Amino.** This compound and benzothiazole, 1-amino-5-chloro are listed as seed disinfectants and as general fungicides for use in orchards and on truck crops under British Patent 407,408.

**Bis(o-amino-phenyl) disulfide.** An efficient mosquito larvicide at a concentration of less than 1 in 10,000 that kills within 18 to 24 hours. Three disulfides, *n*-butyl, phenyl and *p*-tolyl, were found to be efficient larvicides for the flesh fly, *Lucilia sericata.*[193]

**β-Butoxy-β′-thiocyanodiethyl ether,** known as "Lethane" is effective against spider mites at concentrations ranging from 1 to 800 to 1 to 2400.[206] It is used as a household spray for moths, roaches and flies, in combination with pyrethrins. One of a large number of compounds tested against the larvae of the flesh fly, *Lucilia sericata,* which showed average effectiveness.[193] The insecticidal action is more that of hydrocyanic acid than of nicotine or pyrethrum.

**Difluorodiphenyl disulfide.** (See aromatic section, p. 235).

**1,3-Dithiane-2,2-diphenyl,** also known as 2,2-diphenyl-tetramethylene-1,3-disulfide, is reported to have killed 10 per cent of mosquito larvae at a concentration of 1 to 10,000. 1,3-Dithiane-2-phenyl killed 100 per cent of mosquito larvae at a concentration of 1 to 10,000.[208]

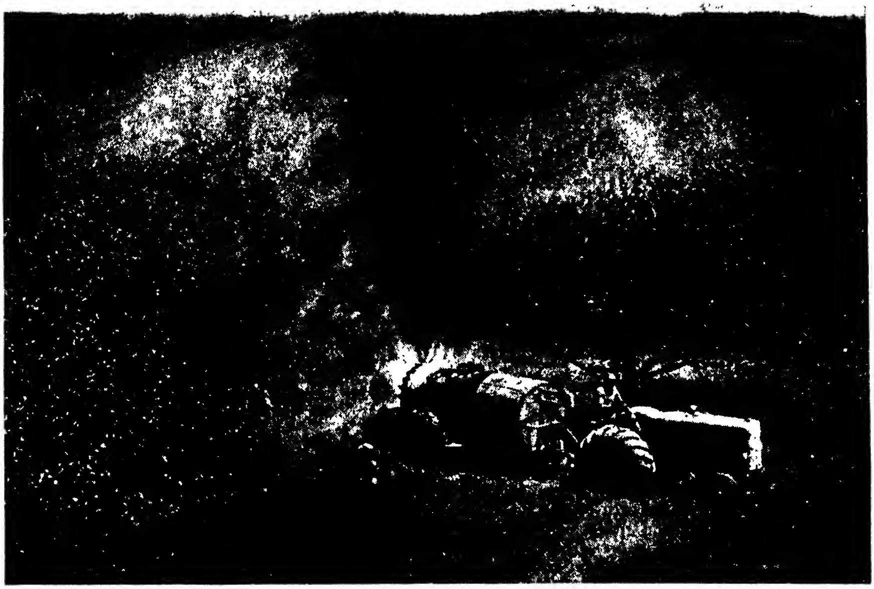
**Dithiocarbamates.** Derivatives of dithiocarbamic acid form at present the most important group of organic fungicides and seed disinfectants. Tisdale and Williams[194] are credited by McCallan[195] as the discoverers of the value of these compounds in a comprehensive review of the dithiocarbamate fungicides. Disodium ethylene bis-dithiocarbame, known as "Dithane," a water-soluble form, was developed by Dimond, Heuberger and Horsfall,[196] while the metal dialkyl dithiocarbamates have been largely developed by Goldsworthy, Green and Smith.[197] Selection of the metallic combining form has been restricted by plant tolerance, the iron and zinc salts being generally considered the safest. The ferric salt is soluble in water to the extent of 120 ppm and the zinc salt at 65 ppm.

These compounds are somewhat unstable, the dialkyl dithiocarbamates oxodizing readily. They adhere well as sprays and dusts but apparently have no residue hazard.[195]

**Tetramethylthiuram disulfide** is an effective control against the Botrytis blight of the tulip is reported in a comparative test of various fungicides.[203] This material, which contains two molecules of dimethyl dithiocarbamic acid, is used against turf diseases,[198] as a seed disinfectant and protectant, particularly on peanuts,[195] many vegetable seeds and on sorghum seed.[180, 181]

**Ferric dimethyldithiocarbamate,** known as "*Fermate,*" is used as a general fungicide in orchards and on truck crops[203] and in place of sulfur applications on apples. It is compatible with lead arsenate, oil emulsions, lime and DDT.[195] It has been reported as not controlling the spider mites on apple; but by combining with oil emulsions effective control is obtained of the mites and certain fungus diseases[199] under Ohio conditions. Similarly good results have been obtained in Oregon on the spray-sensitive Anzou pears against pear scab, *Venturia pyrina.*[200] "Fermate" is proving a satisfactory fungicide for a number of truck crop diseases, including celery blight and anthracnose fruit rot of tomatoes, but it is not as effective on tomato foliage diseases as are the fixed coppers.[201]

**Zinc dithiocarbamate,** known as "Zerlate" and "Methasan," is an orchard and truck crop fungicide but somewhat inferior, in the present state of development, to "Fermate" on apples. It has been used with average control on late blight, *Phytophora infestans*, of potatoes.[137] Wilson[201] reported better results on much of the vegetable spraying than from "Fermate." Diseases controlled included early blight of celery and tomato anthracnose.



(*Courtesy John Bean Manufacturing Co., Lansing, Mich.*)

Figure 18. Speed sprayer in action.

It has also given a long period of protection against copper spot, *Gloeocercospora*, on fine turf grasses.[173]

**Disodium ethylene bisdithiocarbamate** (known also as "Dithane"). This compound combined with zinc sulfate has given effective control of potato early blight. Experiments on this disease in the North Atlantic districts did not give as good control as those in Florida.[194] Nagel reported effective control of late potato blight from three foliage applications of "Dithane."[137] The compound has given good control of certain root rots, *Rhizoctonia solani*, and *Fusarium* spp., on beans and peas in small amounts in the seedling row.

**Isothiocyanates.** Allyl ester of isothiocyanic acid at a concentration of

1 per cent gave a 41 to 48 per cent control of codling moth larvae. The ethyl ester of the acid showed a 53 per cent control and the phenyl ester but 25 per cent control.[203]

Isothiocyanates derived from alkyl radicals, including 2-methylpentamyl-1 and related compounds, are used against flies and aphids.[205]

**Mercaptans.** A number of these compounds were tested on the larvae of the flesh fly, *Lucilia sericata*, but were found of less than average toxicity.[193]

Phenyl mercaptan, *p*-tolyl mercaptan, and *m*-tolyl mercaptan were effective in decreasing order among the more active insecticides tested against mosquito larvicides.[27] In the case of 2-naphthyl mercaptan, a concentration of 1 to 10,000 of water killed 100 per cent of the mosquito larvae.[208](See also Chapter 7, p. 179.)

**Phenothiazine** ($C_6H_4SC_6H_4NH$), also known as thiodiphenylamine, is a yellow, crystalline compound melting at 180°C. It is neutral in reaction, insoluble in water, but slightly soluble in acetone. It is unstable, showing color changes ranging from yellow to green and black. Modification of the structure usually results in lowering the toxicity.[12, 209]

This compound has been reported as highly toxic to a number of insects, including mosquito larvae, aphids, codling moth, and Mexican bean beetle.[13, 27, 208] Difficulty of suspension reduces its value in the control of aphids. Laboratory tests against codling moth, applied both as a paste and a powder, showed a greater efficiency than lead arsenate[12], but field tests in the northwestern apple districts failed to show as good control even at 2 pounds per 100 gallons of spray.[14] This is apparently due to lack of adhesion. Bentonite has been used to improve the physical qualities of this material in applications for codling moth control, but in laboratory studies it has been found that the addition of either or both bentonite and hydrated lime reduces its efficiency.[211] A comparative test of a large number of organic compounds against mosquito larvae, *Culex* spp., showed phenothiazine to be the most toxic, a concentration of 1 ppm giving 100 per cent kill.[27] An average value as a larvicide for the fleshfly, *Lucilia sericata*, has been shown by Hoskins.[193] The toxicity to the screwworm larva, *Cochilomyia americana*, of phenothiazine and 16 related compounds was determined by Bushland to be superior to that of phenothiazine sulfoxide and thianthrene.[15] Knipling later reported apparently acquired resistance to phenothiazine by this insect.[210] Bean foliage injury has been noted from phenothiazine, but none on potato, apple and peach foliage. Lowered efficiency in codling moth control was noted with the addition of lime-sulfur solution or of Bordeaux mixture, but not with precipitated sulfur.[12] Fungicidal value of phenothiazine has been noted by Goldsworthy and Green against apple scab, *Venturia inaequalis*.[212]

The value of phenothiazine as a parasiticide for cattle, sheep and swine has been fully demonstrated. Dosages of 20 grams per 70 pound of sheep removed the nodular worm, *Oesophagostomum columbianum*, the stomach worm, *Haemonchus contortus*, and the lesser stomach worms, *Ostertagia* spp. In 25-gram dosages it was also effective in removing a number of other internal parasites.[16] Treatment of calves with the material at dosages ranging from 0.44 to 1.1 grams per kilogram of body weight gave almost perfect removal of the intestinal worms, *Haemonchus contortus* and *Trichostrongylus axei*. Slightly less efficiency was shown in the removal of a number of other parasites.[18] Swine treatment for intestinal worms shows that phenothiazine has a number of advantages over previously used antihelmintics, being effective over more than one species of parasite.[213]

Phenothiazine sulfoxide, phenothiazone and thionol are oxidation products of phenothiazine of recognized fungicidal value in control of the fungus, *Sclerotinia fructicola*.[20] The toxicology of the two latter compounds and of phenothiazine to the cockroach, *Periplaneta americana*, has been studied by Zukel, and a better understanding of the insecticidal action of the three compounds[214] has thus been gained.

**Phenothioxin** ($C_{12}H_8OS$) is an effective mosquito larvacide tested principally against *Culex quinquefasciatus*.[27] It is also one of the most toxic chemicals tested against the larval stage of the screwworm, *Cochliomyia americana*.[15] Average effectiveness was shown with this material when used against the body louse.[37] Quick and lasting control of the body louse, shaft louse and fluff louse of chickens resulted from the use of a 5 per cent dust of phenothioxin.[150]

**Thioacetamide** ($CH_3CSNH_2$). A dip of a 5 per cent concentration reduced decay in oranges caused by stem end rot and the blue and green molds from about 40 per cent to 2 per cent or less.[215] This compound has given average control of the flesh fly larva, *Lucilia sericata*,[193] but in horticultural work it has shown but little value.

**Thiophene compounds.** 2-Chloromercurithiophene at 1.5 per cent concentration is used as a seed disinfectant. The compounds ethyl, dimethyl and methyl chlorimercurithiophene are also listed as seed disinfectants.[216]

**Thiourea** ($NH_2CSNH_2$) is a water-insoluble compound which is toxic to the fleshfly larva, *Lucilia sericata*, at very low concentrations, 1/128 to 1/512 per cent. It is also very effective against the housefly larva. A number of related compounds, including ethyl, methyl, propyl, butyl and amyl thiourea, were effective against the flesh fly larvae but at slightly higher concentrations than that of thiourea alone.[179] It is equally effective to thioacetamide against decay of oranges.[215] Tetramethylthiuram salts at 5 and 10 per cent concentration gave average control of poultry lice.[160]

**Thiocyanates.** This group includes some of the earliest recognized effective insecticides used against aphids, mealy bugs and spider mites.[22, 217–220] Wilcoxon and Hartzell published a series of papers[17, 19, 21] showing results from the use of various thiocyanates against aphids, and mealy bugs, *Pseudococcus* sp., smaller European elm bark beetle, *Scolytus multistriatus*, potato flea beetle, *Epitrix cucmeris*, and the spider mite, *Tetranychus telarius*. An aliphatic thiocyanate (β-Butoxy-β-thiocyanodiethyl ether) has proved effective against the latter mite at a concentration of 1 to 800 parts of water. Lime-sulfur solution or precipitated sulfur may be added for fungicidal action.[22] It is also an effective ovicide against grain-infesting beetles and moths. Insects of stored products and certain household insects, particularly the bedbug, *Cimex lectularius*, are quite susceptible to the action of normal butylcarbitolthiocyanate.[23]

**Ammonium thiocyanate** is used generally as a herbicide but with greater success on annuals than on perennials. Dosages vary from 3 to 12 pounds per square rod. The results are generally not as permanent as those from sodium arsenite and borax.[222]

## Miscellaneous Organic Compounds

**Formaldehyde** ($HCHO$), also known as formalin and as methanal, is a colorless gas at room temperatures, boiling at −21°C. Polymerization of the gas occurs with the presence of impurities and is hastened by rising temperatures. Commercial formaldehyde consists of a 35 to 40 per cent concentration of the gas in water, usually with small amounts of impurities. The polymerized form is a white, amorphous substance known as paraform or paraformaldehyde. This form is believed to be useless for disinfecting purposes.

The use of formaldehyde as an agricultural disinfectant was developed in treating potato powdery scab, *Spongospora subterranea*, a bacterial disease.[2] Treatment of seed potatoes is both by soaking in formaldehyde solution and by treating with formaldehyde gas. For each 100 bushels of potatoes treated, a concentration of 1½ pints of 40 per cent formaldehyde solution in 100 gallons of water is used.[3] Formaldehyde gas for treating potatoes is generated by combining 3 pints of 40 per cent formaldehyde solution and 23 ounces of potassium permanganate for each 1000 cubic feet of space.[1] The gas treatment is also used for killing seed-borne fungus spores and bacteria as well as a 2 per cent formaldehyde solution for dipping seeds.[4] Formaldehyde is also applied as a dust treatment, using an inert base as the carrier for a 15 per cent concentration of the chemical.[5]

Formaldehyde solution is also used as a fly poison, it being less dangerous to man than arsenical compounds. A common formula is 2½ per cent of commercial formaldehyde in milk and sugar solution; ethyl alcohol, beer or vinegar added to the solution increases the attractiveness. The addition of alkali to commercial formaldehyde solutions causes rapid polymerization and a decrease of repellancy. Both paraformaldehyde solution and neutralized commercial solution are less repellent than unneutralized formaldehyde solutions.

**Metaldehyde** $(C_2H_4O)_4$ is an ingredient of snail and slug baits used both alone and in combination with calcium arsenate. A common formula is 1.5 to 2.5 per cent of powdered metaldehyde and 5 per cent of calcium arsenate in bran, fruit pulp, and molasses. Tests with a number of other aldehydes have shown no attractiveness to snails. Metaldehyde is also used alone at 2.75 per cent concentration.[224] Experiments in the citrus districts of Southern California indicate less efficiency with the metaldehyde bait than with calcium arsenate.[225]

**Hexaethyl Tetraphosphate** $(C_{12}H_{30}O_{13}P_4)$, also known as "Bladan," boils at 150°C and above and solidifies at approximately −40°C. It is a light straw colored liquid at room temperatures. The ester is miscible in all proportions with water, alcohol, acetone and a number of organic solvents. It is stable at room temperature in the absence of moisture, but hydrolyzes in aqueous solutions, leaving no spray residue. The commercial form is apparently a mixture of related esters varying according to manufacturing methods. The material is available in forms both for spraying and dusting and is very promising in its action, particularly against aphids, leaf hoppers, thrips and spider mites. Present indications are that it will supplement our inadequate supply of nicotine.[226] It is incompatible with alkalies and should not be applied over Bordeaux mixture.[126] For aphids difficult to wet, such as the wooly aphid of the apple, *Erisoma lanigerum*, one-half gallon of foliage spray oil may be added to 100 gallons of spray, but this combination is sometimes dangerous to pears.

A form later developed is known as tetraethyl pyrophosphate, $(C_2H_5O)_4P_2O_3$. This is a colorless liquid with a specific gravity of 1.19, boiling at 150°C at 10 mm Hg and soluble in water, acetone, alcohol and many organic solvents, but not miscible in petroleum fractions. It decomposes more slowly than hexaethyl phosphate and remains active for a longer period of time. It has some fumigating action.[229]

Another phosphate compound, *o,o*-diethyl-*o*-*p*-nitrophenyl thiophosphate, known as "Thiophos 3422" or more commonly as "parathion," has been generally tested in 1947 with favorable reports. It has a high boiling point and a specific gravity of 1.26, is quite stable in normal waters and resists oxidation. It is used with DDT in the control of codling moth, as it also acts as check on plant mites and aphids.

**Insect Repellents.** Rapid progress was made during the war in developing effective repellents for blood-sucking insects and mites attacking man and other animals. These compounds have been especially useful in protecting against mosquitoes, horn flies, *Siphona irritans*; stable flies, *Stomoxys calcitrans*; buffalo gnats, *Simuliidae*; fleas and the larval stage of certain mites, *Eutrombicula*, and related genera, known in the United States as "chiggers." Dimethyl phthalate is effective in preventing the attachment of these mites, but is readily lost through leaching and laundering. Dibutyl phthalate is as effective as a repellent, but is not so readily removed by exposure to water and for this reason was adopted by the Australian military forces. These repellents are applied in a broad band to the openings of the outer clothing and as 5 per cent emulsions to the entire uniform. Benzyl benzoate has also been found to be an effective repellent for chiggers, resistant to laundering, readily available and more economical during the war period than the phthalates. Other related, effective products, but not sufficiently tested for recommendation, include benzil (dibenzoyl), and a number of esters of benzoic acid.[50]

Mosquito repellents, first used by the armed forces but now generally available, include dimethyl phthalate, "Rutgers 612" (2-ethyl-1,3-hexanediol) and "Indalone" (N-butyl mesityl oxide oxalate). These substances are also useful as protectants against chiggers and fleas, being applied directly to the person or the clothing.[140] The list now includes dimethyl carbate [*cis*-bicyclo(2,3,1)-5-heptene-2,3-dicarboxylic acid, dimethyl ester]. The materials vary in their effectiveness to different species of insects and hence are recommended to be used in combinations of 2 or 3. They are solvents of paints and certain plastics and should be used with caution, but are considered safe to use on the human body.[227]

Dimethyl phthalate gives a protective period of 4 or more hours against the malaria-carrying mosquito, *Anopheles quadrimaculata*. "Rutgers 612" is preferred for the yellow fever-carrying mosquito, *Aedes aegypti*, with a protective period of about 60 hours. "Indalone" is used against the stable fly, *Stomoxys calcitrans*. All materials are effective against the southern buffalo gnat, *Eusimulium pecuarum*.[73]

Benzyl benzoate and 2-phenylcyclohexanol have been found more effective as clothing treatments against fleas than have dimethyl phthalate, "Indalone" and "Rutgers 612." Two other products, *p*-iso-prophylphenylethyl alcohol and 1,2,3,4-tetrahydro-2-naphthol are also effective repellents, but their possible toxic or irritating properties have not been determined.[228]

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# Chapter 10

# Heat, Cold and Radiation as Insecticides

## HEAT

Increasing recognition is being given to the value of physical processes, as distinguished from chemical treatments, in reducing losses from both insects and fungi. The use of heat treatments for buildings, particularly those infested with stored product insects, has been so standardized as to be largely a process of engineering details, covering heat radiation and loss of energy through the walls. The use of cold-storage warehouses offers a moderate priced and efficient means both of destroying and preventing infestations. Grain and vegetable seeds are disinfected by standard methods of heat treatment. Certain types of infestations by insects, mites and nematodes, of both food and plants, are also readily controlled.

Electric energy as soil sterilizers, colored lights as attractants and ultraviolet rays, within a narrow spectrum, are well recognized as both insecticides and fungicides. More extended uses of physical forces as control agents will no doubt occur with increases in cold-storage plants, drying kilns, and improvements in electrical apparatus. Physical treatment in preference to chemicals is an important contribution toward public health both in preventing infestation and by the absence of dangerous residues.

Dry storage of grain is the cheapest and most efficient preventive of insect infestation and may even be a lethal agent. The successful application of this principle, however, is dependent upon moisture regulation. Standing grain, such as barley and wheat, when grown under the high temperatures and low humidities of the semi-arid districts of western United States, will have a moisture content in the field of 8 to 12 per cent. If after threshing it is stored locally, but little mositure is absorbed until after the cold weather of winter, which prevents insect breeding. Moisture content builds up during the winter and spring; if grain is held until early summer both moisture and temperature favor insect breeding, and heavy losses may occur. The lack of heavy insect infestation during the summer after threshing is due to the inability of grain insects, such as the weevil, *Sitophilus oryza* and *S. granarius*, to breed in grain of such low moisture content. There being insufficient water in the grain for the needs of the adult insects which may contaminate the grain, they can survive only by drawing on the water content of their bodies. This action, if prolonged, results in the death of the insects.*

Artificial drying (dehydration) of grain before storage is being practiced to an increasing extent as a protection against losses from bacteria, molds and insects. This process is almost imperative if the grain is to be stored in sealed tanks.

