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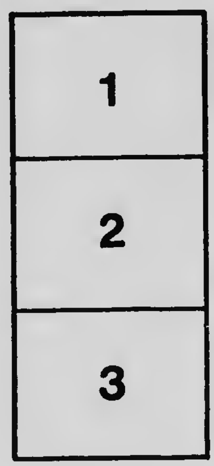
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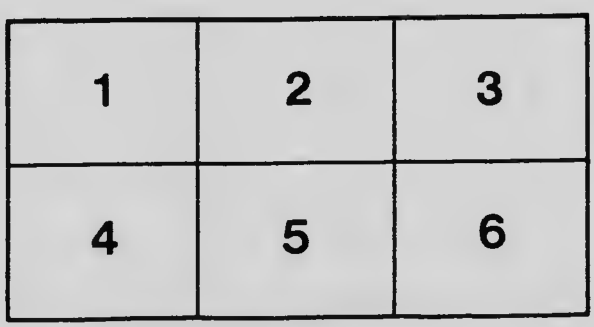
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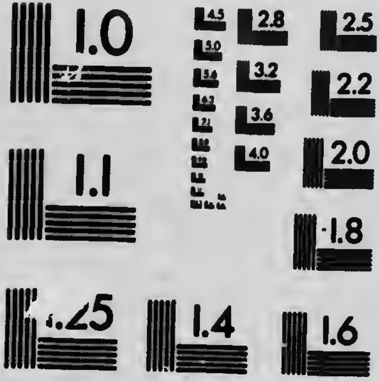

BULLETIN 154.] [FEBRUARY, 1907

Ontario Department of Agriculture.

ONTARIO AGRICULTURAL COLLEGE.

INSECTICIDES AND FUNGICIDES.

By R. Harcourt, Professor of Chemistry,
and H. L. Fulmer, Demonstrator in Chemistry.

OBJECT.

Year by year the damage done to the crops of the farm, orchard, and garden by insects and fungous pests seems to be increasing. Some cf these pests may be a blessing in disguise, in that the remedies used for their eradication have been beneficial in other respects; but, in order that they may be successfully combatted, it is essential that the farmer know how to fight them to the best advantage, and that he have a clear idea of the nature of the remedies employed and the precautions that must be observed in their use. The literature on the subject is voluminous, but it is scattered and not always accessible to those who require it. In this bulletin an attempt has been made to gather the information obtainable on the subject into one publication and present it in a manner that will be helpful, in the hope that it will fill a long felt want.

INTRODUCTION.

To spray with any degree of success requires, besides a knowedge of the acting principle of the remedy which is being employed, a rather intimate acquaintance with the enemy which is being combatted. The different classes of insects and fungous diseases do not show similar characteristics. If it were so, then the question of remedy would resolve itself into a very simple one; the discovery of a single successful one would end our labors. As it is, a great many of these remedial compounds are required in plant economy, the absolute number needed depending entirely upon the different ways in which insects and fungous diseases attack their food or host plants. This results largely from differences in anatomical and physiological structure of these little but often highly destructive animals and plants.

Classes of Insects.

Practically all insects can be divided into two leading groups: (*a*) those which actually chew and swallow their food and have what the entomologist calls *biting mouth parts*, and those which obtain their food by piercing the outer tissues of the plant and sucking up the juice, called insects with ***sucking mouth parts.*** The first group of insects, among which we find grasshoppers, cucumber beetles, codling moth larvæ, currant worm, and a great many others, can be poisoned by covering the surface of the plant upon which they feed with some poisonous material; while the second group, since they do not eat the surface of the plant but feed only on the inside juices, must be destroyed by means of some substance which will act upon their bodies, as caustic washes, or something which will act upon their breathing pores, smothering them, such as a gas.

This, then, divides insecticides into two groups: ***food poisons*** and ***contact insecticides.***

There are some insects, however, owing to their peculiar habits, inaccessibility, or other causes, which require special treatment, such as the cut worms, which work underground, and the grain weevils, which affect stored products; the ones which feed inside the bark or within the stem of the tree or plant, such as the apple tree borer or the raspberry cane borer; the household pests; and the animal parasites.

Classes of Fungi.

A fungus is a plant which feeds upon other plants, and is thus a parasite. It begins with a seed (spore) which germinates and produces a great number of small thread-like structures which correspond to the roots, stem, and leaves of an ordinary plant, and called the mycelium. Sometimes this mycelium develops wholly upon the surface of the plant or fruit, as with the powdery mildew of the grape; while at other times the germ tube of the spore penetrates the skin and produces its mycelium within the tissues, just as happens in the case of the grain rusts and smuts, downy mildew, and a great many others.

Fungi, then, can be classed as ***external*** and ***internal***, and the method of dealing with them varies accordingly. Those of the first kind can be attacked and destroyed by use of proper materials, but the second kind can only be prevented.

INSECTICIDES.

Food Poisons

Food poisons are that class of compounds which contain some poisonous substance that if eaten and absorbed by the system will cause death. The most commonly used material that produces this toxic effect is arsenic, but other materials may be and are used.