Dehydration is usually accomplished by blowing a blast of hot air through the grain while spread in shallow layers. Such treatment may be purely protective, by lowering the moisture content to a point where the grain is not susceptible to insect attack, or it may be continued at 140°F (60°C) for 10 minutes or longer, owing to the depth of grain being treated, until all insects are killed. Longer exposures at 140°F, or the use of slightly higher temperatures will give lethal effects. Compensation should in all cases be made for the chilling effect of the grain and time allowed for taking on the air temperature.[9] Shucked corn spread to a depth of 3 feet can be effectively heat-treated with an exposure of 18 hours, or a 13-hour exposure to a depth of 2½ feet, when air temperatures in the room are maintained close to 181°F (83°C). Unshucked corn cannot be successfully treated.[12]

Table 61. Insect Breeding at Controlled Moisture Contents in Dried Fruits.

| | Moisture Contents in Fruits | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10% | 12% | 14% | 16% | 18% | 20% | 22% | 24% | 26% |
| Average number of living insects found per jar | 0 | 6.4 | 7.4 | 7.8 | 16.0 | 4.7 | 4.6 | 2.3 | 0 |

Small quantities of beans or other seeds, for oven treatment, should be spread thinly in shallow pans and heated to from 120 to 145°F (49 to 63°C) for several hours. Higher temperatures may injure germination. Temperatures below 120°F are ineffective.[11]

Dehydration of fruits (apples, pears, peaches, prunes and apricots) and to a less extent vegetables by sun-drying is a common commercial practice. A preliminary sulfur bleach is usually given to drying fruits, except prunes, to prevent darkening and to give some protection against spoilage. After sulfuring the fruits are dried to a moisture content of 16 to 25 per cent, according to variety. When stored at the latter moisture content, air-drying under semi-arid conditions may continue over a period of months and the moisture content will fall to 12 or 15 per cent. If the moisture is maintained at this level, very little damage from insects, and no molding,

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* The growth and consequent damage from bacteria, fungi and insects in dry-stored grain is largely a question of the moisture content, providing temperatures are above 55°F (13°C). Bacteria may develop and "souring" or "rotting" occur at moisture contents of 18 to 30 per cent. Fungi, including molds, will grow at 15 to 24 per cent and above. Insects will breed at 12 to 18 per cent but at higher moisture concentrations, they are likely to become bedraggled and die.

w ll occur. Much bulk-stored dried fruit is stored at a moisture content of approximately 18 per cent. This, however, has been found to be the optimum moisture content for insect development. The two extremes of moisture at which insects cannot breed is shown in Table 61, giving results obtained when apricots and prunes were stored under moisture control, as indicated, and infested with the Indian Meal moth, *Plodia interpunctella*, and the saw-toothed grain beetle, *Oryzaephilus surinamensis*. Jars containing fruit and insects remained sealed for six months.

In no case, in the data given in this table did fruit containing either 10 or 26 per cent moisture permit the development of the insects present. The insects were unable to secure the needed moisture from fruit containing only 10 per cent, but a moisture content of 26 per cent caused such a sticky condition that both beetles and moths were unable to move about. Insect activity increased at a range from 12 to 18 per cent moisture, while from 18 to 24 per cent it gradually decreased, indicating an optimum moisture content for insect development of the species concerned at about 18 per cent. The dried fruit mite, *Carpoglyphus passularum*, bred rapidly on apricots containing 24 per cent moisture. Molds occurred on apricots at 24 per cent moisture and on prunes at 26 per cent moisture.[13]

The conclusions reached were that the prevention of insect infestation of dried fruit by reducing the moisture to 10 per cent is not practical, because of excessive dehydration cost, darkening of fruit color, large loss in weight, reabsorption of moisture from the air, and loss of palatability of the product.[13] Dehydration checked at 26 per cent as a preventive of insect attack is not practical unless the fruit is sealed in tight containers, because of the tendency to mold. Dehydrated fruit has been shown to be a semi-perishable product, subject to only a small insect hazard, if dried to about 14 to 16 per cent moisture. In this condition it may be stored for a year or more without serious losses if carefully watched.[13]

**Flour Mill Treatment with Heat.** The milling industry early adopted the use of heat as a means of insect control, since the method requires no special apparatus or dangerous chemicals and is without injury to the milling qualities of the wheat.[14] "A temperature of from 120 to 125°F (49–52°C) in all parts of the mill for a period of from 10 to 12 hours is sufficient to destroy all insect life. To obtain these killing temperatures in the parts exposed to the radiation, the air should be kept in circulation by means of fans or by running the machinery. The fans should be so located as to keep the hot air moving away from the radiators. Otherwise the temperature in some parts of the mill will be higher than necessary. Steam heat at a pressure of from 25 to 40 pounds per square inch in well distributed steam pipes is a satisfactory method of obtaining mill temperatures fatal to insects."[15]

The radiation surface required to heat a given surface depends on the construction and condition of the building, windows, machinery, and location of the steam pipes. "Usually one square foot of radiation surface will heat from 50 to 100 cubic feet of space."[9] Steam pipes should be located near the floor and be equipped with traps for drawing off accumulated water and with steam jets for maintaining a humidity of at least 50 per cent during the heating.[9] Extra stocks of flour should be moved out of the mill, as heat penetrates flour very slowly and three or four days' continuous heat exposure may be necessary to kill insects buried in sacked flour.[16] A modification of the methods of flour mill treatment recommended earlier suggests the use of higher temperatures, ranging from 150°F (65°C) floor temperatures to 180°F (82°C) ceiling temperatures. Higher temperatures permit shorter exposures and also aid in penetration of accumulated flour throughout the building.[16]

Sterilization of cereal products is accomplished by passing them through heating chambers held at a range from 125°F to 180°F (52 to 82°C). The length of exposure within the sterilizer depends upon the rapidity of heat transfer from the air to the center of the package or layer of cereal. Flour will require a rather long exposure, but a temperature of 174°F (79°C) must be avoided. Fifteen to 30 minutes' exposure should be given after all the cereal has reached a temperature of 125°F or above. Since the cereal will cool somewhat slowly there will be ample time to transfer it into packages and seal before danger of reinfestation occurs.[18]

Table 62. The Relative Resistance of Different Stages of *Tribolium confusum* Exposed at Several Temperatures.

| Temperature | | Median Lethal exposure | | | |
|---|---|---|---|---|---|
| C° | F° | Eggs | Larvae | Pupae | Adults |
| 44 | 111.2 | 14 hours | 10 hours | 20 hours | 7 hours |
| 46 | 114.8 | 1.2 " | 1.0 " | 1.5 " | 1.2 " |
| 48 | 118.4 | — | 8.0 min. | 12.0 min. | 26.0 min. |
| 50 | 122.0 | — | 4.7 " | 4.5 " | 4.9 " |

**Effect of Heat on the Flour Beetle.** The relative resistance to heat of various stages of the confused flour beetle, *Tribolium confusum*, is shown in Table 62. It will be noted that the data is based on the "median lethal exposure" (approximately 50 per cent mortality).

"At temperatures too low to kill within a reasonable time for practical purposes, it has been shown that the rate of development may be slower than at temperatures in the optimum range, the percentage of eggs hatching is reduced, larvae may not be able to complete their development, and lethal deformities of adults from exposed pupae may occur."[19] Disturbances of physiological processes are also noted in the reaction of different stages of the flour beetle to temperature ranges from 32 to 38.5°C (90 to 101°F).

Egg deposition was reduced from 45 to 50 per cent with exposures to a temperature range above 32°C. Larval development is also retarded by the higher temperature. The fertility of eggs laid by females developing from larvae and pupae, exposed to a temperature of 41°C (106°F), dropped from 80 per cent at 12-hour exposures of the larvae and 24-hour for the pupae to zero at 60- and 72-hour exposures, respectively.[19]

Farrar and Reed[5] have shown that a lower temperature results from heating wet grain than occurs in grain of a lower moisture content. "The process lowers the air temperature, as recorded on the dry bulb thermometer, but does not change the wet bulb reading nor heat the material. As drying progresses, as when material with a low moisture content is used, the rate of drying decreases and the wet bulb reading of the material increases until it is near the dry bulb reading." "Plants operating at dry bulb temperatures of 105 to 110°F and wet bulb temperatures of 70 to 80°F are not likely to secure insect control during the regular drying operations."[5]

**Effect of Heat on Fabric Insects.** "Infested clothing and other articles may be freed from fabric insect by a thorough brushing and exposure to the direct rays of the sun when the outdoor temperature is high. The disturbances of the insects by brushing and subsequent high temperatures will keep down their numbers."[20]

"A temperature of 135°F (57°C) for 6 hours will kill all fabric insects, and this treatment may sometimes be used in the home. The articles to be treated should be placed in a tight room (preferably a room easily heated) during a period when the outside temperature is high. The heating plant of the house should then be used to raise the temperature to 125 to 135°F, but never over 150°F (65.5°C). Ten to 15 hours are often necessary to raise the interior of the upholstery on heavily padded furniture to 135°F. After the articles being treated have reached this temperature, they should be subjected to it at least for 5 or 6 hours."[20]

"Infested articles which will withstand hot water may be rendered free of insects by submerging the articles in hot water (heated to 150°F or over) for at least 10 minutes. The temperature must be maintained at or above 150°F during the entire period of submergence."

**Use of Heat on Lumber and Logs.** Many varieties of trees are subject to attack by certain beetles and a limited number of moths in the larval stage. Such attack may occur on standing, but usually on weakened and fallen trees. The attacking beetles include two general classes; (1) the barkbeetles or "ambrosia" beetles and (2) the wood borers. The first group work within and underneath the bark, while the second group bore into the sapwood and heartwood.

Barkbeetles are controlled by the "solar-heat" method. This consists primarily in utilizing direct sunlight to kill broods of beetles in the inner bark of thin-bark trees, thus eliminating the necessity for peeling them.

This method is effective on the mountain pine beetle, *Dendroctonus monticolae*, in lodgepole pine logs. "Bark temperatures under 110°F (43°C) are not effective. Bark temperatures of 120°F (49°C) or higher will kill the insects with a minimum exposure of 20 minutes."[21] Any temperature between 110 and 120°F will kill the broods if it is maintained for two or three hours. "Killing temperatures are registered in the bark of logs exposed to direct sunlight and lying north and south, during the hours from 10 A.M. to 4 P.M., when the air temperature is 80°F or higher."[21] "The mean difference between air temperatures and the concurrent bark temperatures is 40°F.'[21]

The western pine beetle, *Dendroctonus brevicomis*, feeding on yellow pine, may be controlled by the use of solar heat, when the bark is detached from the log and placed on the ground exposed to the sun's rays. Under such exposure, the temperature of the bark has been found to exceed 120°F (49°C) with an air temperature of 80°F (27°C). Infested bark attached to the standing tree does not become more than 10°F warmer than the air, which is ineffective as a control agent. No mortality to any stage of the insect occurs, during brief exposures, if the acquired temperature of the bark does not exceed 100°F.[22]

The borers in heart and sapwood of hickory, ash, and oak may be controlled by subjecting them to kiln temperatures of 125 to 130°F (52 to 54°C) for a minimum period of 1 hour and 12 minutes to 2 hours. In treating lumber of varying thicknesses, longer exposures than those suggested should be used; the borers are then subjected to live steam for 1½ to 2 hours in a saturated atmosphere.

**Hot-water Treatments.** "The hot-water method of seed treatment is based on the principle that the thermal death point of certain disease germs is lower than that of the seed. The heat treatment has the advantage of being as effective inside the seed as on the surface, which is not true of chemical treatments. Consequently, infections such as black-leg and black-rot of crucifers, which are often introduced with the seed, and which penetrate the seed coat, can be destroyed by hot-water treatment, while surface disinfectants are only partly effective. The margin of safety with hot-water treatments is not large, and any considerable increase in either temperature or exposure will cause serious seed injury."[24]

Seeds of a number of vegetables may be treated at a temperature of 112°F (44.4°C) without immediate injury to germination if the time of exposure is held between 15 to 30 minutes. Hot water-treated seed should be sown soon after treatment, as germination decreases more rapidly than with untreated seed. Hot-water treatment should be made in commercial plants with adequate facilities for both accurate regulation of temperatures and for rapid artificial drying.[25]

Diseases of seed grains are treated in two ways: first by chemicals, as for stinking smut of wheat, the covered smut of barley, and other diseases whose spores are carried on the outside of seed grains; secondly, the loose smuts of wheat and barley which live inside the kernels are controlled by the so-called "modified" hot-water treatment. "The seed is placed in small loose sacks filled only half full, and soaked for from 5 to 7 hours in water at room temperatures."[26] Following the preliminary treatment, barley is dipped in water at a temperature of 124 to 129°F (51 to 54°C) for 13 minutes and wheat is treated for 10 minutes at a temperature of 124 to 131°F (51 to 55°C).[26]

Hot-water treatment of greenhouses as a control for the root-knot nematodes, *Heterodera marioni*, and the fungus, *Rhizoctonia spp.*, has proved successful for small-scale operations. The soil on the benches is treated by pouring on boiling water at the rate of 7 gallons per cubic foot. Treated soil retains a temperature above 60°C (140°F) for over 30 minutes and above 55°C (131°F) for 48 to 65 minutes. These exposures have been found ample for practical control of both the nematode and the fungus.[27] Soil treatments in the field have not shown the same success in nematode control, by the use of hot water, as have greenhouse beds and pots. Steam sterilization, instead of hot water, has been found practical for seed beds under certain methods of application. The inverted steam pan has been found fairly satisfactory for shallow treatments, but for more lasting results dependence is placed on the distribution of steam through tile buried in the ground at depths of 10 to 18 inches. Steam is turned into the lines and treatment continued for from 2 to 10 hours, depending on steam pressure and the amount of soil moisture. A temperature of 150°F (65°C) should be reached at a depth of 12 to 24 inches.[28]

Hot-water dips for controlling the nematode, *Aphelenchoides fragariae*, on begonias has been reported as successful and without injury to the plant except for infested leaves. The entire plant, together with the pot, is submerged in a tub of hot water. The time of submersion recommended is 1 minute at 120 to 121°F, 2 minutes at 117 to 119°F, or 3 minutes at 115 to 118°F. The highest water temperature should prevail at the beginning of the submersion period and the maximum temperature restored for each new lot of plants being treated. "The same temperature-interval water baths are recommended for healthy leaves for propagating stock, where the disease exists."[29] Similar treatments are recommended for Chrysanthemum and strawberry plants.[29]

The Japanese beetle, *Popillia japonica*, when present in the soil and around the roots of plants, may be killed at all stages at a temperature of 112°F (45°C) for 70 minutes. The dipping tank should be equipped with a suitable heating device and a water-circulating system to maintain the desired temperature at all times. All varieties of hydrangeas and Rhododendrons tested were either injured or killed by the treatment, but with these exceptions the greater part of the plants treated were reported as uninjured.[30]

A modification of the water-dip method known as the "vapor-heat" treatment has been developed, particularly for use on bulbs. It consists of circulating through the heating chamber "a mixture of air, saturated water vapor, and water in the form of a fine mist, all at the desired temperature. The mixture is withdrawn from the lower part of the room, circulated through the conditioning machine and reintroduced into the chamber through the ceiling."[31] A standard treatment has been developed of 110 to 111°F (43.3°C) for use on narcissus bulbs, the time of exposure being 1.5 hours for the narcissus fly, *Merodon equestris*, and the lesser bulb flies, *Eumerus tuberculatus*, *E. strigatus* and *E. narcissi*; one-half hour for the bulb mite, *Rhizoglyphus hyacinthi*; and 8 hours for the bulb nematode, *Ditylenchus dipsaci*. The principal advantage of this method of treatment is economy of handling large amounts of bulbs and avoiding the necessity of careful drying of the bulbs after the hot-water dip.[31]

Table 63. Average Time Required to Kill Adult Insects at Low Temperatures,

| Time | 10°F (%) | 25°F (%) | 32°F (%) | 36°F (%) | 45–50°F (%) |
|---|---|---|---|---|---|
| 1 month | 100 | 98.7 | 80.6 | 86.5 | 0 |
| 2 months | — | 99.0 | 88 | 100 | 0 |
| 3 months | 100 | 100 | 100 | 100 | 83 |
| 4 months | 100 | 100 | 100 | 100 | 85.8 |

## Cold

The use of cold storage temperatures of 45 to 58°F (7 to 10°C), as a protection against the clothes moth and insects feeding on stored products has been a common practice for many years. At these temperatures, insects are commonly in a dormant or semi-dormant condition, neither taking food nor increasing in number; hence such storage may be considered as a preventive of insect damage.[32] Prolonged exposure to temperatures of 36°F (2°C) and lower are necessary to kill all stages of the insects feeding on stored products. One of the flour beetles, *Tribolium confusum*, and the rice weevil, *Silophilus oryzae*, are the two known exceptions, a large percentage of all stages of this insect being killed at 45°F (7°C).[33] A summary of the mortality rate of adult insects, exposed to continuous cold, is given in Table 63.[34] Insects used in these experiments are the Indian Meal Moth, *Plodia interpunctella*, saw-toothed grain beetle, *Oryzaephilus surinamensis*, Cadelle beetle, *Tenebroides mauritanicus*, dried fruit beetle, *Carpophilus hemipterus*, and the dried fruit mite, *Carpoglyphus passularum*.[34] Sudden fluctuations in temperature from 35 to 70°F (1.6 to 21°C) and the reverse will considerably shorten the time of exposure necessary to cause death over that given in the table.

Field studies of the effect of low temperatures on insects show[35] that native species are not affected to a great extent by such exposures, but heavy mortalities may occur from sudden thaws followed by decided drops in temperature. "Larvae and adults of the wire worm, *Melanotus communis*, have a sufficiently low freezing point to withstand Minnesota winter temperatures −18 to 2°C (0 to 35°F), if they hibernate below 4 inches in the ground."[35] The June bug, *Phyllophaga implicata*, has a "much higher freezing point than wire worms" . . . and must of necessity hibernate at much lower depths than wire worms if they are to survive winter soil conditions."[35]

Field records in Montana of the effects of low temperatures on the western pine needle, *Dendroctonus brevicornis*, show a heavy mortality of the larvae when bark temperatures are below 0°F (−18°C) and that practically no larvae survive at −10°F (−23°C).[22]

Relationship has frequently been noted between unusually low mean winter temperatures and the control of certain insects. This is illustrated by Rockwood,[4] who finds that outbreaks of the pea aphid, *Macrosiphum pisi*, have not occurred in western Washington when the minimum temperature for the winter fell below 15°F, nor has there been an outbreak "when the lowest monthly mean temperature was 37°F or below."[4]

Technical studies of the actual freezing points of insects are now being made with the aid of the thermocouple. Robinson[1] and Salt[2] have shown a relationship between the undercooling* and freezing points of insects. Ditman concludes that "true freezing points of insects are never more than a degree or so below 0°C." "Freezing point values are of little economic importance. They are of no use in determining lethal low temperatures, the undercooling temperatures being the most important criterion for most insects."[3] The variability of field conditions, however, must be considered in the application of laboratory data to the interpretation of economic problems.

## RADIATION

The use of electricity has been studied in determining the "thermal lethal point" for a number of parasitic fungi attacking living plants. Two methods of application of soil sterilization practices are used: first, use of the

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* The phenomenon of "undercooling", as applied to water in a finely divided condition, is similar to that occurring in a living insect. Water particles, which lack ice crystals or other nuclei, may be undercooled below the freezing point without the formation of ice. Undercooling of insects is probably influenced by the form in which water is present and the colloidal materials in the cells and the intracellular liquid.[3]

soil-resistance principle, in which the current passes directly through the soil; and secondly, employment of the heating-element principle, in which the current passes through resistance heating units properly spaced to impart their heat to the soil by thermal conductivity. Both types were capable of destroying a number of common plant pathogens, including bacteria, *sclerotia fungi*, nematodes and weed seeds.[36] A soil temperature of 70°C (158°F), in the presence of adequate soil moisture, was found to be high enough to kill several soil fungi. All kinds of soil from pure sand to muck were effectively treated in both types of sterilizers. However in the direct-heating or resistance type it was often found necessary to add some dilute electrolyte solution (0.05 per cent of potassium nitrate) to sand to insure heating in a reasonable length of time.[36]

"The current consumed varied with different kinds of soils . . . in general, a 50°C rise in temperature (from initial 20°C to final 70°C) required from 1.0 to 1.3 kilowatt hours. Where only nematodes and damping-off organisms are being combatted, lower final temperatures are permissible, at a saving of current, if more time is employed."[35]

Light traps, with electrocuting attachments, have been found of value in controlling the grape-leaf hopper, *Erythroneura comes*, artichoke plume moth, *Platyptilia carduidactyla*, and other economic insects.[37,38] A combination light and suction-fan trap is being used as a control for a non-blood-sucking gnat, *Chaoborus astictopus*, present in such swarms as to be a serious nuisance in certain California resorts.[39] Brilliancy of light has been found to act as a deterrent in preventing the codling moth from entering and depositing eggs in the artificially lighted area, but the resulting reduction in worminess of fruit was not as great as in the sprayed blocks.[40]

Light traps are being used both alone and in combination with baits for the control of several species of insects. Experiments in the control of codling moth, *Carpocapsa pomonella*, have shown the greatest efficiency with "the mercury vapor type of lamp producing 300 to 700 lumens in the visible region within wave lengths of 3000 to 7000 Angstrom units.* Electrified grids or suction fan retrieving devices were about as effective as attachments for capturing moths attracted to baits or lights."[41] "Although the fruit in baited and illuminated trees was often less wormy than in neighboring unsprayed trees, the benefit was not so great as . . . to warrant at present the recommendation of bait or light trapping as a substitute for spraying."[41]

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* The Angstrom unit (Å), used to express the wave length of light and ultraviolet radiations, is equal to 1/10,000,000th millimeter, or 1/250,000,000th inch.

Light Spectrum Divided According to Angstrom Units.

| Ultraviolet Spectrum | | Visible Rays | |
|---|---|---|---|
| X-rays | Bactericidal and Fungicidal | Stimulative | Violet to Red |
| 136–1000 | 2000–2800 | 3130–3787 | 4000–8000 |

Physiological reactions, ranging from increased growth of certain plants to lethal reactions of bacteria, mold spores and certain insect eggs, are reported from irradiation by ultraviolet rays in the light spectrum between 2000 and 3780 Angstrom units. Bactericidal value has been associated with the short wave lengths of light for many years, but with the use of the quartz mercury vapor lamps, measurements first began to be made of the effect of different parts of the spectrum on living organisms. The high cost of the quartz lamp and the great length of its spectrum (2000 to 6000 Å) limited its usefulness. Passing the rays through glass screens of varying permeability made it possible to use selected portions of the spectrum and in this way to distinguish between the fields of harmful, beneficial and neutral rays. The results from unscreened and screened light on various plants were as follows: "Raying with an unscreened, quartz, mercury vapor light, (2000 to 5780 Å units) caused injury in all plants used."[42] Raying with a screened light (2894 to 3780 Å) "was beneficial for some plants but it produced little visible effect in others."[42] "Raying with a screened light (3136 to 5780 Å) injured none and benefited many of the plants."[42] ("It will be noted that the latter treatment is outside that portion of the spectrum, 2000 to 3130 A units, indicated in the diagram as injurious. Ed.")[42]

Experiments with ultraviolet rays on the larvae of the honey bee have shown that exposures ranging from a few seconds to 10 minutes may be harmful at 2970 Å. The longer rays had little or no effect on the larvae of either worker or queen bees. "There was no shortening of the development period by any sort of irradiation used, and no significant difference in the weight of emerging queens."[43]

Ova of two species of ascarids (roundworms), *Toxascaris leonina*, and *T. canis*, were rayed for from 1 to 20 hours from a quartz monochromator and a quartz mercury arc with wave lengths ranging from 2652 to 3650 Å. Excepting slight variations in the degree of energy used and the susceptibility of the two species, the range of lethal rays was from 2652 to 3022 Å. The spectrum from 3130 to 3650 Å was generally without effect.[44]

In experiments with eggs, larvae, and adults of the bean weevil, the author found the eggs and first, instar larvae to be killed by exposure to wave-lengths of light shorter than 3126 Å from a quartz mercury arc. "Adults exposed to these same rays exhibited no marked effects, but eggs from these forms were largely sterile. Sublethal dosages produced forms which were defective in their metabolic processes, as was evidenced by the excessive amount of food consumed and failure to build a correspondingly greater bodily weight. Abnormalities of external structures were apparent in forms both from irradiated eggs and adults. Shortened elytra, or swollen abdomens—an abnormality accentuated in the third and fourth generations—were very common in progeny of all irradiated forms. Larvae developing as progeny of irradiated adults sometimes had a prolonged pupal period with the resulting forms becoming mixtures of larvae, pupae, and adults."[45]

Extensions of the use of ultraviolet radiation as a lethal agent have resulted from the development of a low-pressure mercury vapor lamp, the tubing of which is made from glass of a special formula, which releases more than 90 per cent of the developed energy at or near 2537 A. These lamps operate at temperatures only slightly above room temperature and for this reason can be placed in vegetable washing machines without danger of breakage from cold liquids. The rays developed by the mercury vapor lamp do not penetrate solids to any appreciable distance, and hence must be so placed as not to cast shadows on any portion of the surface being rayed. The usual practice is to suspend the lamp with an aluminum or magnesium oxide reflector to deflect the rays in the desired direction. For enclosures such as air ducts and water pipes, center the lamp in the tube so that the rays will reach the sidewalls without obstruction and with equal distances from the lamp tube to the surrounding walls. The rays are lethal to air-borne bacteria and the spores of certain fungi at distances from one inch to three or more feet, depending on the time of exposure and the species concerned. A decrease in the toxic action occurs when the relative humidity of the air reaches 80 per cent or above. Mold spores of *Aspergillus niger* required about 45 times as much radiation.[46]

Experiments with this type of lamp on fruit infected with *Monilia* spp. and *Botrytis* spp. gave no appreciable control except on spores placed directly in the rayed area. Spores or mycelium imbedded in the fruit tissue or in shadows were unaffected. There was no injury from the treatment to apricots, plums and strawberries.[6] These finding have been confirmed by English and Gerhardt, who studied the action of irradiation on sweet cherries.[7] Although treatment of infected fruit with ultraviolet light has not as yet proved to be of commercial value there are possibilities of reducing the number of air-borne spores in packing houses by properly placed lamps.

Fungi vary in spore production and vegetative growth with changes in the quality and the intensity of the light. "The quality as well as the quantity of the light affects the growth and development of fungi. Ultraviolet wave lengths cause greater material changes than do those of the visible spectrum."[47]

The bactericidal value of ultraviolet light (2500 A.) in clear water is shown in Table 64. The bacteria used for contaminating the water was *Serratia marcesens.*

In the above experiments, the lamp was fixed in the center of a 4-inch horizontal pipe with 20 gallons of water in the tank. The water was pumped repeatedly past the lamp at the rates indicated. "The ultraviolet rays exerted a marked lethal action, at least on *Serratia marcescens*, when the tube was immersed in the water. At the highest speed possible this lethal action was, furthermore, still found. . . . At this high rate of speed the percentage of bacteria killed at any one passage by the light was lower than that at the slower speeds, although the continued circulation naturally resulted in a comparably low count."[48] The light was found to penetrate clear water to a distance of 13 centimeters "without apparent dimunition of energy."[48] Turbid water quickly decreased the effectiveness of the light. "At very low temperatures, 1° to 2°C (33.8 to 35.6°F), the action of the light was greatly decreased. This decreased activity resulted from a decrease in the energy coming from the lamp."[48]

Table 64. Effect of Ultraviolet Light on Bacterial Content of Water

| Rate of Flow | | Light on (min.) | Bacteria per ml. | | Per cent of kill | Remarks |
|---|---|---|---|---|---|---|
| (gals. per min.) | (Feet per sec. at lamp) | | Before passing light | After passing light | | |
| 20 | 0.53 | 0 | 36,000 | — | — | Water before inoculation |
| 48 | 1.24 | 0 | 650,000 | — | — | Water inoculated |
| 13 | 0.32 | 2 | 33,000 | 1,500 | 95 | |
| 13 | 0.32 | 5 | 970 | 240 | 75 | |
| 13 | 0.32 | 10 | 260 | 160 | 38 | |
| 48 | 1.24 | 0 | 680,000 | — | — | Water inoculated |
| 24 | 0.62 | 2 | 28,000 | 9,600 | 66 | |
| 24 | 0.62 | 5 | 890 | 440 | 41 | |
| 24 | 0.62 | 10 | 390 | 290 | 26 | |
| 58 | 1.50 | 0 | 480,000 | — | — | Water inoculated |
| 58 | 1.50 | 2 | 5,200 | 2,900 | 44 | |
| 58 | 1.50 | 5 | 5,000 | 1,000 | 80 | |
| 58 | 1.50 | 10 | 710 | 540 | 24 | |

Experiments with high-frequency radio waves on insects have shown a lethal action with exposures to wave lengths of 24 meters and 12,000,000 cycles per second, with the ammeter reading about $1\frac{3}{4}$ amperes. The lethal action is due to the development of internal heat. Such internal heat, when subjected to high-frequency waves, was found to be more or less characteristic of certain chemical compounds found in living tissue, particularly cholesterol.[42] It has been found that "electric energy, propagated in an static electric field at the rate of from 1,000,000 to 3,000,000 cycles per second with a field strength of 4,000 volts per inch can be used to destroy certain insects, enclosed in the electrostatic field, without damage to their host plants."[50]

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# Appendixes

DICTIONARY OF INSECTICIDES

GLOSSARY

LEGAL REQUIREMENTS COVERING THE MANUFACTURE AND SALE OF INSECTICIDES

OFFICIAL ANTIDOTES

ASTM STANDARDS

CONVERSION TABLES

MISCELLANEOUS DATA

# Dictionary of Insecticides

**2-Acetamidofluorene** ($C_6H_4CH_2C_6H_3NHCOCH_3$): Stomach insecticide.

**acetic acid** [1-trichloromethyl-2, 2-methylene bis (4-dichlorophenyl) diester]: Mosquito larvicide.

**acetic ester**: See **ethyl acetate.**

**acetone semicarbazone** [$(CH_3)_2CNNHCONH_2$]: Stomach insecticide.

**acetophenone oxime** [$C_6H_5O(NOH)CH_3$]: Insecticide; fumigant.

**acetoxy-mercuri-benzo thiophene**: Seed disinfectant.

**1-acetyl-2-phenylhydrazine** ($CH_3CONHNHC_6H_5$): Insecticide.

**acetylene tetrachloride tetrachloroethane** [$CHCl_2CHCl_2$]: Larvicide for blowfly larvae.

**acid arsenic** ($H_3AsO_4 \cdot \frac{1}{2}H_2O$) (orthoarsenic acid): Combining form of arsenic in the production of arsenates.

**acid boric** ($H_3BO_3$): Wood preservative, herbicide.

**acid cresylic** ($CH_3C_6H_4OH$): Insectifuge; herbicide.

**acid hydrocyanic** (acid prussic; hydrogen cyanide) ($HCN$): General fumigant for ships, warehouses, quarantine measures, citrus trees.

**acid hydrofluosilicic** (acid silicofluoric) ($H_2SiF_6$): Wood preservative.

**acid oleic** (red oil) [$C_6H_{17}CHCH(CH_2)_7CO_2H$]: Combining form to produce insecticidal soap.

**acid pyroligneous** ($H_2C_2H_3O_2$): Herbicide.

**acid silicofluoric**: See **acid hydrofluosilicic.**

**acrolein** ($CH_2CHCHO$) (acrylic aldehyde): Fumigant; insecticide.

**acrylonitrile** ($CH_2{:}CHCN$): Fumigant; insecticide.

**acyl sulfide**: Insecticide.

**alkyl mercuriacetates**: Seed disinfectants.

**allyl bromide**: Fumigant; insecticide.

**allyl bromide** (3-bromopropene) [$CH_2{:}CHCH_2Br$]: Soil fungicide, nematicide.

**allyl chlorophenyl carbonate**: Herbicide, selective on grasses.

**allyl isothiocyanate**: Fumigant.

***p*-aminoacetaniliede**: Insecticide used for defoliators.

**aminoacetophenone** ($CH_3COC_6H_4NH_2$): Insecticide.

**1-aminoethyl-2-heptadecylglyoxalidine**: Plant fungicide.

***p*-aminoazobenzene** ($C_6H_5NNC_6H_4NH_2$): Stomach insecticide.

**1-amino-5-hydroxy-benzo-thiazole**: Seed disinfectant.

***p*-aminophenyl cadmium dilactate**: Turf fungicide; control of dollar spot, copper spot, brown and pink patch.

**ammonium bifluoride** ($NH_4HF_2$): Wood preservative.

**ammonium borate**: Herbicide.

**ammonium copper arsenite** ($CuHAsO_3$): Wood preservative.

**ammonium dinitro-*o*-cresol**: Herbicide.

**ammonium fluoride** ($NH_4F$); Water-soluble insecticide.

**ammonium polysulfide**: Fungicide.

**ammonium sulfamate** ($NH_4OSO_2NH_2$): Herbicide.

**ammonium sulfocyanate**: See **ammonium thiocyanate.**

**ammonium thiocyanate** ($NH_4SCN$) (ammonium sulfocyanate): **Herbicide.**
**ammonium trichloroacetate:** Herbicide effective on grasses.
**N,N-amyl-benzyl cyclohexylamine:** Insecticide.
**N,*n*-amyl-*n*-octylamine** ($C_5H_{11}NHC_8H_{17}$): Fly spray.
**anabasine** ($C_{10}H_{14}N_2$): An alkaloid insecticide.
**anabasine sulfate:** Similar value to nicotine sulfate.
**aniline hydrobromide** ($C_6H_5NH_2HBR$): Insecticide.
**aniline hydrochloride:** Insecticide.
**anthracene** (anthracene oil) [$C_6H_4(CH)_2C_6H_4$]: Insecticide.
**antimony-potassium tartrate** (tartar emetic) [$K(SbO)C_4H_4O_6$]: Insecticide; specific for certain thrips.
**antimonyl pyrogallol** [$HOC_6H_3O(SbOH)O$]: Stomach insecticide.
**Antu:** See **α-naphthylthiourea.**
**"Arasan"** (tetramethylthiuramdisulfide): Seed disinfectant.
**areca nut** (betel): Use, internal parasiticide.
**n-armyl carbamate** ($NH_2COOC_5H_{11}$): Fumigant.
**arsanilin acid** ($p$-$H_2NC_6H_4AsO_3H_2$): Grasshopper bait ingredient.
**arsenate of iron, ferric** ($FeAsO_42H_2O$): Insecticide; scorodite ore.
**arsenate of iron, ferrous** [$Fe3(AsO_4)_2 \cdot 6H_2O$]: Insecticide.
**arsenic** ($As_4$): Used in insecticides.
**arsenic oxide:** See **arsenic trioxide.**
**arsenic trioxide** (arsenious acid; white arsenic; arsenious oxide) ($As_2O_3$): Insecticide used in baits; combining form of arsenic.
**arsenic, white:** See **arsenic trioxide.**
**arsine** (arsenic hydride) ($AsH_3$): Fumigant.
**atropine** (daturin) ($C_{17}H_{23}NO_2$): Alkaloid; insecticide.
**azobenzene:** Insecticide.
**azoxybenzene** ($C_{12}H_{10}N_2O$): Louse powder; general insecticide.

**"Barbak C"** (phenyl mercuric cyanamid): Seed disinfectant and protectant.
**barium antimonyl tartrate:** Poultry parasiticide.
**barium antimonyl tartrate** ($Ba[(SbO)C_4H_4O_6]_2$): Stomach insecticide.
**barium carbonate** ($BaCO_3$): Rodenticide.
**barium chloride** ($BaCl_2 \cdot 2H_2O$): Rodenticide; termite repellent.
**barium fluoride** ($BaF_2$): Insecticide.
**barium oxalate** ($BaC_2O_4 \cdot H_2O$): Insecticide.
**barium peroxide** ($BaO_2$): Insecticide.
**barium triphosphate:** Insecticide.
**"Basicop"** (copper basic sulfates): Fungicide used generally.
**benzaldehyde** ($C_6H_5CHO$): Auxiliary fumigant with HCN.
**benzalmalononitrile:** Insecticide.
✓**benzene hexachloride**; gammahexane; 1,2,3,4,5,6-hexachlorocyclohexane ($C_6H_6Cl_6$): Insecticide and fumigant.
**benzene sulfonic acid:** Insecticide, tested on codling moth.
**benzhydrcl:** Fungicide for control of citrus fruit decay fungi. Soluble in isopropyl alcohol but not in water.
**benzil** (dibenzoyl) ($C_6H_5COCOC_6H_5$): Mite repellent.
**benzine** (benzol): See **petrolic ether. Fumigant.**

**benzocaine**: Ovicide used against lice.

**benzoic acid,** 2-chlorophenyl ester: Mite repellent.

**benzoic acid, 3,5-dimethylphenyl ester**: Mite repellent.

**benzoic acid, α-methylbenzyl ester**: Mite repellent.

**benzoic acid, phenyl ester (phenyl benzoate).**: Mite repellent.

**benzoic acid, phenylethyl ester**: Mite repellent.

**benzol** (benzene, phenyl hydride) ($C_6H_6$): Larvicide; combining form of certain organic insecticides.

**benzonitrile**: Fly larvicide.

**benzothiazole, 1-amino**: Seed disinfectant and protectant.

**benzyl benzoate**: Insect repellent.

**benzyl nicotinium chloride**: Fungicide.

**benzyl pyridine**: Insecticide.

**benzyl salicylate**: Fungicide.

**benzyl thiocyanate**: Fly larvicide.

**bis(*o*-amino-phenyl) disulfide**: Mosquito larvicide.

**2,2-bis(*p*-bromophenyl)-1,1,1-trichloroethane**: Insecticide similar to DDT in its action.

**bis(5-chloro-2-hydroxyphenyl) methane** [$C_6H_3Cl(OH)_2CH_2$]: Effective against European corn borer.

**bis(*p*-chloro-phenoxy)methane**: Acaricide.

**bis(*p*-chloro-phenoxy)methane** ("Neotran"): Miticide (acaricide).

**2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethane**: See **DDD.**

**2,2-bis(*p*-fluorophenyl)-1,1,1-trichloroethane**: See **DFDT.**

**2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane**: See **DMDT.**

**bismuth subsalicylate** [$C_6H(OH)CO_2BiO$]: Fungicide, used on tobacco.

**"Black Leaf 40"**: See **nicotine salts.**

**"Black Leaf 155"**: "Fixed" or stable form of nicotine, 14% nicotine.

**"Bladan"**: See **hexaethyl tetraphosphate.**

**blue stone**: See **copper sulfate.**

**borax** ($Na_2O \cdot 2B_2O_3 \cdot 10H_2O$): Herbicide.

**Bordeaux mixture**: Liquid fungicide and insecticide made from copper sulfate and lime.

**"Bordow"** (copper basic sulfate): Fungicide used generally.

**boric acid**: See **acid boric.**

**bornyl thiocyanoacetate**: Fly spray.

**brimstone**: See **sulfur.**

***p*-bromoazobenzene**: Insecticide.

***p*-bromobenzonitrile** ($BrC_6H_4 \cdot CN$): Fumigant.

**2-bromoethyl ethyl ether**: Fumigant.

***p*-bromohydroazobenzene**: Insecticide.

**bromomethane**: See **methyl bromide.**

**2-bromoethyl acetate**: Fumigant.

**β-butoxy-β-thiocyanodiethyl ether**: "Lethane 384"; Used against spider mites and in fly sprays and other household insects.

**butyl carbitol thiocyanate**: Insecticide.

**butyl carbityl (6-propyl piperonyl) ether**: Synergist used with pyrethrins.

***n*-butyl mesityl oxide oxalate**: (Indalone): Insect repellent; mosquitoes, black flies, and other biting flies.

**N-butyl piperonylamide**: Pyrethrum activator.

**cadmium carbonate** ($CdCO_3$): Seed disinfectant.

**cadmium chloride** ($CdCl_2$:) Mildew preventive.

**cadmium cyanide** [$Cd(CN)_2$]: Seed disinfectant.

**cadmium oxide** ($CdO$): Seed disinfectant.

**cadmium nitrate** [$Cd(NO_3)_2 \cdot 4H_2O$]: Termite repellent.

**cadmium soap**: Mildew preventive.

**calcium arsenate** (tricalcium orthoarsenate) [$Ca_3(AsO_4)_2$]: Insecticide for defoliators and fruit and boll worm.

**calcium arsenite** ($CaAsO_3H$): Fungicide for dormant trees.

**calcium carbonate** (chalk; limestone) ($CaCO_3$): Seed protectant.

**calcium chlorate** [$Ca(ClO_3)_2 \cdot 2H_2O$]: Herbicide.

**calcium chloride** ($CaCl_2$, $CaCl_2 \cdot H_2O$, $CaCl_2 \cdot 6H_2O$): Herbicide.

**calcium cromate** ($CaCrO_4 \cdot 2H_2O$): Wood preservative.

**calcium cyanamide** ($CaCN_2$): Herbicide.

**calcium fluoride** ($CaF_2$): Wood preservative.

**calcium hydroxide**: (calcium hydrate; slaked lime) [$Ca(OH_2)$]: Fungicide; wood preservative.

**calcium hypochlorite** (bleaching powder) [$Ca(ClO)_2 \cdot 4H_2O$]: Fungicide for control of fruit rots.

**calcium polysulfides** ($CaS_5$): Insecticide; active ingredient of lime-sulfur solution.

**calcium silicofluoride** ($CaSiF_6$): Insecticide.

**"Calo-Chlor"** (mercurous and mercuric chloride): Fungicide for general use.

**Calomel** (mercurous chloride): Fungicide; insectifuge.

**camphor** (gum camphor) ($C_9H_{16}CO$): Mothproofing.

**carbon dichloride** (tetrachloroethylene): Fumigant.

**carbon disulfide** (carbon bisulfide) ($CS_2$): Fumigant; rodenticide; herbicide.

**carbon monoxide**: Rodenticide.

**carbon tetrachloride** (tetrachloromethane) ($CCl_4$): Fumigant; parasiticide. Combined with flammable fumigants to reduce hazard.

**"Castrix"**: See **2-chloro-4-dimethylamino-6-methylpyrimidine**.

**cedar wood oil**: Moth repellent.

**"Ceresan (New Improved)"** (ethyl mercury phosphate): Seed disinfectant.

**cetyl isoquinolinium bromide**: Fungicide.

**chenopodium oil** (oil of American wormseed): Parasiticide.

**Chloranil**: See **tetrachloro *p*-benzoquinone**.

**"Chlordane"***: ("Velsicol 1068," "Octo-Klor") 1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane ($C_{10}H_6Cl_8$): General insecticide, used against insects of household and field. Technical product is not pure but associated with related compounds.

**chlorinated camphene**: See **octachloro-camphene.**

**chloroacetonitrile** ($CH_2ClCN$): Fumigant.

***p*-chlorobenzenesulfonamide** ($ClC_6H_4SO_2NH_2$): Stomach insecticide.

***o*-chlorobenzonitrile** ($ClC_6H_4 \cdot CN$): Fumigant.

***p*-chlorobenzonitrile** ($ClC_6H_4 \cdot CN$): Fumigant.

**chloro cyanohydrin**: See **trichloroacetonitrile.**

**2-chloro-4-dimethylamino-6-methylpyrimidine** ("castrix"): A very toxic rodenticide. Substitute for thallium. Developed in Germany.

**2-chloroethyl ether**: Fumigant.

**2-chlorofluorene**: Insecticide; used against the European corn borer.

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* Official name now changed to "Chlordan".