"White Arsenic," known also as arsenious acid, arsenious oxide, As_2O_3, is the basis of practically all food poisons. It is a white powder,

but occurs also in two crystalline forms. It is soluble in water, to a certain extent, the solubility varying with circumstances. If water at 15° C. be shaken for a long time with the solids, 100 parts of the water will dissolve .28 parts of the crystalline and .92 parts of the powder, while if saturated solutions at 100° C. be cooled at 15° C., 2.18 parts of the crystalline and 3.33 parts of the powder form remain in solution. Water containing carbon dioxide, however, dissolves much greater quantities than does pure water. White arsenic completely and readily dissolves in solutions of caustic alkalies, such as ammonia, and in solutions of alkaline carbonates, such as washing soda. To both plants and animals it is, along with its compounds, a powerful poison, two or three grains being sufficient to cause death with the human being.

What is important to know about arsenious oxide in this connection, however, is that with water it forms an *acid*. For this reason it cannot be used separately as a spray, for it would burn and destroy foliage; it must have its acid or scorching property removed. Now we have in chemistry, compounds which are known as *bases*, and which combine with acids to form neutral substances called *salts*. If we treat arsenious acid with a base, we form a salt, termed an arsenite, and this arsenite may be used with water as a spray without fear of doing harm to foliage. This is what is done, and we have a great many salts of arsenic, such as Paris green, calcium arsenite, sodium arsenite, lead arsenite, etc. In general, all substances containing arsenic are called *Arsenic or Arsenical Compounds*.

But all salts of arsenious acid cannot be used for spraying purposes. Those which are *soluble in water*, such as sodium arsenite, cannot be employed, and *only those which do not dissolve but remain in suspension as solid particles* are of use.

Arsenical Compounds.

Paris Green.

This substance is used as an insecticide more largely than any other in the Province of Ontario, due to the fact that it was the first introduced, and, therefore, better known. It is an olive green material consisting of a combination of arsenic, copper, and acetic acid or "vinegar," called by chemists copper aceto-arsenite, along with varying quantities of other substances present as impurities. Theoretically, pure Paris green contains 58.65 per cent. arsenious oxide (As_2O_3), 31.29 per cent. copper oxide (CuO), and 10.06 per cent. acetic acid. Commercially, however, these proportions do not obtain, since there is always a small amount of moisture present in the green together with some sodium sulphate or glauber salt, a compound formed in the process of manufacture and never afterwards completely removed. This latter substance has no insecticidal value, and if present in more than normal quantity only increases the cost of the green and should be classed as a mere "make weight." If care is used in the manufacture, there is no reason for it being present in more than very small amounts, say one-half of one per cent.

Free or Soluble Arsenious Oxide in Paris Green. It is on account of the presence of this substance in Paris green that we sometimes find that after spraying, the leaves of the plant treated turn black, having the appearance of being burnt, or even, in more extreme cases, drop off altogether, leaving the plant defoliated. This, of course, is very objectionable, since the physiological functions of the plant are thus severely checked, a case where the cure is as bad, or worse than, the evil.

To account for the occurrence of this scorching, J. K. Haywood, of Washington, D.C., states three causes.*

(1) There may be a certain amount of arsenious oxide over and above that combined with the other constituents. This is "free" arsenious oxide and until recently it has been considered the only cause of the scorching of the foliage by Paris green.

(2) The greens may be poorly made, so that the constituents are very loosely held together. When such greens are brought in contact with water, especially water containing carbon dioxide, they soon break up and arsenious oxide is set free. Between the water of the spray, and the action of dew and rain, enough oxide may be liberated to severely scorch the foliage.

(3) The green may be extremely fine. The best greens when ground to a fine powder and applied to foliage will scorch. This is doubtless due to the fact that more surface is exposed to the action of water which, containing carbon dioxide, would soon set enough arsenious oxide free to cause serious damage.

Following up these statements, however, Mr. Haywood says: "It is a very common occurrence to secure a commercial Paris green that scalds because of one of the first two causes, but the writer has never found a commercial sample of green that scorched because it was in too fine a condition."

As to the breaking up of Paris green when in contact with water, with the liberation of free arsenious oxide, Colby, of California,† expresses some doubt, since, as he says, "aceto-arsenite of copper, as manufactured to-day, is instantaneously precipitated from complex solutions containing alkali and often excessive quantities of various acids." However, as this may be, we do know that Paris green often destroys foliage and that it is due to free arsenious oxide. There is no sure and ready method by which the free arsenic content of Paris green can be ascertained. Reagents, such as ammonia, which dissolve Paris green also dissolve the oxide almost or quite as readily. The microscope has been highly recommended, especially for the detection of "white arsenic" which has been added as an adulterant, but not for that which has been

* U. S. Dept. Agri., Bureau of Chemistry, Bull. 82, pp. 5-6.

† College of Agriculture, Bull. 151. p, 19.

retained in the process of manufacture. No doubt this is a valuable aid, still the actual amount present cannot be determined in this way. The only way to decide whether this substance is present in injurious quantities or not is by an actual estimation through the means of chemical analysis.

Precautions in the Use of Paris Green. Since the last method of estimating the free arsenious oxide of Paris green is not within the ready reach of all it is well to assume that it is present in harmful quantities and to use something to alleviate the difficulty, if such there be. As before stated, arsenious oxide, or "white arsenic," may be combined with other substances which will neutralize or destroy its acid or burning property. Lime is one of these substances. *If an equal quantity of good, freshly slaked lime be added to the Paris green, in suspension in the water, some little time before spraying, it will combine with the free arsenious oxide and overcome its leaf-scorching power to a great extent.* It is well also to know that some kinds of foliage are much more susceptible to the destroying power of arsenious acid than others; thus the peach tree has foliage which is remarkably tender, whereas the foliage of the apple is very hardy.