**chloroform** (trichloromethane) ($CHCl_3$): Fumigant.

***p*-chlorometacresol**: Wood preservative.

**chloromethyl-4-chlorophenyl sulfone** ($ClC_6H_4SO_2CH_2Cl$): Insecticide used against the European corn borer.

**2-chloro-6-nitrotoluene**: Termite and wood rot control.

**chlorophenyl carbamate**: Selective herbicide for grasses.

**2-chloro-*o*-phenylphenol**: Mildew preventive.

***p*-chlorophenoxyethoxyethyl chloride**: Wood preservative.

**chloropicrin**: See **nitrotrichloromethane.**

**2-chloro-2-tetrachloro-phenoxy diethyl ether** [$Cl(C_2H_4)_2\ O_2Cl_4$]: Household insecticide.

**chlorothymol**: Mildew preventive.

**chromated zinc chloride**: Wood preservative.

**chromic oxide** (chrome green) ($Cr_2O_3$): Wood preservative.

**chromic sulfate** (chromium sulfate): (a) $Cr_2(SO_4)_3$; (b) $Cr_2(SO_4)_3.15H_2O$: Wood preservative.

**cinnamamide**: Insecticide.

**citronella oil**: Fly and mosquito repellent.

**clove, powdered**: Mothproofing.

**cobaltous oxide** (cobalt oxide) ($CoO$): Fungicide.

**cobaltous sulfate** (cobalt sulfate) ($CoSO_4$; $CoSO_4 \cdot 7H_2O$): Fungicide.

**"Compound A"** (copper oxychloride): Fungicide for general use.

**"Copofilm"** (copper salts): Fungicide for general use.

**copper** ($Cu$): Active fungicide alone and combined.

**copper abietinate** (cupric abietinate) [$Cu(C_{19}H_{27}O_2)_2$]: Wood preservative.

**copper acetate**: (cupric acetate; green verdigris) [$Cu(C_2H_3O_2)_2 \cdot H_2O$]: Insecticide; fungicide.

**copper acetoarsenite** (cupric acetoarsenite; Paris green) [$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$]: Insecticide for use against defoliators; mosquito larvicide.

**copper acetonate**: Fungicide.

**copper-ammonium sulfate** (cupric-ammonium sulfate) ($CuSO_4 \cdot 4NH_3 \cdot H_2O$): Insecticide; fungicide.

**copper arsenate, basic** [$Cu(CuOH)AsO_4$]: Insecticide.

**copper arsenite** (cupric arsenite; Scheele's green) ($CuHAsO_3$): Insecticide.

**copperas**: See **ferrous sulfate.**

**copper basic salts**: See **"Copper Hydro 40."**

**copper basic sulfates**: See **Basicop,** *also* **Bordow.**

**copper carbonate** (cupric carbonate) [$Cu_2(OH)_2CO_3$]: Seed disinfectant.

**copper chloride** (cupric chloride) ($CuCl_2$; $CuCl_2 \cdot 2H_2O$): Insecticide.

**copper chloride, cuprous** ($CuCl$): Insecticide; wood preservative.

**copper-clay** (7% metallic copper): Plant bactericide. Also copper-sulfur and copper-talc with above proportions and for same use.

**copper cyanide** (cupric cyanide) [$Cu(CN)_2$]: Insecticide.

**copper cyanide** (cuprous cyanide) [$Cu_2(CN)_2$]: Anti-fouling paint.

**copper dimethyl dithiocarbamate**: See **Cupramate.**

**copper fluoride** (cupric fluoride) ($CuF_2 \cdot 2H_2O$): Insecticide.

**"Copper Hydro 40"** (copper basic salts): Fungicide for general use.

**copper hydroarsenate**: A compound containing basic cupric arsenate; insecticide.

**copper hydroarsenate-arsenite**: A compound containing basic cupric arsenate and basic cupric arsenite; insecticide.

**copper hydroxide** (cupric hydroxide; copper hydrate) [$Cu(OH)_2$]: Fungicide.

**copper metaarsenite** [$Cu(AsO_3)_2 \cdot H_2O$]: Insecticide.

**copper naphthenate**: Fungicide, cloth treatment; wood decay control.

**copper nitrate** (cupric nitrate) [$Cu(NO_3)_2 \cdot 3H_2O$; $Cu(NO_3)_2 \cdot 6H_2O$]: Fungicide; mildew proofing of textiles.

**copper oleate** (cupric oleate) [$Cu(C_{18}H_{33}O_2)_2$]: Oil-soluble fungicide.

**copper oxalate** [$(COO)_2Cu$]: Fungicide.

**copper oxide, red** (cuprous oxide); "Cuprocide" ($Cu_2O$): Seed disinfectant, protectant; general fungicide; ship bottom paint.

**copper oxychloride** ($CuCl_2 \cdot 2CuO \cdot 4H_2O$): Fungicide.

**copper phosphate** ($Cu_3(PO_4)_2$: Fungicide; insecticide for dusting grain.

**copper phosphate** [$Cu_3(PO_4)_2 \cdot 3H_2O$): Fungicide.

**copper phosphide** (cuprous phosphide) ($Cu_3P_2$): Fungicide.

**copper polysulfide**: Insecticide.

**copper propionyl acetate**: Mildew preventive.

**copper 8-quinolinolate**: Fungicide.

**copper resinate** (cupric resinate) [$Cu(C_{20}H_{29}O_2)_2$]: Oil-soluble fungicide.

**copper sebacate**: Fungicide.

**copper silicate** ($CuSiO_3$): Fungicide.

**copper silicofluoride** (cupric silicofluoride) ($CuF_2SiF_4 \cdot 6H_2O$): Fungicide.

**copper stearate** (cupric stearate) [$Cu(C_{18}H_{36}O_2)_2$]: Oil-soluble fungicide.

**copper sulfate, basic** ($4CuO \cdot SO_3$): Fungicide; reaction product between copper sulfate and calcium hydroxide.

**copper sulfate** (cupric sulfate; blue stone) ($CuSO_4 \cdot 5H_2O$): Fungicide; combined with lime to form Bordeaux mixture; insecticide; wood preservative.

**copper sulfate, monohydrate** ($CuSO_4 \cdot H_2O$): Fungicide used in dusting operations.

**copper sulfate, tribasic**: Fungicide.

**copper sulfide** (cupric sulfide) ($CuS$): Fungicide; ship bottom paint.

**copper thiocyanate** (cuprous thiocyanate) ($CuCNS$): Fungicide.

**copper trichlorophenate**: Seed disinfectant.

**corn oil** (maize oil): Fungicide used on plants; insecticide.

**corrosive sublimate**: See **mercuric chloride.**

**cotton-seed oil** (seed oil): Fungicide used on plants; insecticide.

**creosote, coal-tar**: Wood preservative.

**cryolite**: Insecticide; moth proofing; natural formation of sodium fluoaluminate.

**"Cupramate"** (copper dimethyl dithiocarbamate): Fungicide.

**cupric acetoarsenite**: See **copper acetoarsenite.**

**cupric arsenate, basic** [$Cu_3(AsO_4)_2 \cdot Cu(OH)_2$: Insecticide.

**cupric metaarsenite** [$Cu(AsO_2)_2 \cdot H_2O$]: Insecticide.

**"Cuprocide"**; See **copper oxide.**

**cuprous thiocyanate** ($CuCNS$): Insecticide.

**cyanamide**: See **calcium cyanamide.**

**cyanogen** ($C_2N_2$): Insecticide; fumigant.

**cyanogen chloride** ($CNCl$): Insecticide; fumigant.

**cyanogen iodide**: See **iodine cyanide.**

**1-$\alpha$-cyclohexylpyrrolidine**: Insecticide.

**$\alpha$-cyclohexylpyrroline**: Insecticide.

**cyclopentadiene**: Insecticide; fungicide.

**cyclopropyl ethyl ether** ($C_3H_5OC_2H_5$): Fumigant.

**cyclopropyl methyl ether** ($C_3H_5OCH_3$): Fumigant.

**cyclopropyl propyl ether** ($C_3H_5OC_3H_7$): Fumigant.

**2,4-D**: See **dichlorophenoxyacetic acid.**

D-D (2 parts of 1,3-dichloropropylene and 1 part of 2-dichloropropane): Soil fumigant.

DDD [2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethane] ($(ClC_6H_4)_2HCCHCl_2$): Insecticide similar in action to DDT but considered less toxic to mammals.

DDT (*p,p'*-DDT; dichloro-diphenyl-trichloroethane; 1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane) [$(ClC_6H_4)_2HCCCl_3$]: General insecticide, noted particularly for its persistent residual value.

DDT **(technical)** (isomers of **dichloro-diphenyl-trichloroethane**, principally *p,p'* DDT and *o,p'* DDT and with a setting point of 89°C): Insecticide, see **DDT.**

**delphinium** (larkspur): Alkaloidal extract used in lotion for lice.

DFDT [2,2-bis-(*p*-fluorophenyl)-1,1,1-trichloroethane], $(FC_6H_4)_2CHCCl_3$: Insecticide developed in Germany. Used principally against household insects. Has fumigating action but not a long residual value.

**diamylphenol**: Fly spray.

**2,2-di-*p*-anisyl-1,1,1-trichloroethane**: Insecticide.

**diazoaminobenzene** ($C_6H_5N_2NHC_6H_5$): Stomach insecticide.

**dibasic sodium *o*-arsenate** ($Na_2HAsO_4 \cdot 7H_2O$): Insecticide.

**dibasic sodium *o*-arsenite** ($Na_2HAsO_3$): Insecticide; grasshopper and ant baits; herbicide.

***p*-dibromobenzene** ($BrC_6H_4Br$): Fumigant.

**1,2-dibromoethane**: See **Ethylene dibromide.**

**1,2-dibromoethyl benzene**: Styrene dibromide. Insecticide; used against corn earworm.

**dibromo-nitroethylbenzene**: Insecticide.

**N-*n*-dibutyl amine** [$(C_4H_9)_2NH$]: Fumigant, grain.

**dibutyl oxalate**: Insect repellent.

**dibutyl phthalate**: Repellent for chiggers.

**dichloroacetonitrile** ($CHCl_2CN$): Fumigant.

**2,5-dichloroaniline** ($Cl_2C_6H_3NH_2$): Fumigant.

**dichlorobenzene** ($C_6H_4Cl_2$): Insecticide; fumigant for clothes moth; soil fumigant. The para form is used as a tree fumigant for the peach crown borer and for museum pests. The ortho form is used as a fumigant for wood borers.

**3,4-dichlorobenzyl alcohol**: Insecticide.

**dichlorodiphenyl dichloroethane**: See **DDD.**

**dichlorodiphenyl oxide**: Wood preservative.

**dichloro-diphenyl-trichloroethane**: See **DDT.**

**dichloroethane**: See **Ethylene dichloride.**

**dichloroether**: See **α-β-dichloro-ethyl ethyl ether.**

**1,2-dichloro-1-ethoxy ethane**: See **α,β-dichloroethyl ethyl ether.**

**α,β-dichloroethyl ether**: See **α,β-dichloroethyl ethyl ether.**

**α,β-dichloroethyl ethyl ether** (1,2-dichloro-1-ethoxy ethane; dichloro ether; α,β-dichloroethyl ether) ($CH_2ClCHClOC_2H_5$): Fumigant.

**dichloro-isopropyl ether** ($C_6H_{12}OCl_2$): Soil fumigant.

**2,3-dichloro-1,4-naphthoquinone** ("Phygon"): Seed disinfectant and protectant; fungicide for foliage and textile treatment. Promising material for apple scab and potato blight.

**1,1-dichloro-1-nitroethane** ($CH_3CCl_2NO_2$): Fumigant.

**1,1-dichloro-1-nitropropane** [$CH_3CH_2C(NO_2)Cl_2$]: Fumigant.

**2 dichlorophenoxyacetic acid** (2,4-D): Hormone spray; herbicide.

**di(4-chlorophenoxy) methane** ($C_{13}H_{10}O_2Cl_2$): General insecticide, effective on mites, and as mosquito larvicide.

**$\alpha$,$\alpha$-di-(4-chloro-phenyl)-diethyl ether**: Fumigant.

**3,4-dichlorophenyl-N-methyl sulfonamide**: Moth repellent.

**1,2-dichloropropane** (propylene dichloride) combined with 1,3-dichloropropene to form **D-D** mixture of commerce: Soil fumigant.

**1,3-dichloropropene**: Two isomers combined with dichloropropane to form **D-D** mixture of commerce. Soil fumigant for nematodes and wire worms.

***o*-dicyanobenzene** [$C_6H_4(CN_2)$]: Insecticide.

***p*-dicyanobenzene** [$C_6H_4(CN)_2$]: Fumigant.

**di-*n*-decylamine** [$(C_{10}H_{21})_2NH$]: Fly spray.

***o*,*o*-diethyl-*o*,*p*-nitrophenyl thiophosphate** (3422): General insecticide; used against spider mites, defoliators, and cockroaches.

**N,N-diethyl-piperonylamide**: Insecticide.

**diethylene glycol monobutyl ether acetate**: Mosquito repellent.

**diethylene glycol monoethyl ether**: Mosquito repellent.

**diethylene oxide**: Fumigant.

**difluorodiphenyl disulfide**: Insecticide; specific for body louse.

**difluorodiphenyl trichloroethane**: Insecticide.

**di-*n*-heptylamine** [$(C_7H_{15})_2NH$]: Fly spray.

**9,10-dihydroanthracene** ($C_6H_4CH_2C_6H_4CH_2$): Insecticide.

**1,2-Dihydro-4-methoxy-1-methyl-2-oxonicotinineo nitrile** (Ricinine): Insecticide derived from castor bean plant.

**1,2-Dihydro-1,4,6-trimethyl-2-oxonicotinonitrile**: Insecticide.

**di-hydrogen potassium arsenate** ($KH_2AsO_4$): Insecticide.

**di(*p*-methoxyphenyl) trichloroethane,** also called 1-trichloro-2,2-bis (*p*-methoxyphenyl) ethane: Methoxy analog of **DDT**.

***p*-dimethylaminobenzene diazosulfonic acid, sodium salt**: Rodenticide of moderate toxicity, developed in Germany.

***p*-dimethylaminophenyl diazo sodium sulfonate**: Rodenticide.

**dimethylbenzylcetyl ammonium chloride** [$(CH_3)_2$ $(C_6H_5CH_2)$ $C_{16}H_{33}NCL$]: Textile fungicide.

**dimethyl carbate** [*cis*-bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, dimethyl ester]: Insect repellent; mosquitoes, black flies and other biting flies.

**dimethyldidodecylammonium chloride**: Fungicide.

**dimethyl dilauryl ammonium chloride**: Turf fungicide.

**dimethyl phthalate**: Insect repellent.

**dimethylethanoloctodecylammonium chloride**: Fungicide.

**dimorpholinethiuram disulfide**: Fungicide.

**2,4-dinitro anisole** ($CH_3OC_6H_3(NO_2)_2$]: louse powder.

**2,4-dinitro-6-cyclohexyl phenol** (2,4-dinitro-*o*-cyclohexyl phenol): Specific in control of spider mites.

**2,4-dinitro-*o*-cyclohexylphenol**: Insecticide; ovicide.

**dinitronaphthalene** [$C_{10}H_6(NO_2)_2$]: Termite repellent.

**4,6-dinitro-*o*-cresol** (2-methyl-4,6-dinitrophenol) [$(NO_2)_2C_6H_2(CH_3)OH$]: This compound and its salts are toxic to aphids and their eggs; used as dormant sprays; wood preservative.

**3,5-dinitro-*o*-cresyl acetate**: Louse powder.

**dinitro-*o*-secondary butyl phenol** (also the ammonium salt of): Insecticide; used in dust barriers for chinch bugs; herbicide.

**2,4-dinitrophenetole**: Louse powder.

**dinitrophenol**: Wood preservative.

**1,4-dinitrosopiperazine** $[ONN(CH_2CH_2)_2NNO]$: Stomach insecticide.

**di-*n*-octylamine** $[(C_8H_{17})_2NH]$: Fly spray.

**diphenyl** $(C_6H_5 \cdot C_6H_5)$: Fungistat (preventing or retarding the growth of fungi) for checking fruit decay.

**diphenyl guanidine phthalate**: See **Guantol.**

**diphenylamine (phenylaniline)** $[(C_6H_5)_2NH]$: Larvicide.

**diphenylamine arsenious oxide**: Repellent for marine pile borer.

**diphenylene oxide**: Household insecticide. Larvicide of medium toxicity to screw worm fly.

**1,4-diphenylsemicarbazide** $(C_6H_5NHNHCONHC_6H_5)$: Stomach insecticide.

**diphenyl sulfoxide**: Fungicide for control of citrus fruit decay fungi. Soluble in isopropyl alcohol but not in water.

**1,10-dipiperidinodecane**: Specific for body louse.

**disodium ethylene bisdithiocarbamate**: Fungicide.

**Dithane**: (disodium ethylene bisdithiocarbamate); Fungicide.

**"dithane Z-78"** (zinc ethylene bisdithiocarbamate): Fungicide for truck crops.

**1,3-dithiane,2,2-diphenyl**: Mosquito larvicide.

**dithiocarbamic acid**: Fungicide.

**β-dithiocyanoethyl ether** ("Lethane A70"): Insecticide.

**2,2-di-*p*-tolyl-1,1,1-trichloroethane**: Insecticide.

**2,4-dinitrophenyl ester of acetic acid** $[CH_3CO_2C_6H_5(NO_2)_2]$: Moth repellent.

**DMDT** (Methoxychlor) 2,2-bis-(*p*-methoxyphenyl)-1,1,1-trichloroethane $[(CH_3OC_6H_4)_2CHCCl_3]$: Methoxy analog of DDT. Insecticide similar to DDT but thought to be less toxic to mammals.

**"Dow 9B"** (zinc-2,4,5-trichlorophenate): Fungicide; seed protectant.

**"Dowfume W-40"** (ethylene dibromide 40 per cent by weight): Soil fumigant; insecticide; nematicide.

**dry lime sulfur** (calcium polysulfides): Fungicide; insecticide.

**"Elgetol"** (sodium dinitro-*o*-cresolate): Fungicide used on dormant trees.

**epichlorohydrin**: Fumigant.

**ethanol mercuric chloride** ("Sanoseed"): Seed disinfectant.

**ethene** (ethylene) $(CH_2 \cdot CH_2)$: Fungicide; used as a fungicide for fruit rot.

**ethyl acetate** (acetic ester) $(CH_3COOC_2H_5)$: Fumigant.

**ethyl formate** $(C_2H_5CO_2H)$: Insecticide; grain fumigant.

**2-ethyl-1,3-hexanediol** ("Rutgers 612"): Insect repellent; mosquitoes, black flies and other biting flies.

**ethyl isothiocyanate**: Fumigant.

**ethyl mercaptan**: Fumigant.

**ethyl mercury chloride** $(C_2H_5HgCl)$: Seed disinfectant.

**ethyl mercury cresol**: Seed disinfectant.

**ethyl mercury nitro phenol**: Seed disinfectant.

**ethyl mercury phosphate** ("New improved Ceresan"): Seed disinfectant.

**ethyl mercury sulfate**: Seed disinfectant.

**ethyl mercury *p*-toluene sulfonanilide** ("DuBay 1452-C"): Seed disinfectant.
**ethylene** (ethene) ($CH_2 \cdot CH_2$): Fungicide used as a fumigant for fruit rot.
**ethylene chlorobromide:** Nematicide.
**ethylene chlorohydrin** ($C_2H_5OCl$): Fumigant.
**ethylene dibromide** (dibromoethane) ($CH_2BrCH_2Br$): Insecticide; soil fumigant.
**ethylene dichloride** (dichloroethane) ($C_2H_4Cl_2$): Fumigant, soil.
**ethylene monochlorochloride** (monochloroethylene chloride) ($CH_2Cl \cdot CH_2Cl_2$): Fumigant.
**ethylene oxide** [$(CH_2)_2O$]: Fumigant.
**eucalyptus oil**: Insectifuge.

**fenchyl thiocyanoacetate** ("Thanite"): Insecticide; fly spray ingredient.
**"Fermate"** (ferricdimethyl dithiocarbamate): Seed disinfectant.
**ferric dimethyl dithiocarbamate** ("Fermate"): Fungicide.
**ferrous arsenate** (iron arsenate) [$Fe_3(AsO_4)_2 \cdot 6H_2O$]: Insecticide.
**ferrous sulfate** (iron sulfate; copperas; green vitriol) ($FeSO_4$): Herbicide.
**fish oil** (herring oil): Insecticide; combined with sodium or potassium base as a soap.
**flowers of sulfur** (sublimed sulfur), See **sulfur.**
**fluorene** ($C_{13}H_{10}$): Larvicide for European corn borer.
**2-fluorylamine** ($C_6H_4CH_2C_6H_3NH_2$): Stomach insecticide.
**formaldehyde** (formalin; formic aldehyde) ($H \cdot CO \cdot H$): Fungicide; soil sterilant; used in baits for flies.
**formalin**: See **formaldehyde.**
**formic aldehyde**: See **formaldehyde.**

**gamma-hexachloride**: See **benzene hexachloride.**
**"Genecop"** (copper salts): Fungicide for general use.
**glyoxalidine derivatives** as fungicides: See **1-hydroxethyl-2-heptadecylglyoxalidine.**
**green vitriol**: See **ferrous sulfate.**
**"Guantol"** (diphenyl guanadine phthalate): Fungicide for general use.

**heptachloropropane**: fly larvicide.
**2-heptadecylglyoxalidine**: Plant fungicide.
**N,*n*-heptyl-*n*-octylamine** ($C_7H_{15}$ $NHC_8H_{17}$): Fly spray.
**herring oil**: See **fish oil.**
**HETP**: See **hexaethyl tetraphosphate.**
**hexachlorocyclohexane**: See **benzene hexachloride.**
**hexachloroethane** ($C_2Cl_6$): Fumigant for ear corn; cattle vermifuge.
**hexachloropropene**: Fly larvicide.
**hexaethyl tetraphosphate** (HETP) $OP[OPO(OC_2H_5)_2]_3$: Insecticide; substitute for nicotine.
**N,*n*-hexyl-2-aminoheptane** ($C_6H_{13}NHCH_3CHC_5H_{11}$): Fly spray.

**N,*n*-hexyl-*n*-heptylamine** ($C_6H_{13}NHC_7H_{15}$): Fly spray.

**hydrocyanic acid**: See **acid hydrocyanic.**

**hydrogen cyanide**: See **acid hydrocyanic.**

**1-hyroxyethyl-2-heptadecylglyoxalidine**: Plant fungicide.

**hydroxymercurichlorophenol** ("Semesan"): Seed disinfectant.

**hydroxypentamethylflavan** (2-hydroxy-2,4,4,4,7-pentamethylflavan): Insecticide.

**Indalone** (*n*-butyl mesityl oxide oxalate): Insect repellent; mosquitoes, black flies and other biting flies.

**"Indole"** ($C_6H_4CHCHNH$): Fumigant.

**INPC**: See ***o*-isopropyl-N-phenylcarbamate.**

***p*-iodazobenzene**: Insecticide; larvicide for the European corn borer.

**iodine cyanide** (cyanogen iodide) ($ICN$): Insecticide; taxidermists' preservative.

***p*-iodonitrobenzene**: Insecticide; larvicide for the European corn borer.

**4(*p*-iodophenylazo)-*o*-cresol** ($C_{13}H_{11}IN_2O$): Insecticide; larvicide for the European corn borer.

**iron arsenate**: See **ferrous arsenate.**

**iron sulfate**: See **ferrous sulfate.**

**isobornyl thiocyanoacetate** ("Thanite"): Fly spray.

**N-isobutyl piperonylamide**: Pyrethrum activator.

**N-isobutyl undecylenamide**: Insecticide; used in fly spray and louse powders.

**2-isobutyryl-1-phenylhydrazine** $[C_6H_5NHNHCOCH(CH_3)_2]$: Larvicide for the European corn borer.

***o*-isopropyl-*n*-phenylcarbamate**: Herbicide used on quack and other grasses.

***p*-isopropylphenylethyl alcohol**: Insect repellent.

**isopropyl thiocyanate**: Fumigant.

**isothiocyanates**: General insecticide.

**isovaleryl-2-phenylhydrazine**: Larvicide for codling moth.

**jervine** ($C_{26}H_{37}O_3N$): Alkaloid derived from white hellebore.

**"Karbam (black)"**: See **Ferric dimethyl dithiocarbamate.**

**kerosene** (coal oil): A petroleum fraction; insecticide; ingredient of fly sprays.

**larkspur**: See **delphinium.**

**lauryl quinaldinium bromide**: Fungicide.

**lauryl quinolinium chloride**: Fungicide.

**lauryl thiocyanate** $[CH_3(CH_2)_{10}CH_2SCN]$: Insecticide.

**lead arsenate, basic**: The commercial compound is apparently a mixture of lead hydroxy arsenates. Insecticide; used on plants of tender foliage such as bean, peach and English walnut.

**lead arsenate,** standard (acid)($PBHAsO_4$): Insecticide; the principal lead arsenate of commerce.
**lead arsenite** [$Pb(AsO_2)_2$]: Insecticide.
**lead dimethyl dithiocarbamate**: Fungicide.
**lead fluoride** ($PbF_2$): Insecticide.
**lead mercaptide**: Insecticide.
"**Lethane** 384" (β,β-tubutoxythiocyanodiethyl ether): Insecticide.
"**Leytosan**" (phenyl mercury urea): Seed disinfectant.

**malachite green**: [$(C_{23}H_{25}N_2Cl)_3 \cdot 2ZnCl_2 \cdot 2H_2O$]: Fungicide.
**manganese arsenate**: The commercial product is a mixture of trimanganoarsenate [$Mn_3(AsO_4)_2$] and dimanganoarsenate ($MnHAsO_4$). Insecticide; used in orchard and truck crops.
**magnesium arsenate**: The commercial produce is a mixture of trimagnesium orthoarsenate [$Mg_3(AsO_4)2$] and dimagnesium acid arsenate ($MgHAsO_4$). Insecticide; used largely on truck crops.
**manganese ethylene bisdithiocarbamate**: Fungicide for general use.
**mannitan monolaurate**: Fly spray.
**mercuric chloride** (corrosive sublimate) ($HgCl_2$): Wood preservative.
**mercuric cyanide** [$Hg(CN)_2$]: Wood preservative.
**mercuric oxide, red** ($HgO$): Used in ship bottom paint.
**mercuric phenyl cyanamide** ("Barbak D"): Seed disinfectant.
**mercurous chloride** (calomel) ($HgCl$): Insectifuge.
**mercurous iodide** ($HgI$): Seed disinfectant.
**mercury acetamide**: Seed disinfectant.
**mercury benzamide**: Seed disinfectant.
**mercury phthalimide**: Seed disinfectant.
**mercury** (quicksilver) ($Hg$): Insecticide; ointment for lice.
**mercury succinimide**: Seed disinfectant.
**merthiolate** (sodium ethyl mercurithiosalicylate): Fungicide; dip for citrus fruit.
**mesityl oxide**: Insect repellent.
**2-mesityl-α-pyrrolidine**: Insecticide.
**2-mesityl-α-pyrroline**: Insecticide.
**metaldehyde** ($(C_2H_4O)_4$): Insecticide; used in snail and slug baits.
"**Methoxon**" (See **2-methyl-4-chlorophenoxyacetic acid**): Herbicide.
**methoxy analog of DDT**: See **DMDT**.
"**Methoxychlor**": See **DMDT.**
**p-methoxydiphenyl**: Mite repellent.
**methyl acetate** ($CH_3COOCH_3$): Fumigant.
**methyl p-amino benzoate**: Louse powder.
**methyl bromide** (bromomethane) ($CH_3Br$): Fumigant.
**2-methyl-4-chlorophenoxyacetic acid**: See "**Methoxon**".
**2-methylcyclohexanone semicarbazone**: Insecticide; defoliator control on cabbage.
**methylallyl bromide** (3-bromo-2-methylpropene-1) [$CH_2 \cdot C(CH_3)CH_2Br$]: Fumigant.
**methalallyl chloride** (3-chloro-2-methyl propene-1) [$CH_2 \cdot C(CH_3)CH_2Cl$]: Fumigant.
**methyl disulfide** ($CH_3SSCH_3$): Fumigant.
**methyl formate** ($HCOOCH_3$): Fumigant.
**methyl naphthalene** ("Velsicol"): Insecticide.
**2,2-methylene-bis-(4-chlorophenol)**: Textile mildew preventive.

**"Milban"**: Textile preservative. See **Zinc dimethyl dithiocarbamate.**

**mineral** (or petroleum) **oil:** Insecticide used for scale insects and mealy bugs. Ovicide for leafroller, aphids, spider mites and codling moth. Kerosene used as a base for fly sprays.

**monochloroacetonitrile** ($CH_2ClCN$): Fumigant.

**mono-ethanolammonium fluoride,** also **di** and **tri** forms: Mothproofing substance.

**monohydroxy diarylamine**: Fungicide.

**morpholine thiuramdisulfide** (M.T.D.S.): Seed disinfectant.

**naphthalene** ($C_{10}H_8$): Insecticide; soil, household and greenhouse fumigant.

**$\alpha$-naphthol** ($C_{10}H_7OH$): Insecticide; used in codling moth bands.

**$\beta$-naphthol** ($C_{10}H_7OH$): Insecticide; used in codling moth bands.

**$\alpha$-naphthyl isothiocyanate**: Insecticide.

**2-naphthyl mercaptan**: Mosquito larvicide.

**$\alpha$-naphthylthiourea** (ANTU; $\alpha$-naphthylthiocarbamide): Rodenticide, for Norway rat.

**"Neotran"**: See **bis (*p*-chlorophenoxy methane).**

**"New Improved Ceresan"** (ethyl mercury phosphate): Seed disinfectant.

**nickel carbonate** ($NiCO_3$): Fungicide.

**nickel cyanide** [$Ni(CN)_2 \cdot 4H_2O$]: Fungicide.

**nickel sulfate** ($NiSO_4 \cdot 6H_2O$): Fungicide.

**nicotine** ($\beta$-pyridyl-$\alpha$-methyl pyrrolidine) ($C_{10}H_{14}N_2$): Insecticide; principal alkaloid of tobacco used in volatile and fixed form.

**nicotine cuprocyanide**: Insecticide for control of codling moth.

**nicotine salts**: **hydrochloride** ($C_{10}H_{14}N_2 \cdot HCl$); **sulfate** [$(C_{10}H_{14}N_2)_2 \cdot H_2SO_4$]: Forms used for storage as being non-volatile and less toxic than the alkaloid.

**"Nifos-T"**: See **tetraethyl pyrophosphate.**

**nitrobenzene** (nitrobenzol): Insecticide.

***p*-nitrobenzoic acid, ethyl ester**: Larvicide for European corn borer.

**nitrobenzol**: See **nitrobenzene.**

**6-nitro-2,4-bis(trichloromethyl)-1,3-benzodioxane**: Larvicide for European corn borer.

**2-nitrobutane** ($CH_3CHNO_2CH_2CH_3$): Fumigant.

**o-nitrochlorobenzene** ($ClC_6H_4NO_2$): Fumigant.

***p*-nitrochlorobenzene** ($ClC_6H_4NO_2$): Fumigant.

**nitrotrichloromethane** (chloropicrin) ($CCl_3NO_2$): General and soil fumigant; insecticide, nematicide, fungicide, herbicide.

**nitrodiphenyl**: Wood preservative; specific for poultry lice.

**4-nitrodiphenylamine** ($C_6H_5NHC_6H_4NO_2$): Fumigant.

**nitroethane** ($CH_2NO_2CH_3$): Fumigant.

**nitromethane** ($CH_3NO_2$): Fumigant.

**$\alpha$-nitronaphthalene**: Household insecticide.

**p-nitrophenol**: Wood preservative.

**1-nitropropane** ($CH_2NO_2CH_2CH_3$): Fumigant.

**2-nitropropane** ($CH_3CHNO_2CH_3$): Fumigant.

**nitrostyrene**: Fly larvicide.

**nitrotrichloro methane: See Chloropicrin.**

**nornicotine**: (β-pyridyl-α-pyrrolidine) ($C_9H_{12}N_2$): A commonly occurring alkaloid in tobacco, but because of low volatility and difficulty of recovery by steam distillation the insecticidal value was not recognized for many years.

**octachloro-camphene** ("Toxaphene") ($C_{10}H_{10}Cl_8$): Insecticide, apparently a mixture of isomers of octachloro-camphenes. Similar in action to DDT but with very adhesive residual films.

**1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane**: See **"Chlordan."**

**"Octa-Klor"**: See **"Chlordan."**

**oleic acid**: Insecticide; combined with sodium or potassium base to form soap.

**"Omilite"** (polyethylene polysulfide): Fungicide, used on grapes.

**8-oxyquinoline benzoate**: Fungicide and fungistat, used for "elm disease."

**paraffin oil**: See **petroleum oil.**

**paraformaldehyde** (polyoxymethylene): See **formaldehyde.**

**Paris Green**: See **copper acetoarsenite.**

**pentachloroethane** ($C_2HCl_5$): Soil fumigant.

**pentachloronitrobenzene**: Insecticide.

**pentachlorophenol** ($C_6Cl_5OH$): Wood preservative; herbicide.

**pepper, black**: Insecticide for stored product insects.

**peppermint oil**: Insectifuge.

**petroleum oil (crude, refined)**: See **Mineral oil.**

**phenazine** ($C_{12}H_8N_2$): Larvicide for European corn borer.

**phenazine oxide**: Insecticide; used against European corn borer.

**phenothiazine** (thiodiphenylamine) ($C_6H_4NHC_6H_4S$): Parasiticide; insecticide.

**phenothiazone**: Oxidation product of phenothiazine; insecticide.

**phenothioxin** (dibenzothioxin) ($C_{12}H_8OS$): Louse powder.

**phenoxathiin**: Insecticide.

**phenylacetonitrile**: Fly larvicide.

**phenyl benzoate**: Mite repellent.

**1-phenylbenzothiazole**: Larvicide.

**phenylchlorophenyltrichloroethane**: Insecticide.

**phenyl mercaptan**: Mosquito larvicide.

**phenylmercuri-2,2,2-nitrilotriethanol lactate**: Fungicide for dipping citrus fruit.

**phenyl mercuri triethanol ammonium lactate**: Turf fungicide.

**phenyl mercuric acetate**: Industrial fungicide.

**phenyl mercuric cyanamide**: See **Barbak C.**

**phenylmercuritriethanol ammonium chloride**: See **"Puratized agricultural spray."**

**phenyl mercury oleate**: Mildew preventive.

**phenyl mercury urea** ("Leytosan"): Seed disinfectant.

**4-phenylmorpholine**: Insecticide.

**o-phenyl phenol**: Mildew preventive.

**phenyl salicylate**: Mildew preventive.

**phenylthiourea**: Rodenticide.

**phenylurethane**: Fungicide for control of citrus fruit decay fungi; soluble in isopropyl alcohol, but not in water.
**phosphorus pentoxide**: Slug and snail remedy; ingredient of bait.
**phthalonitrile** (orthodicyanobenzene) [$C_6H_4(CN_2)_2$]: Insecticide.
**"Phygon"**: See **2,3-dichloro-1,4-naphthoquinone**.
**picric acid** (trinitrophenol): Fungicide.
**pine oil**: Insecticide; insectifuge.
**pine tar oil** (destructively distilled): Insecticide; fungicide; insectifuge.
**piperidine** ($C_5H_{11}N$). Insecticide.
**piperine**: Alkaloid found in black pepper; synergist for pyrethrum.
**piperonal** (3,4-methylene-dioxy benzaldehyde): Mosquito repellent.
**piperonyl butoxide** [butylcarbityl (6-propyl piperonyl) ether]: Insecticide used with pyrethrins. Technical product is impure and associated with related compounds.
**piperonyl cyclohexenone**: Insecticide used with pyrethrins in flea powders.
**polychlor**: Group name for the chlorinated hydrocarbons, including DDT, analogs, BHC, Chlordane, and Toxaphene.
**polyethylene polysulfide**: See **Omilite.**
**potassium ammonium selenosulfide** [$(KNH_4S)_5Se$]: Insecticide; used for spider mites.
**potassium cyanide** (KCN): Fumigant; insecticide; largely displaced by sodium cyanide.
**potassium fluoride** (KF): Wood preservative; fungicide.
**potassium fluosilicate** ($K_3AlF_6$): Insecticide; limited in use because of solubility.
**potassium permanganate** ($KMnO_4$): Fungicide.
**potassium polysulfides**: An ingredient of ointment for scab mite control.
**potassium sulfocarbonate** ($K_2CS_3 \cdot H_2O$): Soil fumigant used in France in the early campaign against the root aphid, *Phylloxera.*
**potassium xanthate** ($KS_2COC_2H_5$): Soil fumigant. Carbon disulfide is released by decomposition of the compound.
**propyl thiocyanate** ($CH_3CH_2CH_2SCN$): Insecticide; paralytic action.
**propylene chloride**: See **1,2-dichloropropane.**
**propylene dichloride** (1,2-dichloropropane): Insecticide.
**propylene glycol** [$CH_3 \cdot CH(OH) \cdot CH_2OH$]: Fungicide used in cosmetics.
**propylene oxide** ($C_3H_6O$): Fumigant used in sterilizing spices and as an insecticide.
**"Puratized agricultural spray"** (phenylmercuritriethanol ammonium chloride): Fungicide, used especially for apple scab.
**"Puratized N5E"**: See **phenylmercuritriethanol ammonium lactate.**
**pyrethrins**: **Pyrethrin 1,** ($C_{21}H_{30}O_3$); **Pyrethrin 2,** ($C_{22}H_{30}O_5$). Toxic extracts from pyrethrum flowers. Insecticide; fly sprays horticultural sprays and dusts.
**pyrethrum flowers**: Insecticide; powdered for use in insect powders and for extraction.
**pyridine** [$CH(CH \cdot CH)_2N$]: Insecticide.
**pyridyl mercuric chloride** ($C_5H_4NHgCl$): Textile fungicide.
**β-pyridyl-α-methyl pyrrolidine**: See nicotine.

**quassia** (bitterwood tree): Wood or bark of **Quassia amara.** Insecticide.
**quassin**: Extract of **Quassia amara.** Insecticide.

**quicksilver**: See **mercury.**

**8-quinolinol**: Fungicide; toxic to apple scab and blotch but this was largely lost in the field.

**8-quinolinol benzoate:** Specific used against "Dutch elm disease".

**quinosol**: Control of orange decay.

**rape-seed oil**: Fungicide used on plants.

**"Rothane"**: See **dichlorodiphenyldichloroethane.**

**ricinine**: Alkaloid derived from castor bean plant; synthetic ricinine (1,2-dihydro-4-methoxy-1-methyl-2-oxonicotinonitrile. Insecticide.

**"Rutgers 612"** (2-ethyl-1, 3-hexanediol): Insect repellent; mosquitoes, black flies, and other biting flies; mites (chiggers).

**ryania**: Ground wood of the tropical plant **Ryania speciosa**. Specific for European corn borer.

**sabadilla seed** (powdered): Insecticide.

**salicyanilide**: Mildew preventive.

**salicyl aldehyde** ($C_6H_4OHCOH$): Auxiliary fumigant with HCN.

**"Sanoseed"**: See **ethanol mercuric chloride.**

**"Santobane"**: See **DDT.**

**Scheele's green**: See copper arsenite.

**"Semesan"** (hydroxymercurichlorophenol): Seed disinfectant.

**sesamin** ($C_{20}H_{18}O_6$): Ingredient of fly sprays.

**silver chloride** (AgCl): Fungicide.

**silver chromate** ($Ag_2CrO_4$): silver oxide ($Ag_2O$); silver carbonate ($Ag_2CO_3$). Seed disinfectants.

**"Sinox"**: See **sodium dinitro-*o*-cresylate.**

**soap** (laundry, potassium, potassium fish oil, sodium oleate): Insecticide.

**sodium arsenate**: See dibasic sodium ortho-arsenate.

  **arsenite**: See **dibasic sodium ortho-arsenite.**

  **benzoate** ($NaC_7H_5O_2$): Fungicide; food preservative.

  **bisulfite** ($NaHSO_3$): Fumigant for fresh fruit; seed disinfectant.

  **chlorate** ($NaClO_3$): Herbicide.

  **4-chloro-2-methylphenoxyacetate**: Herbicide.

  **chloro-2-phenylphenate**: Fungicide.

  **chromate** ($Na_2CrO_4$): Fungicide; wood preservative.

  **cyanide** (NaCN): Fumigant; insecticide, warehouse, ship and citrus trees.

  **dinitro-*o*-cresylate** ("Sinox"): Insecticide; herbicide.

  **dinitrophenolate**: Insecticide.

  **ethyl mercurithiosalicylate**: Fungicide for dipping citrus fruits.

  **ethyl xanthate** ($C_2H_5O \cdot CS:SNa$): Soil fumigant.

  **fluoaluminate** (cryolite ($Na_3A_6F$,): Insecticide for general use on plants.

  **fluoride** (NaF): Insecticide; used in insect powders.

  **fluoroacetate** ("1080"): Rodenticide.

  **fluosilicate** (sodium silicofluoride) ($Na_2SiF_6$): Insecticide used on plants.

  **hypochlorite** (hydrated) ($NaClO \cdot 2\frac{1}{2}H_2O$): Fungicide.

**isopropyl xanthate**: Herbicide.

**metaborate** ($NaBO_2$): Fungicide for dipping citrus fruit.

**monosulfide** (sodium sulfide) ($Na_2S$): Insecticide; fungicide.

**orthophenylphenate**: Fungicide for dipping citrus fruit.

**pentachlorophenol**: Herbicide.

**pentaborate**: Herbicide.

**pentachlorophenate**: Fungicide for dormant applications.

**perborate** ($NaBO_3 \cdot H_2O$): Fungicide.

**o-phenylphenate**: Textile fungicide.

**selenate**: Insecticide for soil treatment of plants against spider mites and aphids.

**silicofluoride**: See **sodium fluosilicate.**

**sulfide**: See **sodium monosulfide.**

**xanthate** ($NaS \cdot CS \cdot OC_2H_5$): Soil fumigant.

**soluble sulfur**: Fungicide for general use.

**"Spergon"**: See **tetrachloro-*p*-benzoquinone.**

**squill, red** (sea onion): Rodenticide; fortified squill powder used in rat and mice baits.

**Stoddard solvent**: Refined petroleum fraction with boiling range of 150–200°C.

**strychnine** ($C_{21}H_{22}N_2O_2$): Rodenticide; used for rats and ground squirrels.

**strychnine sulfate** [$(C_{21}H_{22}N_2O_2)_2 \cdot H_2SO_4$]: Alkaloid combined with sulfuric acid. Rodenticide.

**styrene dibromide** ($\alpha$-$\beta$-dibromoethyl benzene): Insecticide used against corn earworm.

**sulfaguanidine**: Sterilant.

**1-sulfocyano-2,4-dinitrobenzene**: Insecticide.

**sulfur**(S): Fungicide; insecticide.

**sulfur dioxide** ($SO_2$): Fumigant, insecticide and fungicide.

**"Tanatox"**: See **trichlorochlorophenyl phenylethane.**

**tar, pine**: Fly repellent.

**TDE**: See **DDD.**

**"Ten Eighty"**: Sodium fluoroacetate; rodenticide.

**"Ten-six-eight"** ("Velsicol 1068") Also known as **"Chlordane"**: General insecticide.

**TEP**: See **tetraethyl pyrophosphate.**

*tert.* **butyl bromide**: Fumigant.