From investigations carried on in 1902-3, the results of which are embodied in Bulletin 82 of the Bureau of Chemistry, Washington, D.C., J. K. Haywood was enabled to make out a schedule showing the amount of free arsenious oxide which the foliage of the more common fruit trees will withstand. His results, which also give figures showing the influence which lime exerts, and are thus doubly valuable, are summarized in the following table:

Average Percentages of Soluble Arsenious Acid Allowable.

	Apple	Pear	Peach	Plum
Without Lime................	6	6	[illegible]	4
With Lime....................	7	7	4.5	6

This shows plainly that the orchardist must consider the kind of foliage he is spraying as carefully as the kind of Paris green he is using.

Total Arsenious Oxide in Paris Green. Since Paris green owes its insecticidal value to the arsenic which it contains, it follows that the larger the proportion of arsenious oxide there is present in it, the more effective it will be when used against insects. The value of any arsenical is determined by its arsenic content. Pure Paris green contains 58.65 per cent. As_2O_3. Any quantity above that must be present in the free state, and any quantity below that lowers the insecticidal, and, thus, the market value, just to the extent to which it is deficient. The commercial article is never ideal; in reality its manufacture is difficult and many chemicals enter into the process. However, from analyses which we have made here and from results obtained elsewhere, most Paris greens contain at least 56 per cent., and there is no reason why they should contain less than 56 per cent. of arsenious oxide, providing any reasonable degree of care be exercised in the making.

Total Copper Oxide in Paris Green. Copper aceto-arsenite contains 31.29 per cent. CuO, which bears a relation to the total arsenious oxide present of 1 : 1.87. Since it is necessary that arsenious oxide be combined with copper in order that it be not in the free state, then, any result of analysis showing a greater factor than 1.87 indicates free arsenic. White arsenic cannot be added as an adulterant without seriously disturbing this ratio.

Physical Conditions. The best grade of Paris green is a powder which will pass through a sieve of not less than 100 meshes to a square inch. A coarse green is one that will settle rapidly from its suspension in water and will require constant agitation during the spraying operation in order that it may be distributed evenly over the foliage.

Adulterants and their Detection. The more common ones occurring in Paris green are white arsenic, barium carbonate, barium sulphate, gypsum, and road dust. The white arsenic may be added to bring the arsenic content up to the standard, but the presence of any of them is fradulent, and they can only be classed as mere "make weights" which increase the cost of purchase for actual insecticidal value received. As previously stated, white arsenic may be detected under the microscope, when it appears in the shape of white octohedral crystals. The other adulterants mentioned are all insoluble in ammonia, thus any quantity of residue left on dissolving the green in ammonia gives good ground for rejecting a sample on account of adulteration. This test is simple and can be applied by any one. A teaspoonful of the sample is placed in some receptacle, preferably glass, and about ten teaspoonsful of strong ammonia added and the whole then thoroughly stirred. The Paris green readily dissolves to form a deep blue solution, whereas the adulterants present are left as solid particles in the bottom of the vessel. As before stated, white arsenic is also quite readily soluble in ammonia, and a complete solution does not show the absence of this material.

Paris Green in Ontario.

The consumption of Paris green in this Province amounts to between 100 and 120 tons annually. Although the demand is so good, still the product put upon the market is of a very favorable quality. The Inland Revenue Department at Ottawa reports that the samples which they examined in 1902-3 were 95.8 per cent. genuine. The samples analyzed in this department were also of a highly satisfactory standard.

Some Paris Greens Analysed in 1905.

No.	Moisture 100°C	Sand	Sod. Sulphate	Copper oxide	Total arsenious acid As_2O_3	Acetic acid by difference	Soluble arsenious acid As_2O_3
1	1.29	.11	.34	30.68	56.55	11.03	2.36
2	.99	.23	.13	31.62	56.91	10.12	2.73
3	1.25	.26	.37	30.59	56.8	10.73	2.11
4	1.26	.15	.36	30.39	56.12	11.72	2.85
5	1.20	.71	.57	30.23	56.01	11.19	2.73
6	1.41	.12	1.80	30.29	56.33	10.05	4.35

These greens are all as satisfactory as we can expect the commercial article ever to be. Probably No. 6 contains somewhat more sodium sulphate than there is any need for, and is also somewhat high in free arsenious acid; otherwise there are none of them but could be highly recommended for spraying purposes.

London Purple.

London purple is prepared by boiling a purple residue from the dye industry, containing free arsenious acid, with slaked lime. In this way calcium arsenite and calcium arsenate are formed, and these are the poisonous compounds of this insecticide. As the dye residue has accumulated some dirt during the process of manufacture, a sandy substance will always be present in the London purple. It will thus be seen that London purple consists of calcium arsenite, calcium arsenate, a dye residue, and small amounts of sand and moisture. In case not enough lime is added to the dye residue or the boiling is not continued long enough, varying quantities of the arsenious acid will be left in the free condition, and thus in a form which will scorch the foliage to which it may be applied.