*tert.* **butyl valone**: Louse powder.

**tetrachloro *p*-benzoquinone** ("Spergon"; "Chloranil") ($C_6Cl_2O_2$): Seed disinfectant and protectant; fungicide.

**tetrachloroethane**: See **Acetylene tetrachloride.**

**tetrachloromethane**: See **Carbon tetrachloride.**

**tetrachloroquinone** ($C_6O_2Cl_4$): Fungicide; used as a protectant for citrus fruit.

**tetrachlororesorcinal**: Seed disinfectant.

**tetraethyl pyrophosphate** (TEP) [$O[PO(OC_2H_5)_2]_2$]: Insecticide similar to hexaethyl tetraphosphate, but hydrolyzes less rapidly in solution; also a fumigant.

**1,2,5,6-tetrahydro-*o*-methylbenzoic acid, 1,2,5,6-tetrahydro-*o*-methylbenzyl ester**: Mite repellent.

**tetramethylthiuram disulfide** ("Thiosan"): Fungicide; seed disinfectant.

**tetramethylthiuram monosulfide**: Insecticide.

**tetranaphthene** ($C_6H_3C_4H_7C_2H_4$): Insecticide.
**tetranitrocarbazole**: Insecticide.
**thallium acetate** ($TlC_2H_3O_2$): Insecticide, used in ant baits; rodenticide.
**thallium sulfate** ($Tl_2SO_4$): Insecticide, used in ant baits; rodenticide.
**"Thanite"** (fenchyl thiocyanoacetate): Insecticide; fly spray ingredient, activator of pyrethrum.
**thienyl-α-pyrrolidine**: Insecticide.
**thiocarbamosulfonamides**: Fungicide.
**thioacetamide**: Control of decay of orange.
***p*-thiocyanochlorobenzene** ($ClC_6H_4SCN$): Fumigant.
**β-thiocyanoethyl laurate**: Insecticide.
**thiocyanopropyl phenyl ether**: Insecticide.
**thiodiphenylamine**: Mosquito larvicide.
**"Thiosan"**(tetramethylthiuram disulfide): Fungicide.
**thiosemicarbazones**: Insecticide.
**thiourea** ($NH_2CSNH_2$): Insecticide.
**"Three-four-two-two"**: See **diethyl, nitrolphenyl thiophosphate**.
**tolyl mercury salicylate**: Mildew preventive.
***p*-toluene sulfonylamide**: Fungicide.
**"Toxaphene"**: See **octachloro-camphenes.**
**trichloroacetonitrile** (chlorocyanohydrin) [$CCl_3CH(OH)CN$]: Fumigant, house and warehouse.
**trichloroacetyl chloroethylamide**: Mosquito repellent.
**trichlorobenzene** ($C_6H_3Cl_3$): Insecticide; termite proofing.
**1-trichloro-2,2-bis(*p*-bromophenyl) ethane**: Bromine analog of **DDT**.
**1-trichloro-2,2-bis(*p*-chlorophenyl) ethane**: See **DDT.**
**1-trichloro-2,2-bis(*p*-fluorophenyl)ethane**: Fluorine analog of **DDT**.
**1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane** (DMDT) [(di(*p*-methoxyphenyl) trichloroethane: Methoxy analog of **DDT.**
**α,α,β-trichlorobutyramide** ($CH_3CHClCCl_2CONH_2$): Stomach insecticide used in the laboratory with medium success against the European corn borer.
**1-trichloro-2-(*p*-chlorophenyl)-2-phenylethane** [$(ClC_6H_5)\ (C_6H_5)\ CHCCl_3$].
**1,2,4-trichloro-3,5-dinitrobenzene**: Insecticide.
**1,1,2-trichloroethane**: Fumigant.
**trichloroethylene** ($C_2HCl_3$): Fumigant.
**trichloronitromethane**: See **chloropicrin.**
**trichlorochlorophenyl phenylethane**: Insecticide, used for aphids.
**2,4,5-trichlorophenol**: Seed disinfectant.
**2,4,5-trichlorophenoxyacetic acid**: Herbicide used on bindweed.
**triethylene glycol**: Volatile fungicide.
**2,4,4′-trinitrodiphenylamine** [$C_6H_3(NO_2)_2NHC_6H_4NO_2$]: Insecticide tested against codling moth larva, slightly superior to lead arsenate.
**triphenyl-3,4-dichlorophenyl phosphonium chloride**: Moth repellent.
**"Two, Four, D"**: See **2,4-dichlorophenoxyacetic acid.**

**"Velsicol 1068"**: See **"Chlordan."**
**veratridine** (alkaloid-active principle of sabadilla seed): **Insecticide.**

**wintergreen oil**: Insectifuge.
**wood tar acid**: Herbicide, fungicide, insecticide.
**wood tar oil**: Fungicide; insecticide.

**xanthene**: Insecticide; used against screwworm larvae.
**xanthone** (benzophenone oxide) [$(C_{13}H_8O_2)\cdot CO, (C_6H_4)_2O$]: Insecticide.
**xanthydrol**: [$HCOH(C_6H_4)_2O$]: Ovicide of body louse.
**2,6-xylenol** [$(CH_3)_2C_6H_3OH$]: Fumigant.
**xylidene acetate** [$(CH_3)C_6H_3NH_2\cdot CH_3COOH$]: Insecticide.

**"Zerlate"** ("Zimate"). See **Zinc dimethyl dithiocarbamate.**
**zinc arsenate** ($5ZnO\cdot 2As_2O_5\cdot 4H_2O$): Insecticide, used on plants of hardy foliage.
**zinc arsenite**: See **Zinc meta-arsenite.**
**zinc borate** ($ZnBO_3$): Fungicide, for textile treatment.
**zinc chloride** ($ZnCl_2$): Disinfectant for pear blight.
**zinc chromate** ($ZnCrO_4$): Fungicide, used on truck crops.
**zinc dimethyl dithiocarbamate** ("Zerlate"): Seed disinfectant; fungicide.
**zinc dithiocarbamate** ("Zerlate"): Fungicide used for late blight of tomatoes.
**zinc ethylene bisdithiocarbamate**: Fungicide (control potato blight).
**zinc fluoride** ($ZnF_2$): Wood preservative.
**zinc hydroxide** [$Zn(OH)_2$]: Seed disinfectant and protectant.
**zinc mercaptobenzothiazole**: Fungicide.
**zinc metaarsenite** [$Zn(AsO_2)_2$]. Wood preservative.
**zinc naphthenate**: Mildew preventive.
**zinc oxide** ($ZnO$): Seed disinfectant.
**zinc phosphide** ($Zn_3P_2$): Rodenticide used as a substitute for strychnine and thallium sulfate.
**zinc 2,4,5-trichlorophenate**: Seed disinfectant.
**zinc sulfate** ($ZnSO_4\cdot 7H_2O$): Fungicide, supplementing copper for citrus treatments.

# Glossary

**Bordeaux mixture 5–5–100.** Five pounds of copper sulfate, 5 pounds of hydrated or burnt lime to make 100 gallons of spray mixture.

**Burgundy mixture.** A mixture of copper sulfate and sodium carbonate.

**Copper-lime dust, 20–80.** An intimate mixture of 20 pounds of monohydrated copper sulfate and 80 pounds of hydrated lime.

**Emulsive petroleum oil.** One to which an oil soluble emulsifier has been added.

**Fungicide.** Lethal in action.

**Fungistatic.** Preventing growth of fungus and spore.

**Genestatic.** Preventing sporulation or fruition.

**LD 50.** The lethal dose for 50 per cent of the spores or insects under experimentation.

**Mass Median diameter.** Designates the diameter that is the boundary between the coarser and the finer half of the sample by weight (mass). It is measured by sieves without the application of a shape factor.

**Rotenoids.** Organic compounds structurally related to rotenone which occur principally in the semi-tropical plants, *Derris*, *Lonchocarpus* and *Tephrosia*. Rotenoid examples include sumatrol, elliptone and laevodegulin.[113]

**Solubilizer.** A mutual solvent which in very small amounts produces a stable colloidal solution of insoluble or slightly soluble materials. Used in connection with solutions of toxicants in petroleum oil fractions.

**Synergism.** An increase in toxicity, resulting from the combined use of two forms of chemicals, greater than the simple additive effects of the two chemicals.

**Unsulfonated residue.** That portion of petroleum oil which remains unaffected by treatment with sulfuric acid (37N $H_2SO_4$) according to standard methods. Used to indicate that fraction of petroleum oil of decided plant tolerance.

"**Flammable Liquid.** An inflammable liquid is any liquid which give off inflammable vapors (as determined by flash point from Tagliabue's open-cup tester, as used for test of burning oils) at or below a temperature of 80°F."

"**Dusts.** Solid particles generated by handling, crushing, grinding, rapid impact, detonation and decrepitation of organic or inorganic materials such as rock, ore, metal, coal, wood, grain, etc. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse in air but settle under the influence of gravity."

"**Fumes.** Solid particles generated by condensation from the gaseous state, generally after volatilization from molten metals, etc., and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce."

"**Mists.** Suspended liquid droplets generated by condensation from the gaseous to the liquid state or by breaking up a liquid into a dispersed state, such as by splashing, foaming and atomizing."

"**Gases.** Normally formless fluids which occupy the space of enclosure and which can be changed to the liquid or solid state only by the combined effect of increased pressure and decreased temperature. Gases diffuse."

"**Vapors.** The gaseous form of substances which are normally in the solid or liquid state and which can be changed to these states either by increasing the pressure or decreasing the temperature alone. Vapors diffuse."

"**Poison.** Poison means a substance which, when taken by mouth in amounts of 60 grains (4 grams) or less, or when inhaled in concentrations of less than 200 parts per million by volume in the air, rapidly (within 5 or 10 minutes) jeopardizes life by other than mechanical or physical action."*

*Manufacturing Chemists Assoc. of U. S, Washington, D. C., "Warning Labels" (1946).

# Legal Requirements Covering the Manufacture and Sale of Insecticides and Fungicides

Early insecticide laws in the United States were devoted largely to the standardization and purity of Paris Green (copper aceto-arsenite). A compilation of state laws published in 1903* shows six states with statutes formally establishing standards of purity for this widely used insecticide and generally providing for the assembling and analysis of a number of other insecticides. The State of New York was one of the earliest to frame an insecticide law in 1898, and was followed quickly by Oregon, California, Louisiana and Washington. In addition, provisions were being made for the registration of manufacturers' guarantees and for the detection of adulterated materials. With the increased demand for accurate statements of ingredients, as a means of protecting the public, the Federal Insecticide Act was approved April 26, 1910, effective Jan. 1, 1911. This law, commonly known as the "Insecticide Act of 1910", was the basis for Federal action in the supervision of manufacturing and distribution of insecticides and fungicides. Regulations interpreting the Act were released as occasion demanded.

The "Federal Insecticide, Fungicide, and Rodenticide Act", superseding the "Insecticide Act of 1910", was passed in 1947. This Act, among other provisions, establishes the legal definition of "Economic Poisons" as any substance used against insects, fungi, weeds, and other pests. "Rodenticide" refers to substances used against rodents or other vertebrate animals listed as pests. "Labeling" refers not only to the attached label but also to literature referring to the label which may accompany the economic poison.

Provision is made for coloring or discoloring white powders such as the arsenicals, certain fluorine compounds or other substances required to be colored or discolored. Registration of economic poisons in interstate commerce is also required. The restrictions on the sale of broken or unsealed containers, as found in a number of state laws, is included in the new Federal Act. This is helpful both to the manufacturer and to the public in the sale of materials of guarateed quality. By contrast, "bulk sales" permits the dealer to retail from a wholesale size package, thus greatly increasing the possibility of fraud or adulteration.

In addition to the Insecticide, Fungicide, and Rodenticide Act, insecticides are subject to the following Federal regulations:

Interstate Commerce Commission Regulations for Transportation of Explosives and Other Dangerous Articles.

Federal Caustic Poison Act and Regulations: Food and Drug Administration, Federal Security Agency.

Agricultural Marketing Administration, U. S. Department of Agriculture.

Federal Food and Drug and Cosmetic Act and Regulations: Food and Drug Administration, Federal Security Agency.

U. S. Post Office Regulations.

Abstracts of the latter and of the Interstate Commerce Commission Regulations, as illustrative of their application to the shipping of insecticides, are appended:

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* Haywood, J. K., U. S. Dept. Agr. Bur. Chem. Bull. 76, 1903.

## Interstate Commerce Regulations (1941) for Transportation of Explosives and Other Dangerous Articles by Freight

### Regulations, Specifications and Supplements

### (Abstracts of Regulations Pertaining to Typical Insecticides)

**Arsenate,** Calcium and Lead, Paris Green, and arsenical mixtures.

Specification 44B. Paper Bags. Bags must be at least 4 thicknesses of No. 1 Kraft bag paper or equivalent with a minimum total basis weight of 200 pounds.

Regulated closure of top and bottom.

Net weight not over 50 pounds each. For carload and truckload shipments. Smaller packages are packed inside fiber cartons, cans or boxes.

**Sodium Arsenite, Liquid.**

Glass or earthenware containers not over 1 gallon capacity.

Specifications 5, 5A, and 5B. Steel Barrels or Drums.

Regulated closure.

Specifications 17C, 17D and 17E. Metal drums (single trip containers).

**Carbon disulfide** (Carbon Bisulfide)

Specifications 15a, 15B, 15C, 16a or 19a. Wooden boxes with inside metal containers; or with glass or earthenware containers not over 5 pints capacity each.

Specification 17E. Metal drums (single trip) not over 5 gallon capacity each.

Specification 5, 5A, or 17C (single trip). Metal barrels or drums not over 55 gallons capacity each.

Tank cars.

Carbon disulfide (bisulfide) must not be offered for transportation by *rail express*.

**Chlorates, potash, soda.** Inflammable solids, and oxidizing materials in inner containers not over 1 pound weight each in outside containers not exceeding 25 pounds weight are exempt from specification packaging and labeling requirements for transportation by rail freight, highway or by carrier by water.

Specification 6A, 6B, or 6C (returnable). Metal barrels or drums.

Specification 17E, 37D, 37E, or 37F (single trip). Metal drums.

Specification 21A, 22A, or 22B. Fiber or plywood drums with inside metal drums, Specification 2F.

**Cyanides, Sodium, Potassium** or **Cyanide Mixtures.**

Specification 15A, 15B, or 15C. Wooden boxes with metal inside containers, Specification 2F, not over 25 pounds capacity each; or hermetically sealed (soldered) metal lining.

Specification 2F, or in glass bottles not over 5 pounds capacity each.

Specification 5, 5A, 5B, 6A, 6B, or 6C. Metal barrels or drums.

Specification 37H. Metal drums (single trip container), made watertight; hermetically sealed (soldered) when used for calcium cyanide.

**Hydrocyanic acid** (prussic acid).

Specification 33 or 3D. Packed in metal cylinders of not over 125 pounds water capacity. Gaskets renewed for each shipment. Service pressure must be 480 pounds per square inch.

Regulated construction and valves. *Not accepted for transportation by railway express.*

**Mercury compounds, solid.** In tightly closed inside containers securely cushioned. In inside glass, earthenware or metal containers or sliding lid wooden boxes of not over 5 pounds capacity or fiber cartons of not over 1 pound capacity and packed in wooden or fiberboard boxes.

Specification 5, 5A, 5B, 6A, 6B, or 6C. Metal barrels or drums.

Specification 10A, 10B, or 10C. Wooden barrels, or kegs lined with creped-paper bag, Specification 2J.

Specification 11A. Wooden barrels or kegs, tongue and grooved, net weight of contents not over 115 pounds each.

**Methyl Bromide.** Specification 3A300, 3B300, or 4B300.

Metal cylinders of not over 125 pounds water capacity. Regulated valves.

Specification 15A, 15B, 15C, 16A, 19A, or 12B. Wooden, wirebound wooden, or fiberboard boxes with inside metal cans containing not over 1 pound each.

**Nicotine, liquid.** Glass or earthenware containers not over 1 quart capacity each or in metal containers not over 1 gallon capacity each, packed in strong outside wooden boxes or barrels.

Specification 5, 5A, or 5B. Metal barrels or drums.

Specification 17C, or 17E. Metal drums (single trip containers).

Specification 10A, 10B, or 10C. Wooden barrels or kegs. Linings as prescribed in the regulations.

**Strychnine.** Similar to Mercury compounds.

**Thallium salts,** solid. Similar to Mercury compounds.

The label designs shown illustrate the requirements for various types of insecticides, fungicides, and rodenticides, including poison labels (red on white background), inflammable (red), non-inflammable (green), oxidizables and explosives (yellow), and acid (white). See pages 298, 299 and 300.

In addition to the labels required by legal regulations a guide to the preparation of a series of labels for hazardous chemicals has been developed by the Manufacturing Chemists Association of the United States, Washington, D. C., 1946.

### United States Postal Regulations* (Abstract)

Section 588. All kinds of poisons and all articles and compositions containing poison . . . and explosives of all kinds, and inflammable materials and all materials or articles which may kill, damage or injure the mails or other property . . . are hereby declared to be nonmailable or delivered from any Post Office.

Exceptions: 4. (b) Insecticides, fungicides and germicides not outwardly or of their own force dangerous or injurious to life, health, or property and not in themselves unmailable (sec. 569 and 598), shall be admitted to the mails when securely packed for safe transmission: *Provided*, that the container of the article mailed is plainly labeled to show its contents, is also marked "Poisonous Composition", and bears the label or superscription of the manufacturer thereof.

Poisonous preparations, such as raticides . . . are not mailable.

(c) Poisonous drugs and medicines . . . which are not outwardly or of their own force dangerous or injurious to life, health or property and not otherwise unmailable . . . when securely packed for safe transmission shall be admitted to the mails . . . when sent by the manufacturer thereof or dealer therein to licensed physicians, dentists, druggists . . . and veternarians, when addressed as such: *Provided*, That the container of the article mailed is plainly labeled to show its contents, is marked "Poison", and bears the label or superscription of the manufacturer . . .

Section 590. (f) Insecticides, fungicides and germicides, when accepted for mailing, must be inside containers of metal, glass or fiber cans or boxes and in outside containers of metal, wood, or fiberboard, tightly closed and securely fastened. . . Liquids must not only be surrounded with sufficient absorbent material to absorb all the liquid should the container be broken but packed in cushioning material. . . Solids or powders must be surrounded by cushioning material.

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* Edition 1940. The complete file of regulations should be consulted.

WARNING

POISON

CAUTION—DO NOT DROP

IF LEAKING DON'T BREATH FUMES
TOUCH CONTENTS
SWALLOW

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for transportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required hereon for shipments by EXPRESS

*red on white background*

Keep
AWAY
From FIRE,
HEAT and OPEN-flame
LIGHTS

CAUTION

Sweep Up and Remove Carefully
the Contents of Broken Packages

DO NOT DROP

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for transportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required hereon for shipments by EXPRESS

*yellow background*

Labels conforming to Interstate Commerce Commission Regulations.

**KEEP COOL**

**CAUTION**

Name of Contents

**Non-Inflammable---Compressed Gas**

**DO NOT DROP**

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for transportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required
hereon for Ship-
ments by
EXPRESS

*green background*

**Keep**
**AWAY**
**From FIRE,**
**HEAT and OPEN-flame**
**LIGHTS**

**CAUTION**

**LEAKING Packages Must be Removed to a Safe Place**

**DO NOT DROP**

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for transportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required
hereon for ship-
ments by
EXPRESS

*red background*

Labels conforming to Interstate Commerce Commission Regulations.

**WARNING!**

**BEWARE OF FUMES**

**POISON GAS**

Name of Contents

**CAUTION - KEEP COOL - DO NOT DROP**

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for tansportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required hereon for shipments by EXPRESS

*red on white background*

**Remove**
**LEAKING Packages**
**Wash Acid Off with Water**

**CAUTION**

**ACID** DO NOT DROP

**Do not load with Explosives or near articles bearing YELLOW labels**

This is to certify that the contents of this package are properly described by name and are packed and marked and are in proper condition for transportation according to the Regulations prescribed by the Interstate Commerce Commission.

Shipper's name required hereon for shipments by EXPRESS

*white background*

Labels conforming to Interstate Commerce Commission Regulations.

# *Official Antidotes**

## General Instructions

In case of poisoning call a physician or an emergency hospital immediately.

### Removal of Poisons

If patient is vomiting do not give an emetic but give large amounts of warm water, then follow specific directions suggested. If an emetic is needed—GIVE SODIUM CHLORIDE 15 GM. (ONE-HALF OUNCE) IN GLASS OF WARM WATER AND REPEAT UNTIL VOMIT FLUID IS CLEAR. Gentle stroking or a touching of the throat with the finger or a tongue depressor will aid in inducing vomiting when the stomach is full of fluid.

An emetic of one to three teaspoonsful of powdered mustard in a glass of warm water may also be used. Apomorphine hydrochloride, 5 mgm. (1/12 grain), injected hypodermically, may be used with care. Caution: Do not use in morphine poisoning.

An emetic should not be given after poisoning by corrosive acids or caustic alkalies, since perforation of an eroded esophagus or stomach may occur.

### "Universal Antidote"

Activated Charcoal 2 parts, Magnesium Oxide 1 part, Tannic Acid 1 part, in a mixture, and given as 15 Gm. (½ ounce) in a half glass of warm water may be used to adsorb or neutralize poisons. This mixture is useful in poisoning by acids, alkaloids, glycosides, and the heavy metals. Except after corrosive substances it is to be followed by gastric lavage or an emetic. Gastric Lavage (cleansing the walls of the stomach by injections with the stomach tube).