According to Haywood,* about one-third of London purple is made up of the dye residue, sand, and moisture, and that it contains from 31 to 51 per cent. of total arsenic, figured as arsenious oxide; whereas Paris green contains the equivalent of about 56 per cent. of the arsenious oxide. The value of these two insecticides will thus be in proportion to these figures. However, one other point must be considered in valuing this substance, that is, its effect on foliage. According to Haywood, a very much larger amount of the arsenic of London purple is soluble in water

* U.S. Department of Agriculture, Bureau of Chemistry, Bull. No. 68.

than with Paris green. It seems probable that a part of this is made up of calcium arsenite and arsenate, which have gone into solution, but at the same time, it is safe to say that Paris green is the safer insecticide. *The addition of lime to the water mixture of the London purple is even more essential than with Paris green.*

Commercial Substitutes for Paris Green.

The fact that the use of lime along with Paris green and London purple has been so generally recommended has given the manufacturer or arsenical insecticides an excuse for making and offering for sale many mixtures containing widely different forms and quantities of arsenic compounds. Many of these substances are poor substitutes for good Paris green. Some of them contain very little arsenic or any other form of poison, while in others there is a large amount of arsenic; but, unfortunately, it is not always in such a state of combination as to be safe for use as an insecticide.

Among the mixtures poor in arsenic, the following have been analyzed in our own laboratory:—

Black Death: One of the newer insecticides recently offered for sale in this Province is "Black Death." It is sold at 2 cents per pound, or 15 pounds for 25 cents. The composition of this substance, according to our own analysis, is as follows:—

Moisture	10.42
Sand, etc.	6.37
Carbon	17.39
Sulphur trioxide	23.72
Calcium oxide	23.30
Magnesium oxide	2.16
Carbon dioxide	7.90
*Paris green	0.43
Undetermined (volatile matter, water of crystallization).	8.31
	100.00

This insecticide is composed almost entirely of charcoal, sand, and gypsum. The only substance present which will poison insects is the Paris green. If mixtures with so small an amount of poison will kill insects, it will be cheaper to buy a pound of Paris green and mix it with 200 pounds of gypsum. Paris green can be bought for 20 cents per pound. In Black Death it costs $3.86 per pound.

* Copper oxide .13 per cent.; Arsenic trioxide .12 per cent.

Potato Bug Finish: "Bug Finish" is another insecticide that is now on sale in various localities. It is sold at the same price as "Black Death." The following is the composition of the sample analyzed:

Moisture	12.49
Sand, etc.	17.57
Insoluble organic matter	0.69
Sulphur trioxide	30.47
Calcium oxide	25.79
Carbon dioxide	5.77
Magnesium oxide	1.49
*Paris green	1.06
Iron and aluminum oxides	1.13
Undetermined (water of crystallization, volatile matter, etc.)	3.54
	100.00

One hundred pounds of this mixture contains only a little over one pound of Paris green; the remainder is largely sand and gypsum. The Paris green in it costs $1.56 per pound.

Kno Bug: The manufacturers of this insecticide claim that it kills the bugs, stimulates the plant, and improves the quality of the crop. It sells in 20-pound boxes at 6 cents per pound. According to our analysis, it has the following composition:—

Moisture	10.89
Insoluble matter	10.55
Sulphur trioxide	26.10
Calcium oxide	26.73
Carbon dioxide	11.95
Magnesium oxide	3.09
Iron and aluminum oxides	4.03
Potash, nitrogen-potassium nitrate	4.50
†Paris green	2.49
	100.00

It is essentially crude gypsum with 2½ per cent. of Paris green, and potash and nitrogen equal to about 4.5 per cent. of potassium nitrate. The latter is a valuable plant food; but, as there is only about 25 cents' worth in 100 pounds of the mixture, it does not add very much to its cost. Anyway, it would appear to be a better practice to keep insecticides and fertilizers separate. Without allowing any value for the other materials, the Paris green in this mixture would cost $2.41 per pound.

* Copper oxide .32 per cent.; Arsenious oxide, .70 per cent.

† Arsenious oxide 1.46 per cent.

Slug Shot: Slug Shot is essentially crude gypsum mixed with small quantities of Paris green, tobacco, and carbolic acid. It is sold in Guelph at 10 cents per pound, or 3 pounds for 25 cents. In larger quantities it can be bought for much less. The detailed results of our analysis are as follows:—

Moisture	13.55
Sand, etc.	3.53
Insoluble matter (sulphur, tobacco, etc.)	5.69
Calcium oxide	30.10
Sulphur trioxide	37.93
Iron and aluminum oxides	0.80
Carbon dioxide	2.79
*Paris green	2.13
Phenol, soluble organic matter, etc. (by difference)	3.38
	100.00

Carbolic acid is a poison, and as such will, no doubt, destroy insects as well as the Paris green; but this mixture at even 5 cents per pound is rather an expensive substance to use in destroying potato bugs.

Bug Death.

Another insecticide, containing no arsenic, that has recently come into great prominence, is Bug Death. It is claimed that it kills the bugs, feeds the plant, increases the yield, and improves the quality. It is sold at the rate of 12 pounds for $1, or 100 pounds for $7. The following is the composition of samples secured in 1902 and 1903:—

	1902.	1903.
Moisture	0.32	0.38
Volatile matter	2.67	2.87
Sand, etc.	3.17	4.26
Lead oxide	3.17	4.70
Zinc oxide	87.47	83.04
Iron oxide	3.84	4.09
	100.64	99.34

It is composed largely of crude zinc oxide with small quantities of lead oxide and iron oxide. It also contains nitrogen equivalent to about one-half of one per cent. of ammonium sulphate. This latter substance is a plant food; but there is so little of it in the mixture that it cannot have much value. Bug Death has considerable fungicidal value, and destroys the bugs. It has to be applied in fairly large quantities and it is rather an expensive substance; but it has given good results when used on potatoes.

* Copper oxide .64 per cent ; arsenic trioxide .82 per cent.

Among the most important Paris green substitutes which contain large quantities of arsenic are the various "arsenoids." All of these insecticides are advertised as containing no leaf-scorching materials, but analyses by Haywood* and Colby† show that some of them are not by any means free of soluble forms of arsenic. The gray and white arsenoids are especially bad in this respect. The former is reported as containing arsenic equivalent to 35 per cent. of arsenious oxide, fully one-third of which is soluble in water;, while the latter has the equivalent of over 25 per cent. of the oxide, all of which is in a soluble form, and is, consequently, sure to burn the foliage.

The green arsenoid, copper arsenite, is reported as being as rich in arsenic as Paris green, and does not contain an excessive amount in the soluble condition. Pink arsenoid, or lead arsenite, while poorer in arsenic, is a safe insecticide in that very little of it is in a form that will scorch the leaf.

Bowker's Disprene and Swift's Arsenate of Lead are convenient substances, and are among the safest forms of insecticides. The chief advantages of the lead compounds are that they may be applied to all kinds of foliage with less danger of injury than is the case with Paris green, and, because of this fine state of division, they cling to the foliage better, and remain in suspension in water for a longer time.

Of the lead compounds, the arsenate is most used. In the pure form, it contains arsenic equivalent to about 37 per cent. of arsenious oxide, but in the condition in which it is placed on the market, the arsenic content will be lower. According to an analysis made by Haywood, the Swift's Arsenate of Lead contains only 25.62 per cent. of arsenic oxide and 13 per cent. of organic matter. The organic substance consists of dextrose and dextrin, and are apparently used to make the material stick to the foliage. Colby states that in the form of paste this insecticide contains only 12 per cent. of arsenic oxide and 43 per cent. of water. Consequently, proportionately larger quantities of this substance will have to be used than with Paris green.

Home Made Arsenicals.

There is no good reason why farmers, gardeners, and fruit growers should not prepare the arsenical poisons they require just as they do the Bordeaux and lime-sulphur mixture. The work involved in their preparation is no more difficult, and when properly made they are fully as efficient, and, possibly, safer than the best Paris green.

Arsenate of Lead. The formulæ for the preparation of this compound vary slightly; but in the following is the one given by the United

* U.S. Department of Agriculture, Bureau of Chemistry, Bull. No. 68.
† California Agri. Experiment Station Bull. No. 151

States Division of Entomology,* Colby, of California,† and others :—

Arsenate of soda	10 ounces.
Acetate of lead	24 "
Water	150-200 gallons.

The arsenate of soda and the acetate of lead (sugar of lead) should be dissolved separately and then poured into a tank containing the required amount of water. A white precipitate of lead arsenate is immediately formed, and when thoroughly stirred, is ready for spraying. Its finely divided condition keeps it in suspension for hours and thus simplifies the work of spraying. The preparation may be used several times stronger without the least danger of scorching the most delicate plants. When sprayed upon the foliage, it forms a coating which adheres so firmly that it is but little affected by ordinary rains.

The average wholesale price of the arsenate of soda and acetate of lead, as given by an Ontario wholesale drug firm, is 9 and 7 cents per pound, respectively. This would make the cost of the materials used on the above formula a little over 16 cents, which would be as cheap, if not cheaper, than Paris green.

Arsenite of Lead. Prof. Colby, California Agricultural Experiment Station, Bulletin No. 151, gives the following formula and directions for the preparation of arsenite of lead :—

Arsenite of soda	12 ounces.
Acetate of lead	4 pounds.
Water	150 gallons.

Dissolve the ingredients separately and then pour them into a 150-gallon spray tank filled with water. A milky mixture ready for spraying is obtained. This mixture is said to remain in suspension fifteen times as long as the finest grained Paris green.

Calcium Arsenite. Several formulæ for making this compound have been published. There appears to be no doubt about the insolubility of the compound when it is used immediately after it is prepared, but when allowed to stand for days or weeks before applying, there may be some decomposition take place and soluble arsenites be formed which will destroy foliage.

The formula proposed by Prof. Taft of Michigan is as follows: "Boil one pound of white arsenic and two pounds of lime in two gallons of water for forty minutes and then dilute as required." He further states that when one pound of the arsenic, prepared as above, is used in every 300 to 400 gallons of water, it has been equal to Paris green for destroying the codling-moth and curculio, while one pound in 150 to 200 gallons of water is used upon potatoes. When used in Bordeaux mixture it is not necessary to use any more lime, otherwise he recommends the addition of a small amount of lime when diluting.

* U. S. Department of Agriculture, Division of Entomology, Bull. 41.
† California Experiment Station, Bull. No. 151.

Another formula proposed by Professor Kedzie, of Michigan, is as follows: "Boil two pounds of white arsenic with eight pounds of sal soda (washing soda) in two gallons of water. Boil for 15 minutes in an iron pot, or until the arsenic dissolves, leaving only a small amount of muddy sediment. Put the solution into a two-gallon jug and label *'Poison—Stock Solution for Spraying Mixture.'* The spraying mixture can be prepared whenever required in the quantity needed at any time by slaking two pounds of lime, and adding this to 40 gallons of water; pour into this one pint of the stock arsenic solution; stir thoroughly and the spraying mixture is ready for use. The arsenic in this mixture is equal to four ounces of Paris green."