The "Universal Antidote" or a specific antidote should be administered orally with water before the tube is passed. With the tube in place a lavage fluid is introduced, then the funnel end is lowered to siphon off the contents, being assisted by compression and stripping of the tube toward the funnel end. The washing should be repeated, finally leaving a small quantity, about 60 cc. (2 fluid ounces) of the lavage solution in the stomach. Warm water or a teaspoonful of sodium chloride to a pint of warm water may be used for lavage. For an alkaline wash a 5% sodium bicarbonate solution may be used. One of the most effective solutions for oxidizable poisons is potassium permanganate solution, 1:1000 for adults and 1:2000 for children. This solution keeps well and can be used in the recommended amounts without concern as to toxicity.

The stomach tube should not be used after poisoning by corrosive acids or caustic alkalies, since perforation of an eroded esophagus or stomach may occur.

### Demulcents

1. Mucilaginous
   (a) Raw egg white mixed with water
   (b) Gelatin, 10 to 20 Gm. dissolved in a pint of warm water
2. Fatty
   (a) Butter
   (b) Olive or salad oil
   (c) Cream or milk
3. Starchy
   (a) Mashed potatoes
   (b) Flour and water
   (c) Cornstarch

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* Calif. St. Bd. Pharmacy, Official Antidotes, 1948. (*Selected Subjects*).

### General Methods to Prevent Collapse

1. Cover with a light blanket. Do not use a hot water bottle.
2. Raise foot of bed. Apply elastic binders to arms and legs.
3. Give strong tea or coffee. Tea is useful for children.
4. Hypodermic injection of stimulants—caffeine, epinephrine.
5. Fluid administration—dextrose 5% intravenously.
6. Blood or plasma transfusion.

Do not exhaust patient by too much or too vigorous treatment.

### Artificial Respiration

Avoid harmful forced methods of artificial respiration. Use inhalation apparatus with face mask and rubber balloon to provide a rhythmic intake of oxygen at about 20 inspirations per minute or place patient on a stretcher or board supported in center and rock at 45 degree angle at the same rate. As an alternate method, apply gentle pressure on lower ribs intermittently, with head turned toward the side and supported by the arm. Keep air passages open. Avoid vigorous application of pressure to the chest. Rectum may be dilated manually to stimulate respiration. The procedures described are less harmful and more effective than the use of the pulmotor.

## Antidotes for the Common Poisons

**Acids, Corrosive** (Acetic, Hydrochloric, Muriatic, Lactic, Nitric, Phosphoric, Sulfuric)

External: Flood with water, then cover with moistened sodium bicarbonate. If eyes are involved wash first with water, then with 1 per cent solution of sodium bicarbonate (freshly prepared).

Internal: Do not use emetics, stomach tube, carbonates or bicarbonates. Give at least 20 to 30 cc. (⅔ to 1 ounce) of milk of magnesia or preferably aluminum hydroxide gel well diluted with water. If these alkalies are not available, the whites of eggs (2 or 3) well beaten may be used. Give large quantities of water. Prevent collapse.

**Alkalies, Caustic** (Lye, Soda, Soda Ash, Sodium Carbonate, Sodium Hydroxide, Potassium Hydroxide.)

External: Flood with water, then wash with vinegar or if eyes are involved, wash with saturated boric acid solution or normal saline solution.

Internal: Do not use emetics or stomach tube. Give vinegar 15 to 30 cc. (1½ to 1 ounce) in a large quantity of water. Diluted orange or lemon juice is useful. Follow with demulcent. Patient should not be left alone for 24 hours, because of danger of collapse.

**Alkaloidal Poisons** (not specifically covered)

Give "Universal Antidote," then gastric lavage with 240 cc. (8 ounces) of potassium permanganate solution 1:1000, leaving 60 cc. (2 ounces) in the stomach. Have patient lie down and keep warm. Combat collapse by giving warm stimulating drinks such as strong tea or coffee.

**Antimony Compounds**: Same as for Arsenic Compounds (notably Tartar Emetic)

**Arsenic Compounds and Preparations** (Arsenious Acid, White Arsenic, Fowler's Solution, certain insect and rodent poisons, such as Ant Pastes, Paris Green, "Rough on Rats," Snail Baits, etc.)

Give "Universal Antidote," followed by gastric lavage with 240 cc. (8 ounces) of 5% sodium bicarbonate solution diluted to 1 liter (1 quart) with warm water, Magnesium sulfate 30 Gm. (1 ounce). Force fluids.

Dimercaprol (BAL) is indicated except in presence of known liver damage. A 10 per cent solution in oil is available for intramuscular injection only. The recommended dose is 0.25 cc. (4 minims) per 10 kg. (22 pounds) of body weight, repeated four times at 4 hourly intervals during the first day, and once daily for the following 6 days. Minor toxic reactions consisting of nausea associated with aches and pains may occur. Experimental evidence indicates this antidote may also be effective for other heavy metals, such as antimony, bismuth, lead, mercury, and zinc.

**Barium Compounds Soluble in Water**

Give magnesium sulfate or sodium sulfate, 15 to 30 gm. (½ to 1 ounce) in water. Emetic of mustard. Demulcent drinks and aromatic spirit of ammonia in water.

**Benzene and Derivatives** (Benzol, Toluene, Toluol, Xylene, Xylol)

If inhaled, promptly remove from exposure; 5% carbon dioxide in oxygen inhalation or artificial respiration, if necessary.

If swallowed, give gastric lavage with 240 cc. (8 ounces) of 5% sodium bicarbonate solution diluted to 1 liter (1 quart) with warm water, or give an emetic. Blood transfusion in severe cases. Later, folic acid, 15 mgm. (¼ grain) intravenously, or liver extract (5 to 10 cc.) intramuscularly with a high caloric diet.

**Bichloride of Mercury**: See **Mercury Compounds**

**Bitter Almonds, Oil of**: See **Cyanides**

**Blue Stone, Blue Vitriol**: See **Copper Compounds**

**Boric Acid and Soluble Borates**

Give gastric lavage with 240 cc. (8 ounces) of 5% sodium bicarbonate solution diluted to one liter (1 quart) with warm water. Normal saline solution 1 liter intravenously, or preferably Ringer's solution U.S.P. 1 liter intravenously. Promote diuresis with sodium citrate 1 Gm., (15 grains) repeated as necessary.

**Carbon Disulfide** (Carbon Bisulfide, certain rubber solvents.)

If inhaled, promptly remove from exposure and give 5% carbon dioxide in oxygen or artificial respiration if necessary. If swallowed, give 120 cc. (4 ounces) of liquid petrolatum, then gastric lavage with large quantities of warm water. Hot tea or coffee, caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously.

**Carbon Tetrachloride and Tetrachloroethylene** (Non-inflammable cleaning fluids, fire extinguisher fluids, certain hookworm remedies.)

If inhaled, promptly remove from exposure and give 5% carbon dioxide in oxygen or artificial respiration if necessary. If swallowed, give 120 cc. (4 ounces) liquid petrolatum, then gastric lavage with large quantities of warm water. Calcium gluconate, 5 to 10 Gm. (1¼ to 2½ drams) intramuscularly or intravenously. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. Later, treatment for liver damage. Methionine or choline 2 Gm. (30 grains) by mouth every 2 hours with high carbohydrate diet. Blood transfusion if needed.

**Chlorates Soluble in Water** (Potassium Chlorate, certain dentifrices, gargles, mouthwashes)

Give sodium chloride 15 Gm. (½ ounce) in a glass of warm water and repeat until vomiting occurs. Give milk or white of eggs beaten with water. Give gastric lavage with large quantities of warm water. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm.(7 ½ grains) subcutaneously or intravenously. Keep patient warm and treat as for potential nephritis, giving alkaline salts and milk diet.

**Chloroform.**

Same as for **Carbon Tetrachloride** and **Tetrachloroethylene.**

**Copper Compounds Soluble in Water** (Copper Acetate, Copper Sulfate, Blue Stone, Blue Vitriol)

Lavage with large quantities of water, preferably containing 30 cc. (1 ounce) of milk of magnesia. Give milk or white of eggs beaten with water as a demulcent. Give potassium ferrocyanide, 0.5 Gm. (7½ grains) in water.

**Corrosive Sublimate**: See **Mercury Compounds**

**Creosote** and **Cresols**: See **Phenols**

**Cyanides**: Soluble in Water, Including Hydrocyanic Acid. (Calcium Cyanide, Potassium Cyanide, Silver Cyanide, Sodium Cyanide, Oil of Bitter Almonds, certain fumigating agents)

Speed in giving the antidote treatment is essential. Give amyl nitrate inhalation. Then inject intravenously 10 cc. (2½ drams) of 3% sodium nitrite solution at the rate of 2½ to 5 cc. (½ to 1¼ drams) per minute, then inject intravenously 50 cc. (1⅔ ounces) of 25% sodium thiosulfate solution. (Caution: Avoid circulatory failure.) As an alternate treatment, inject intravenously 50 cc. (1⅔ ounces) of 1% methylene blue in 1.8% sodium sulfate solution. If cyanide was swallowed, gastric lavage with 5% sodium thiosulfate solution should be carried out along with either injection procedure. 5% carbon dioxide in oxygen or oxygen inhalation or artificial respiration if necessary. If signs of poisoning reappear, injection of the solutions should be repeated, using one-half the original doses.

**DDT: Dichlorodiphenyltrichloroethane**

Give "Universal Antidote," followed by gastric lavage. Magnesium sulfate 30 Gm. (1 ounce) in water as a cathartic and force fluids. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. Calcium gluconate 10 cc. (2½ drams) of 10% solution intravenously for incoordination and tremors or pentobarital sodium 0.1 Gm. (1½ grains) intravenously if necessary. For prevention of liver damage, high carbohydrate and calcium diet.

**Digitalis, Derivatives and Preparations**

Give "Universal Antidote" followed by gastric lavage with warm water. 5% carbon dioxide in oxygen inhalation or artificial respiration if necessary.

**Dinitronaphthol**: Same as for Dinitrophenol

**Dinitro-Ortho-Cresol**: Same as for Dinitrophenol

**Dinitrophenol**

Gastric lavage with 5% sodium bicarbonate solution. Give two tablespoonsful of Epsom salt in water as a cathartic and force fluids. Immerse patient in cold bath to reduce body temperature. Normal saline solution, 1 liter (1 quart) intravenously. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. Oxygen inhalation for cyanosis.

**Ether**

If inhaled, promptly remove from exposure. Give 5% carbon dioxide in oxygen inhalation or artificial respiration, if necessary. If swallowed, give sodium chloride 15 Gm. (½ ounce) in a glass of warm water and repeat until vomit fluid is clear. Give aromatic spirit of ammonia, 4 cc. (1 teaspoonful) in water. Caffeine with sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously.

**Fluorides Soluble in Water** (Insect and rodent poisons)

Give gastric lavage with lime water or 1% calcium chloride solution. Give 10 cc. (2½ drams) of 10% calcium gluconate solution intramuscularly. 5% carbon dioxide in oxygen inhalation or artificial respiration if necessary. Demulcent drinks and external heat.

**Formaldehyde Solution** (Formalin)

Give aromatic spirit of ammonia 8 cc. (2 teaspoonsful) in water, then sodium chloride 15 gm. (½ ounce) in a glass of warm water and repeat until vomit fluid is clear. Give milk or white of eggs beaten with water.

**Fowler's Solution**: See **Arsenic**

**Gasoline or Kerosene**: Same as for **Carbon Disulfide**

**Hydrocyanic Acid**: See **Cyanides**

**Kerosene**: Same as for **Carbon Disulfide**

**Lead Compounds Soluble in Water**: Same as for **Barium** (Lead Acetate, Sugar of Lead)

**Mercury Compounds** (Antiseptic Tablets, Bichloride of Mercury, Corrosive Sublimate, Mercuric Chloride, Mercuric Cyanide, Mercuric Oxide, Red Precipitate, White Precipitate.)

Give "Universal Antidote" followed by gastric lavage with 5% sodium formaldehyde sulfoxylate solution, allowing a small amount to remain in the stomach. Inject 100 cc. to 200 cc. (3⅓ to 6⅔ ounces) of freshly prepared 5% to 10% sodium formaldehyde sulfoxylate solution intravenously. For later treatment give sodium citrate 1 to 4 Gm. (15 to 60 grains) every 4 hours by mouth. Give high colonic irrigation with 1% sodium formaldehyde sulfoxylate solution. Calcium gluconate 10 cc. (2½ drams) of 10% solution intrasmuscularly or intravenously for muscle spasm. See **Dimercaprol** under **Arsenic**.

**Metaldehyde** (Certain Snail Baits)

Give sodium chloride 15 Gm. (½ ounce) in a glass of warm water and repeat until vomit fluid is clear. Then give magnesium sulfate 30 Gm. (1 ounce) in water. Have patient lie down and keep warm. Give strong tea or coffee or aromatic spirit of ammonia, 4 cc. (1 teaspoonful) in water.

**Moth Balls**: See **Naphthalene**

**Naphthalene** (Moth Balls)

Give sodium chloride 15 Gm. (½ ounce) in a glass of warm water and repeat until vomit fluid is clear. Demulcent drinks such as milk or white of eggs beaten with water. Have patient lie down and keep warm. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) intramuscularly.

**Nicotine, Derivatives** or **Preparations** (Nicotine Sulfate, "Black Leaf 40", certain garden sprays and insecticides)

Give "Universal Antidote" followed by gastric lavage of 240 cc. (8 ounces) of potassium permanganate solution 1:1000 leaving 60 cc. (2 ounces) in the stomach. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. 5% carbon dioxide in oxygen inhalation or artificial respiration if necessary.

**Nux Vomica Derivatives** or **Preparations** (Strychnine)

Give "Universal Antidote" followed by gastric lavage with 240 cc. (8 ounces) of potassium permanganate solution 1:1000, leaving 60 cc. (2 ounces) in the stomach. Pentobarbital sodium 0.1 gm. (1½ grains) may be given intravenously. Do not use morphine or derivatives.

**Ortho-Dinitrocresol**: Same as for **Dinitrophenol**

**Para-Dichlorobenzene**: Same as for **DDT**

**Paris Green**: See **Arsenic**

**Phosphorus**, or **Preparations** (Certain fireworks, matches, rat pastes)

Give copper sulfate 0.3 Gm. (5 grains) in water, which must be followed by gastric lavage with 1 liter (1 quart) of 1% sodium bicarbonate solution. Give 120 cc. (4 ounces) of liquid petrolatum as a demulcent. Do not use animal or vegetable fats or oils. Later, treatment for liver damage with high carbohydrate diet.

**Potassium Chlorate**: See **Chlorates**

**Potassium Cyanide**: See **Cyanides**

**Roach Powders**: See **Fluorides**

**Rodent Poisons**: See **Arsenic, Phosphorus** or **Thallium**

**Sheep Dip**: See **Phenols**

**Sodium Cyanide**: See **Cyanides**

**Sodium Hydroxide**: See **Alkalies, Caustic**

**Squill**: Same as for **Digitalis**

**Strychnine**: See **Nux Vomica**

**Sulfur Dioxide**

Remove promptly from exposure. 5% carbon dioxide in oxygen inhalation or artificial respiration if necessary. Normal saline solution, 1 liter (1 quart) intravenously. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. Epinephrine 0.5 cc. (7½ minims) of 1:1000 solution subcutaneously for bronchial spasm. If evidence of acidosis, give sodium r-lactate (1.87%) intravenously to restore plasma carbon dioxide combining power.

**Tartar Emetic**: See **Antimony**

**Tetrachloroethylene**: See **Carbon Tetrachloride**

**Thallium Compounds** (Certain Rodent Poisons, "Thalgrain")

Give gastric lavage with a 1% sodium iodide solution. For shock, an intravenous injection of 50 cc. (2 ounces) of 50% dextrose solution may be given. Hot tea or coffee, or caffeine sodium benzoate 0.5 Gm. (7½ grains) subcutaneously or intravenously. Later, treatment to control mobilization of thallium. Daily intravenous injection of 10 cc. (2½ drams) of 10% sodium iodide solution until daily urine test shows absence of thallium. When symptoms subside, thallium elimination may be increased by intravenous injection of 10 cc. (2½ drams) of 10% sodium thiosulfate solution. Give dilute hydrochloric acid by mouth for achlorhydria. Treat for liver injury and nephritis if necessary.

**Toluene, Toluol**: See **Benzene.**

**Xylene, Xylol**: See **Benzene.**

**Zinc Compounds Soluble in Water** (Zinc Acetate, Zinc Chloride, Zinc Sulfate)

Give a teaspoonful of dibasic sodium phosphate in water, followed by sodium chloride 15 Gm. (½ ounce) in a glass of warm water and repeat until vomit fluid is clear. Have patient lie down and keep warm. Give strong tea or coffee or aromatic spirit of ammonia, 4 cc. (1 teaspoonful) in water. Give milk or white of eggs beaten with water. See **Dimercaprol** under **Arsenic.**

## A.S.T.M. Standards

Sieve Mesh Sizes in Microns

| Sieve No. | Screen Mesh Size (microns) |
|---|---|
| 10 | 2000 |
| 20 | 840 |
| 50 | 297 |
| 100 | 149 |
| 120 | 125 |
| 140 | 105 |
| 170 | 88 |
| 200 | 74 |
| 230 | 62 |
| 270 | 53 |
| 325 | 44 |
| 400 | 37 |

U. S. Standard (ASTM E 11–39) for Testing Sieves.

U. S. Bureau of Standards Sieve Series and Equivalents.

The following standards, bearing on insecticides, have also been established.

| | |
|---|---|
| Petroleum Products and Lubricants | 1946 |
| Petroleum, Terms Relating to | D 288–39 |
| Aniline Point, Test for (Tentative) | D 611–46 T |
| Distillation of Gas and Fuel Oil, Test for. | D 158–41 |
| Distillation of Plant Spray Oils, Test for | D 447–41 |
| Unsulfonated Residue of Plant Spray Oils, Test for. | D 483–40 |
| Viscosity Index, Method for Calculating | D 567–41 |

# Conversion Tables and Equivalents; Volume and Linear*

## WEIGHT TABLES

### *United States Avoirdupois Weight*

$27\frac{11}{32}$ grains (gr.) = 1 dram (dr.)
16 drams = 1 ounce (oz.)
16 ounces = 1 pound (lb.) = 7,000 grains
100 pounds = 1 hundredweight (cwt.)
2,000 pounds = 1 short ton
2,240 pounds = 1 long ton

### *Metric Weight*

1,000 micrograms = 1 milligram (mg.)
1,000 milligrams = 1 gram (gm.)
1,000 grams = 1 kilogram (kg.)
1,000 kilograms = 1 metric ton

### *Imperial (British) Avoirdupois Weight*

$27\frac{11}{32}$ grains = 1 dram
16 drams = 1 ounce
16 ounces = 1 pound = 7,000 grains
14 pounds = 1 stone
8 stone
112 pounds = 1 hundredweight
20 hundredweight
2,240 pounds = 1 ton

The imperial avoirdupois units, although differing in definition, are for practical purposes equal to the United States units of the same name. The same conversion values may be used with either. This table is included to show certain variations in terminology between this system and that commonly used in the United States.

### Equivalents of Weight of the Four Systems

| Avoirdupois, United States and Imperial | Metric | Apothecaries' |
|---|---|---|
| *1 grain* | 64.7989 milligrams | 1 grain |
| *1 dram* | 1,771.85 milligrams<br>1.77185 grams | 0.4557 dram |
| *1 ounce* | 28.3495 grams | 0.9115 ounce |
| *1 pound* | 453.59 grams<br>0.45359 kilogram | 1.21528 pounds |

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* U. S. Dept. Agr. Bur. Ent. and Plt. Quar. E-517 (1940).

## CAPACITY TABLES (LIQUID)

### *United States Liquid Measure*

8 fluid drams (fl. dr.) = 1 fluid ounce (fl. oz.)
4 fluid ounces = 1 gill
4 gills = 1 pint (pt.)
2 pints = 1 quart (qt.)
4 quarts = 1 gallon (gal.) = 231 cubic inches

At maximum density, 39.164°F (3.98°C), a gallon of pure water weighs 8.345 pounds; at 59°F (15°C) the weight is 8.338 pounds.

### *Metric Capacity Measure*

1,000 milliliters (ml.)[1] = 1 liter (l.) = 1,000.027 cubic centimeters
10 liters = 1 dekaliter (dkl.)
100 liters = 1 hectoliter (hl.)
1,000 liters = 1 kiloliter (kl.)

### *Imperial Capacity Measure*

8 fluid drams = 1 fluid ounce
5 fluid ounces = 1 gill
4 gills = 1 pint
2 pints = 1 quart
4 quarts = 1 gallon = 277.42 cubic inches

An imperial gallon of pure water weighs 10 pounds at 62°F (16.67°C).

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[1] The term "milliliter (ml.)" should be used for measures of capacity as "cubic centimeter (cc.)" is a measure of volume.