Other writers have recommended the use of larger quantities of lime, even up to eight pounds instead of two to 40 gallons. The additional lime is used to prevent burning of the foliage. Larger quantities of the poison solution may be used if desired.

The mistake has been made in applying the soda stock solution of arsenic without the addition of any lime. The *arsenite of soda thus formed is soluble and will burn the leaf,* thus destroying the plant upon which it is placed.

The chief advantages of these calcium arsenite preparations are that the materials are easily procured, it is easily prepared, it is cheap, and it is a safe and reliable insecticide.

The average wholesale price in original package quoted to the writer for white arsenic is 8 cents per pound, and for sal soda 1 cent per pound. It will thus be seen that the cost of the material required to make calcium arsenite by either of these formulæ is not excessive.

Contact Remedies.

As previously stated, these remedies are employed to destroy sucking insects, which must be killed by contact. They kill by clogging the breathing pores of the insects, and, to some extent, by their corrosive action. *To be effective, the plant or tree must be very thoroughly covered.* In the case of the San José Scale, which may exist in a spot no larger than a pin-head, one scale left untouched may produce as many as a million offspring during the season. Consequently, *thorough spraying is essential to success.*

Sulphur.

Sulphur is a yellowish, brittle substance which melts to a thin straw-colored liquid at 114.5° C. and boils at 448.4° C., changing to a brownish yellow vapor. When these vapors strike a cool surface, they are condensed and deposited as a fine amorphous powder, called "Flowers of sulphur." It is this form which is useful for combatting insects and for manufacturing the lime-sulphur washes. Sulphur also appears on the market in sticks, called "sulphur rolls," and in the shape of needle-shaped crystals and rhombic prisms, but these forms are not of use in dealing with insects and fungous diseases. The powder is very valuable for combatting surface fungi (external) and was long used for that purpose in Europe, but of late years the copper compounds have been more commonly used. When burned, its fumes form a very active disinfectant, but, since moisture must be present in the atmosphere before it will act (at which time it will also bleach colored fabrics, wall paper, etc.), its use in this way has been largely replaced by formaldehyde, mercuric chloride, and other substances.

Lime Sulphur Washes.

These washes have come into use during the last few years in combatting the San José Scale. They have also been found to be very effective in destroying other kinds of the smaller insects, and are considered by many to be one of the best general "cleaning up" sprays that have been devised. In addition to their insecticidal value, they are efficient fungicides.

A number of formulæ have been recommended for the preparation of these washes. Those usually adopted in Ontario, as given by Prof. Lochhead,* are as follows:

Boiled Wash:

Fresh lime	20 pounds.
Sulphur (flowers)	15 "
Water	40 gallons.

"With warm water make the sulphur into a paste, put in the lime and add about 15 gallons of warm water with stirring. The sulphur paste may be added after the lime has been slaked. Boil for an hour and a half in a kettle, or, better, in a barrel with live steam. Make up to 40 gallons with hot water; strain into spray tank and apply while warm."

Some of our fruit growers were at first inclined to use even larger quantities of lime; but this past season many of them increased the amount of sulphur, using the following formula:

Fresh lime	20 pounds.
Sulphur (flowers)	18 "
Water	40 gallons.

The length of time recommended for cooking the wash varies from one-half hour to two hours. Possibly the best plan is to boil until the color of the whole mass is tinged with green. This is undoubtedly the best way to prepare the wash, for the boiling insures the combination of the sulphur and lime. Very little is prepared by boiling in a kettle, the live steam method is much more convenient and cheaper. Where small quantities are wanted, one of the following methods, in which the heat

*Thirty-sixth Annual Report of the Entomological Society of Ontario.

formed by the lime as it slakes is used to boil the mixture, may be used:
Lime Sulphur Wash (Self Cooked):

Formula No. 1—Fresh lime	....	35 pounds.
Sulphur	....	17 "
Water	....	40 gallons.

Put the sulphur into a vessel and add 2 gallons of boiling water, a little at a time, stirring vigorously until a smooth paste is obtained. In another vessel large enough to hold 40 gallons, place the lime, pour onto it 12 gallons of boiling water, and then add the sulphur paste previously prepared. Place a hoe in the mixture, quickly cover the barrel with heavy burlap sack, and allow to cook for half an hour. During the cooking period, occasionally raise the mixture from the bottom to prevent it "caking." Nothing must be done to interrupt the boiling, as that will affect the quality of the wash. After the mixture has cooked for 30 minutes, add 28 gallons of warm water, strain into spray tank, and apply at once.

In preparing this wash many fruit growers have found the 35 pounds of lime excessive, and have reduced the quantity to 25 to 30 pounds:

Formula No. 2—Fresh lime	....	25 pounds.
Sulphur (flowers)	....	20 "
Sal soda	....	12½ "
Water	....	40 gallons.

Put 5 or 6 gallons of hot water into a barrel, add the lime, quickly following with the sulphur and sal soda, and stir until the slaking is practically completed. If necessary, add cold water to prevent the mixture boiling over. After the violent action has ceased, cover the barrel, allow to stand half an hour, dilute to full quantity, strain, and apply while hot:

Formula No. 3—Fresh lime	....	30 pounds.
Sulphur (flowers)	....	15 "
Caustic soda	....	4-6 "
Water	....	40 gallons.

In preparing this mixture, proceed as with lime-sulphur-sal soda wash, only add the caustic soda instead of the sal soda. The granulated caustic soda is the most efficient. It has been recommended that this wash be boiled with steam for 20 minutes.

These methods of preparing the mixtures are very convenient where small quantities are required, but it is hardly possible to make a wash in this way that is as reliable as by boiling with live steam. Much will depend upon the quality of the lime used. It must be *strictly fresh* and of a *very quick slaking* kind. That obtained from the Port Colborne and Beachville lime kilns apparently gives the best results.

It will be noted that salt is not given in any of the above formulæ. The American bulletins nearly all recommended its use, but in the preliminary xperiments conducted in this Province by Mr. G. E. Fisher, it was concluded that the presence of salt added to the cost, made the wash more difficult to spray, and increased its corrosive action on the metal parts of the pump; while it failed to be any more effective as a de..troyer of scale, or more adhesive to the bark of the tree. Following these conclusions, no salt has been used in the washes in this Province.

Prof. Lochhead lately stated that, "My observations incline me to believe that the presence of the salt renders the wash more adhesive, and hence more effective." This is still an unsettled point; but it is evident that anything which will improve the adhesiveness of the wash will increase its effectiveness.

Recently Mr. J. K. Haywood reported the results of a chemical study of the lime-sulphur washes.* In this work it was found that when the wash was prepared according to the following formula: lime, 10 pounds; sulphur, 6⅔ pounds; salt, 5 pounds, and water, 20 gallons, it was found that a 60 minute period of boiling was sufficient to get practically all sulphur in solution. But when the wash was prepared as follows: lime, 10 pounds; sulphur, 6⅔ pounds; caustic soda, 3⅓ pounds; salt, 5 pounds, and water, 20 gallons, and the ingredients put together according to directions given above for lime-sulphur-caustic soda wash, about 8 per cent. of the sulphur remained undissolved. Yet when the wash prepared as above is allowed to cool somewhat and then heated so as to bring it to the boiling point in 20 minutes, it was found that practically all the sulphur was in solution. Further, it was found that so far as the sulphur acids were concerned, it was the same as the wash prepared by the boiling process, only that the sodium salt of the sulphur acids instead of the calcium salts are formed and that it is more caustic. The investigation failed to prove that the added salt materially affected the composition of the wash.

This investigation also proved that when these washes are exposed to the air, the various sulphides formed in preparing the mixture are slowly oxidized through thio-sulphates, sulphites into the inert sulphates, and that sulphur is liberated. In this respect the action was the same whether caustic soda was used in the preparation or not. It seems quite probable that the beneficial action of these washes is due to the finely divided sulphur gradually liberated and to the action of the sulphides and sulphites formed.

All these washes must be applied while still warm, as when the solution cools many of the compounds are precipitated. This is because cold water will not hold as much in solution as the hot; consequently, if strained cold the efficiency of the mixture is weakened.

*Journal American Chem. Society, Vol. XXVII, No. 3, 1905.

A disagreeable feature of these washes is that they are very caustic, and their application is often attended with considerable discomfort, especially in windy weather. Some of the irritation to the face and hands of the operator may be avoided by smearing the former with vaseline and covering the latter with rubber gloves. Leather, is easily corroded by these washes, and care should be taken that the spray does not come in contact with the harness. Unless it is a still day, the horses should be covered with blankets, or always kept to the windward.

Other Insecticides Recommended for Destroying the San Jose Scale.

With the spread of the scale, a large number of remedies of various kinds have been placed on the market. Among the more important of these are "Kil-o-scale," and "Anit-Scale," or "Scalecide," "Emulsified Con-Sol"; (also known as "Target Brand Scale Emulsion," "Con-Sol," the "Webcide Solutions," "Zanoleum," and caustic soda and water. From the results of experiments conducted in this Province and elsewhere, it does not appear that these insecticides are any more effective, if as much so, as the lime-sulphur washes in destroying scale. Prof. C. O. Houghton states that* the so-called "soluble oils," "Kil-o Scale" and "Emulsified Con-Sol," give satisfactory results when applied in the spring. Fall applications of "Kil-o-Scale" were satisfactory in one case, but not entirely so in another. "Scalecide" applied once as a fall spray was quite unsatisfactory so far as could be determined after a period of three months had elapsed. Applied to apple trees as a summer spray, at the rate of 1 part to 28 parts of water, "Scalecide" gave valuable results. "Con-scale," the "Webcide Solutions" and caustic soda in water failed to give satisfactory results in any instance."

Crude Petroleum.

This material was first recommended for use against scale enemies by Dr. J. B. Smith, of the New Jersey Experiment Station. In the hands of many orchardists, however, it has been found to be decidedly damaging to many kinds of foliage, especially the more tender varieties, the apple and pear being the only ones able to withstand its destructive power to any successful degree.

It is a very effective remedy, nevertheless, and whenever applied destroys the scale; but because of its general destroying tendencies, it cannot be recommended except for the most hardy trees.

Kerosene Emulsions.