### Equivalents of Capacity in the Three Systems

| United States | Metric | Imperial |
|---|---|---|
| *1 fluid dram* | 3.6966 milliliters | 1.0408 fluid drams |
| *1 fluid ounce* | 29.5729 milliliters | 1.0408 fluid ounces |
| *1 gill* | 118.292 milliliters<br>0.118292 liter | 0.83268 gill |
| *1 pint* | 473.167 milliliters<br>0.473167 liter | 0.83268 pint |
| *1 quart* | 946.33 milliliters<br>0.94633 liter | 0.83268 quart |
| *1 gallon* | 3,785.33 milliliters<br>3.78533 liters | 0.83268 gallon |

## Linear-Measure Tables

### *United States System*

12 inches (in.) = 1 foot (ft.)
3 feet = 1 yard (yd.)
5½ yards = 1 rod (rd.)
16½ feet
320 rods
1,760 yards
5,280 feet
= 1 mile

### *Metric System*

1,000 millimicrons[1] = 1 micron[2]
1,000 microns = 1 millimeter (mm.)
10 millimeters = 1 centimeter (cm.)
10 centimeters = 1 decimeter (dm.)
10 decimeters = 1 meter (m.)
10 meters = 1 dekameter (dkm.)
10 dekameters = 1 hectometer (hm.)
10 hectometers = 1 kilometer (km.)

### *Imperial System*

Except for small differences in standards, this system is the same as that used in the United States and the same conversion values may be used.

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[1] Abbreviation is "m" followed by the greek letter "mu."
[2] Abbreviation is the Greek letter "mu".

### Equivalents of Length in the Three Systems

| United States and Imperial | Metric |
|---|---|
| *1 inch* | 25.4 millimeters<br>2.54 centimeters |
| *1 foot* | 30.48 centimeters<br>3.048 decimeters |
| *1 yard* | 9.144 decimeters<br>0.9144 meter |
| *1 rod* | 5.029 meters<br>0.5029 dekameter |
| *1 mile* | 1,609.35 meters<br>1.60935 kilometers |
| 0.03937 inch | *1 millimeter* |
| 0.3937 inch | *1 centimeter* |
| 3.937 inches<br>0.328 foot | *1 decimeter* |
| 39.37 inches<br>1.0936 yards | *1 meter* |
| 1.98838 rods | *1 dekameter* |
| 19.8838 rods | *1 hectometer* |
| 198.838 rods<br>0.62137 mile | *1 kilometer* |

## Area-Measurement Tables

### *United States System*

144 square inches (sq. in.) = 1 square foot (sq. ft.)
9 square feet = 1 square yard (sq. yd.)
30¼ square yards = 1 square rod (sq. rd.)
43,560 square feet
4,840 square yards = 1 acre
160 square rods

### *Metric System*

100 square millimeters (mm. 2) = 1 square centimeter (cm. 2)
100 square centimeters = 1 square decimeter (dm. 2)
100 square decimeters = 1 square meter (m. 2)
100 square meters = are (a.)
100 ares = 1 hectare (ha.)

### *Imperial System*

Except for slight differences in standards this is the same as the United States system for area measurement, and the two are combined in the following table:

### Equivalents of Area in the Three Systems

| United States and Imperial | Metric | |
|---|---|---|
| *1 square inch* | 6.452 | square centimeters |
| *1 square foot* | 9.2903 | square decimeters |
| *1 square yard* | 0.8361 | square meter |
| | 25.29 | square meters |
| *1 square rod* | 0.2529 | are |
| *1 acre* | 0.40469 | hectare |

## Dusts and Soil Insecticides

### Equivalent small- and large-scale dosages

| Dosage per square foot | Square feet that 1 pound will cover | Pounds per acre |
|---|---|---|
| *Gram* | | |
| 0.1 | 4,536 | 9.6 |
| .10413 | 4,356 | 10.0 |
| .15619 | 2,904 | 15.0 |
| .25 | 1,814 | 24.0 |
| .26032 | 1,742 | 25.0 |
| *Ounce* | | |
| 0.005 | 3,200 | 13.61+ |
| .008 | 2,000 | 21.78 |
| .01 | 1,600 | 27.22+ |
| .016 | 1,000 | 43.56 |
| .025 | 640 | 68.06+ |
| .064 | 250 | 174.24 |
| .16 | 100 | 435.6 |

### Range of Chemical and Physical Characteristics of the Common Non-metalic Mineral Insecticides Diluents[*]

#### CLAYS

| Analysis | Kaolin Type | Fullers Earth Type | Bentonite (Swelling) |
|---|---|---|---|
| $SiO_2$ | 41.60–59.00 | 53.00–64.00 | 59.57–64.32 |
| $Al_2O_3$ | 27.81–42.70 | 10.56–27.37 | 19.67–24.64 |
| MgO | 0.05– 0.77 | 1.51–10.50 | 2.20– 2.67 |
| CaO | 0.00– 1.06 | 0.11– 2.02 | 0.41– 0.72 |
| $K_2O$ | 0.03– 0.53 | 0.33– 3.31 | 0.15– 0.40 |
| $Na_2O$ | 0.01– 1.51 | 0.21– 1.61 | 0.60– 2.60 |
| $Fe_2O_3$ | 0.02– 2.29 | 2.36– 7.69 | 0.26– 3.60 |
| $TiO_2$ | 0.40– 2.30 | 0.39– — | — — |
| $H_2O$ (Free) | 0.50– 7.00 | 1.0 –15.0 | 7.5 – 9.0 |
| Apparent Density[†] | 28 –44 | 38 –59 | 54 –60 |
| Per cent through 325 mesh screen | 92 –99.9 | 80 –96 | 90 –99 |
| pH | 4.5 – 6.8 | 4.5 – 7.4 | 7.5 – 9.2 |

#### TALCS

| Analysis | Fibrous | Lamellar | Crystalline | Soap stone | Pyrophyllite |
|---|---|---|---|---|---|
| $SiO_2$ | 39 –62 | 37 –57 | 43 –61 | 43 –50 | 73 –79 |
| MgO | 23 –33 | 38 –34 | 28 –32 | 23 –32 | 0.1– — |
| $Al_2O_3$ | 1 –10 | 1 – 5 | 0.3– 6.0 | 0.3– 9.0 | 17 –21 |
| CaO | 3 – 6 | 0.1–10.0 | 0.2– 8.0 | 2 – 5 | 0.1– — |
| $Fe_2O_3$ | 0.6– 1.0 | 0.2– 7.0 | 0.1– 7.0 | 6 –10 | 0.1– 0.5 |
| $H_2O$ (Free) | 0.5– 2.0 | 0.5– 3.0 | 0.5– 3.0 | 0.5– 3.0 | 0.5– 3.0 |
| Apparent Density | 51 –62 | 51 –62 | 35 –60 | 42 –60 | 30 –60 |
| Per cent through 325 mesh screen | 98 –99 | 95 –99.7 | 95 –99.7 | 95 –99.7 | 90 –95 |
| pH | 8 – 9.5 | 8 – 9.5 | 7 – 9.5 | 8 – 9.5 | 6 – 8 |

#### SILICAS

| Analysis | Diatomaceous Earth | Pumice and Pumicite |
|---|---|---|
| $SiO_2$ | 73 –91 | 72.90–73.18 |
| $Al_2O_3$ | 2 –10 | 11.20–15.46 |
| MgO | — — | 0.36– 0.40 |
| CaO | 0.1– 2.0 | 0.80– 1.37 |
| $K_2O$ | — — | 3.66– 4.38 |
| $Na_2O$ | — — | 3.66– 3.64 |
| $Fe_2O_3$ | 0.5– 2.0 | 0.86– 1.09 |
| $TiO_2$ | — — | 0.06– — |
| $H_2O$ (Free) | — — | 0.05– 7.0 |
| Apparent Density | 12 –20 | 46 –60 |
| Per cent through 325 mesh screen | 97 –99 | 90 –99.6 |
| pH | 4.5– 7.0 | 5.4 – 8.9 |

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[*] L. R. Moretti. Paper read before Pacific Chemical Exposition, San Francisco, California, 1947.

[†] Also expressed as bulk density, determined by measuring the weight of a powder which fills a specified container in a standard manner. Usually expressed as pounds per cubic foot.

| Material | Weight per cubic foot (pounds) | Weight per cubic inch (grams) | Per cent through a 325-mesh screen, per cent | | Particle size as determined with a microscope† (microns) | | | Rate of flow through duster (pounds per minute) | | Reaction pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Dry | Wet | Large | Small | Average | Peerless | Messinger | |
| Phosphate rock | 64.14 | 10.95 | 70.4 | 89.60 | — | — | — | — | — | 5.76 |
| Cryolite | 41.50 | 6.57 | — | — | 9 | 2.0 | 3.8 | 1.46 | 10.34 | 7.72 |
| Cryolite | 45.06 | 6.75 | — | — | 15 | 2.0 | 5.6 | .48 | 4.79 | 7.18 |
| Cryolite | 35.75 | 5.37 | — | — | — | — | — | .98 | 4.99 | 6.87 |
| Calcium arsenate | 27.94 | 4.44 | 92.9 | 97.20 | 4 | 1.5 | 1.7 | 1.11 | 7.08 | 11.82 |
| Derris root | 20.62 | 3.62 | 89.0 | — | 90 | 2.3 | 16.4 | 1.10 | 6.81 | 8.33 |
| 1 Fixed Coppers | 55.50 | 8.21 | 98.7 | 99.40 | 42 | 1.0 | 8.8 | 1.98 | 15.86 | 6.30 |
| 2 Fixed Coppers | 50.50 | 8.74 | 99.8 | 99.50 | 4 | 1.0 | 1.8 | 2.18 | — | 5.84 |
| 3 Fixed Coppers | 46.88 | 8.27 | 99.3 | 99.42 | 9 | 1.0 | 2.9 | 2.05 | 31.23 | 6.28 |
| 4 Fixed Coppers | 30.56 | 4.93 | 96.7 | 97.20 | 6 | 1.0 | 3.2 | 1.95 | 22.40 | 8.03 |
| 5 Fixed Coppers | 26.12 | 4.41 | 99.4 | 99.10 | 7 | 1.0 | 2.5 | 1.43 | 10.92 | 8.23 |
| 6 Copper oxide | 96.06 | 17.45 | 97.2 | 96.00 | 8 | 1.0 | 2.7 | 2.04 | — | 5.66 |
| Monohydrated copper sulfate | 47.75 | 8.50 | — | — | — | — | — | 2.10 | — | — |

* J. D. Wilson and Frank Irons, Ohio Agr. Exp. Sta. Bimo. Bull. 27; 26, 1942.

† These measurements are at best only approximate. Certain particles of talc, which contained particles 135 microns long but only 15 wide, were measured only in their longest dimension. The average given here represents the particle size which occurred most frequently in the small sample used.

## HUMIDITY REGULATION

Regulated humidities are sometimes desired in biological testing and for such purposes the following data are given. Series I is made up of saturated solutions of the salts listed; 200 ml. of the solution are placed in the bottom of a battery jar and above this is a wide mesh screen upon which the biological specimens are placed. A tight fitting top is sealed on the jar with vaseline. Series II consists of various concentrations of sulfuric acid with the resulting humidities as determined by a hair hygrometer.*

### Series I

| Salt | Humidity Per cent | Salt | Humidity Per cent |
|---|---|---|---|
| $CaCl_2$ | 11 | $NH_4Cl$ | 64 |
| $LiCl\cdot H_2O$ | 20 | $ZnSO_4$ | 68 |
| $K_2CO_3\cdot H_2O$ | 30 | $Na_2SO_4$ | 68 |
| $NaCl$ | 61 | $Zn(NO_3)_2$ | 68 |
| $NaBr\cdot H_2O$ | 62 | $(NH_4)_2PO_4$ | 73 |
| $Mg(C_2H_3O_2)_2\cdot 4H_2O$ | 68 | $NaH_2PO_4$ | 74 |
| | | $KNO_3$ | 84 |

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* *J. Econ. Entom.*, 37, 750, (1944).

### Series II

| Per cent $H_2SO_4$ Concentration | Humidity Per cent — |
|---|---|
| 62 | 15 |
| 56 | 25 |
| 52 | 33 |
| 48 | 42 |
| 44 | 49 |
| 39 | 58 |
| 36 | 66 |
| 33 | 70 |
| 27 | 80 |

### Temperature Conversion

| Fahrenheit Degrees | Centigrade Degrees | Fahrenheit Degrees | Centigrade Degrees |
|---|---|---|---|
| 32 | 0 | 77.0 | 25 |
| 33.8 | 1 | 78.8 | 26 |
| 35.6 | 2 | 80.6 | 27 |
| 37.4 | 3 | 82.4 | 28 |
| 39.2 | 4 | 84.2 | 29 |
| 41.0 | 5 | 86.0 | 30 |
| 42.8 | 6 | 87.8 | 31 |
| 44.6 | 7 | 89.6 | 32 |
| 46.4 | 8 | 91.4 | 33 |
| 48.2 | 9 | 93.2 | 34 |
| 50.0 | 10 | 95.0 | 35 |
| 51.8 | 11 | 96.8 | 36 |
| 53.6 | 12 | 98.6 | 37 |
| 55.4 | 13 | 100.4 | 38 |
| 57.2 | 14 | 102.2 | 39 |
| 59.0 | 15 | 104.0 | 40 |
| 60.8 | 16 | 105.8 | 41 |
| 62.6 | 17 | 107.6 | 42 |
| 64.4 | 18 | 109.4 | 43 |
| 66.2 | 19 | 111.2 | 44 |
| 68.0 | 20 | 113.0 | 45 |
| 69.8 | 21 | 114.8 | 46 |
| 71.6 | 22 | 116.6 | 47 |
| 73.4 | 23 | 118.4 | 48 |
| 75.2 | 24 | 120.2 | 49 |
|  |  | 122.0 | 50 |

### Percentage of Hydrocyanic Acid for Various Temperatures and Specific Gravities

| Spec. Gr. | 22° | 21° | 20° | 19° | 18° | 17° | 16° | 15° | 14° | 13° | 12° | 11° | 10° | 9° | 8° | 7° | 6° |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.698 | 96.9 | 97.3 | 97.7 | 98.1 | 98.5 | 98.9 | 99.3 | 99.7 | | | | | | | | | |
| 0.699 | 96.6 | 97.0 | 97.4 | 97.8 | 98.2 | 98.6 | 99.0 | 99.4 | 99.8 | | | | | | | | |
| 0.700 | 96.3 | 96.7 | 97.1 | 97.5 | 97.9 | 98.3 | 98.7 | 99.1 | 99.5 | 99.9 | | | | | | | |
| 0.701 | 96.0 | 96.4 | 96.8 | 97.2 | 97.6 | 98.0 | 98.4 | 98.8 | 99.2 | 99.6 | 100 | | | | | | |
| 0.702 | 95.7 | 96.1 | 96.5 | 96.9 | 97.3 | 97.7 | 98.1 | 98.5 | 98.9 | 99.3 | 99.7 | | | | | | |
| 0.703 | 95.4 | 95.8 | 96.2 | 96.6 | 97.0 | 97.4 | 97.8 | 98.2 | 98.6 | 99.0 | 99.4 | 99.8 | | | | | |
| 0.704 | 95.1 | 95.5 | 95.9 | 96.3 | 96.7 | 97.1 | 97.5 | 97.9 | 98.3 | 98.7 | 99.1 | 99.5 | 99.9 | | | | |
| 0.705 | 94.8 | 95.2 | 95.6 | 96.0 | 96.4 | 96.8 | 97.2 | 97.6 | 98.0 | 98.4 | 98.8 | 99.2 | 99.6 | 100 | | | |
| 0.706 | 94.5 | 94.9 | 95.3 | 95.7 | 96.1 | 96.5 | 96.9 | 97.3 | 97.7 | 98.1 | 98.5 | 98.9 | 99.3 | 99.7 | | | |
| 0.707 | 94.2 | 94.6 | 95.0 | 95.4 | 95.8 | 96.2 | 96.6 | 97.0 | 97.4 | 97.8 | 98.2 | 98.6 | 99.0 | 99.4 | 99.8 | | |
| 0.708 | 93.9 | 94.3 | 94.7 | 95.1 | 95.5 | 95.9 | 96.3 | 96.7 | 97.1 | 97.5 | 97.9 | 98.3 | 98.7 | 99.1 | 99.5 | 99.9 | |
| 0.709 | 93.6 | 94.0 | 94.4 | 94.8 | 95.2 | 95.6 | 96.0 | 96.4 | 96.8 | 97.2 | 97.6 | 98.0 | 98.4 | 98.8 | 99.2 | 99.6 | 100 |
| 0.710 | 93.3 | 93.7 | 94.1 | 94.5 | 94.9 | 95.3 | 95.7 | 96.1 | 96.5 | 96.9 | 97.3 | 97.7 | 98.1 | 98.5 | 98.9 | 99.3 | 99.7 |
| 0.711 | 93.0 | 93.4 | 93.8 | 94.2 | 94.6 | 95.0 | 95.4 | 95.8 | 96.2 | 96.6 | 97.0 | 97.4 | 97.8 | 98.2 | 98.6 | 99.0 | 99.4 |
| 0.712 | 92.7 | 93.1 | 93.5 | 93.9 | 94.3 | 94.7 | 95.1 | 95.5 | 95.9 | 96.3 | 96.7 | 97.1 | 97.5 | 97.9 | 98.3 | 98.7 | 99.1 |
| 0.713 | 92.4 | 92.8 | 93.2 | 93.6 | 94.0 | 94.4 | 94.8 | 95.2 | 95.6 | 96.0 | 96.4 | 96.8 | 97.2 | 97.6 | 98.0 | 98.4 | 98.8 |
| 0.714 | 92.1 | 92.5 | 92.9 | 93.3 | 93.7 | 94.1 | 94.5 | 94.9 | 95.3 | 95.7 | 96.1 | 96.5 | 96.9 | 97.3 | 97.7 | 98.1 | 98.5 |
| 0.715 | 91.8 | 92.2 | 92.6 | 93.0 | 93.4 | 93.8 | 94.2 | 94.6 | 95.0 | 95.4 | 95.8 | 96.2 | 96.6 | 97.0 | 97.4 | 97.8 | 98.2 |
| 0.716 | 91.5 | 91.9 | 92.3 | 92.7 | 93.1 | 93.5 | 93.9 | 94.3 | 94.7 | 95.1 | 95.5 | 95.9 | 96.3 | 96.7 | 97.1 | 97.5 | 97.9 |
| 0.717 | 91.2 | 91.6 | 92.0 | 92.4 | 92.8 | 93.2 | 93.6 | 94.0 | 94.4 | 94.8 | 95.2 | 95.6 | 96.0 | 96.4 | 96.8 | 97.2 | 97.6 |
| 0.718 | 90.9 | 91.3 | 91.7 | 92.1 | 92.5 | 92.9 | 93.3 | 93.7 | 94.1 | 94.5 | 94.9 | 95.3 | 95.7 | 96.1 | 96.5 | 96.9 | 97.3 |
| 0.719 | 90.6 | 91.0 | 91.4 | 91.8 | 92.2 | 92.6 | 93.0 | 93.4 | 93.8 | 94.2 | 94.6 | 95.0 | 95.4 | 95.8 | 96.2 | 96.6 | 97.0 |
| 0.720 | 90.3 | 90.7 | 91.1 | 91.5 | 91.9 | 92.3 | 92.7 | 93.1 | 93.5 | 93.9 | 94.3 | 94.7 | 95.1 | 95.5 | 95.9 | 96.3 | 96.7 |
| 0.721 | 90.0 | 90.4 | 90.8 | 91.2 | 91.6 | 92.0 | 92.4 | 92.8 | 93.2 | 93.6 | 94.0 | 94.4 | 94.8 | 95.2 | 95.6 | 96.0 | 96.4 |
| 0.722 | 89.7 | 90.1 | 90.5 | 90.0 | 91.3 | 91.7 | 92.1 | 92.5 | 92.9 | 93.3 | 93.7 | 94.1 | 94.5 | 94.9 | 95.3 | 95.7 | 96.1 |
| 0.723 | 89.4 | 89.8 | 90.2 | 90.6 | 91.0 | 91.4 | 91.8 | 92.2 | 92.6 | 93.0 | 93.4 | 93.8 | 94.2 | 94.6 | 95.0 | 95.4 | 95.8 |
| 0.724 | 89.1 | 89.5 | 89.9 | 90.3 | 90.7 | 91.1 | 91.5 | 91.9 | 92.3 | 92.7 | 93.1 | 93.5 | 93.9 | 94.3 | 94.7 | 95.1 | 95.5 |
| 0.725 | 88.8 | 89.2 | 89.6 | 90.0 | 90.4 | 90.8 | 91.2 | 91.6 | 92.0 | 92.4 | 92.8 | 93.2 | 93.6 | 94.0 | 94.4 | 94.8 | 95.2 |
| 0.726 | 88.5 | 88.9 | 89.3 | 89.7 | 90.1 | 90.5 | 90.9 | 91.3 | 91.7 | 92.1 | 92.5 | 92.9 | 93.3 | 93.7 | 94.1 | 94.5 | 94.9 |
| 0.727 | 88.2 | 88.6 | 89.0 | 89.4 | 89.8 | 90.2 | 90.6 | 91.0 | 91.4 | 91.8 | 92.2 | 92.6 | 93.0 | 93.4 | 93.8 | 94.2 | 94.6 |
| 0.728 | 87.9 | 88.3 | 88.7 | 89.1 | 89.5 | 89.9 | 90.3 | 90.7 | 91.1 | 91.5 | 91.9 | 92.3 | 92.7 | 93.1 | 93.5 | 93.9 | 94.3 |
| 0.729 | 87.6 | 88.0 | 88.4 | 88.8 | 89.2 | 89.6 | 90.0 | 90.4 | 90.8 | 91.2 | 91.6 | 92.0 | 92.4 | 92.8 | 93.2 | 93.6 | 94.0 |
| 0.730 | 87.3 | 87.7 | 88.1 | 88.5 | 88.9 | 89.3 | 89.7 | 90.1 | 90.5 | 90.9 | 91.3 | 91.7 | 92.1 | 92.5 | 92.9 | 93.3 | 93.7 |

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(*See also Dictionary of Insecticides on page 273 for names of chemicals*)

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NOT TO BE TAKEN FROM THIS ROOM