The Kerosene Emulsions of various kinds have been recommended for destroying many forms of insect life. The kerosene is, of course, the

Delaware Experiment Station Bull. No. 74, 1906, killing agent. Dr. James Fletcher gives the following formula:

Kerosene (coal oil)	2 gallons.
Rain water	1 "
Soap	½ pound.

"Boil the soap in water till all is dissolved; then, while boiling hot, turn it into the kerosene, and churn the mixture constantly and forcibly with a syringe or force pump for five minutes, when it will be of a smooth, creamy nature. If the emulsion is perfect, it will adhere to the surface of gl .s without oiliness. As it cools, it thickens into a jelly-like mass. This gives the stock emulsion, which must be diluted with nine times its measure of warm water before using on vegetation. The above quantity of 3 gallons of emulsion will make 30 gallons of wash."

Recently the *K-L* (*Kerosene-Lime*) *Emulsion* has been more or less strongly recommended for destroying San José Scale. It is a mixture of kerosene, hydrated lime, and water, the lime acting as a carrier or emulsifier of the kerosene. Prof. C. P. Close gives the following directions for its preparation:† "Pour the kerosene and lime into a barrel and stir together well with a paddle. Add ten or twenty gallons of water and stir to loosen the kerosene and lime from the bottom and sides of the barrel. Pour in water until the barrels is more than three-fourths full, and with a hoe or dasher, churn, splash and pound the K-L four or five minutes to emulsify it, then fill up the barrel with water, and spray. A long up and down stroke of a hoe or dasher is best, and if the hoe is held just right the blade goes straight down instead of glancing to the side of the barrel. *A terrific splashing can and must be made in this way.* A burlap bag or canvas should be thrown over the barrel to prevent the emulsion from splashing out. A board cover is better than burlap or canvas and is easily made by nailing strips at the ends of thin boards three feet long and boring a two-inch hole in the centre. Through this hole the hoe handle projects and the churning is more easily done than when a bag is used.

"Very small lots of two or three gallons can be emulsified by pumping the K-L back into itself through a nozzle throwing a small solid stream, but this method is not recommended for larger quantities. In fact, *the fruit grower is hereby warned not to attempt to make lots larger than two or three gallons by pumping, nor lots of any size by stirring, but always to make K-L by the most violent churning, pounding and splashing with a hoe or dasher.*

"The prepared hydrates of lime on the market, or good stone lime dry slaked, are best for making K-L. Air-slaked lime is not desirable, but may be used. If the lime is fresh four pounds per gallon of kerosene will be ample, but if old, more may be required. Use enough lime to take up all the kerosene and mix into a thin, sloppy mass. If drops of kerosene gather on the top in less than a minute sprinkle on more lime

* Central Experimental Farm, Ottawa, Bull. 52, 1905.
† Delaware Agricultural Experiment Station, Bull. 73.

Proportion of Kerosene, Lime, and Water.

"K-L is kerosene, lime, and water, and the proportion of each in 50* gallons of different strengths, is as follows:

For	10%	K-L use	5	gals. kerosene,	20	lbs. lime,	44½	gals. water.
"	12½	"	6¼	"	25	"	43	"
"	15	"	7½	"	30	"	41½	"
"	17½	"	8¾	"	35	"	40	"
"	20	"	10	"	40	"	38½	"
"	25	"	12½	"	50	"	34½	"
"	30	"	15	"	60	"	30½	"

"The K-L-B is kerosene, lime, and Bordeaux mixture. It is made exactly like the K-L except that Bordeaux is used instead of water. We use the 4-4-50 Bordeaux formula. Four pounds of copper sulphate are dissolved and diluted with water to 25 gallons. Four pounds of stone lime are slaked and diluted with 25 gallons. Four or five pounds hydrated lime or fresh dry slaked lime are usually substituted for the stone lime. The copper solution is then poured into the milk of lime and the mixture is well stirred with a paddle.

"The K-L-B-P is kerosene, lime, Bordeaux, and poison. It is made exactly like K-L-B except that poison is added to the Bordeaux. Paris green is about the most reliable poison, and one pound is used in 75 gallons of Bordeaux."

Fresh lime is not conveniently obtainable in all parts of the Province. Mr. Frank T. Shutt, Chemist at the Central Experimental Farm, Ottawa, has shown that flour may be used instead of lime with equally good results. With reference to the preparation, Prof. Shutt writes as follows: † "The preparation with flour is most simple. The requisite amount of kerosene is placed in the vessel (pail or barrel)—which is preferably dry—and flour added in the proportion stated, viz., eight ounces to the one quart, the whole thoroughly stirred and the water added, two gallons for every quart of kerosene. This is then vigorously churned. The time necessary to churn will vary from two to four minutes, according to the quantity to be emulsified, and the emulsion is then ready for use.

"When the emulsion is required for immediate use, the quantity of flour may be further reduced. It was found that as small a quantity as two ounces would emulsify one quart of kerosene, but that on standing a few hours a perceptible layer of kerosene had separated.

"It has, further, been found that by scalding the flour before adding the kerosene a less weight is required. An excellent emulsion, which showed not the slightest separation of kerosene after one week, was prepared by scalding two ounces of flour, mixing the resulting paste with one quart of kerosene and emulsifying with two gallons of water.

* Wine measure.

† The Canadian Horticulturist, May

"The flour emulsion is smooth, readily and easily atomized, and does not clog the nozzle. Any separation into layers (no free kerosene will appear for several days, at least) may be readily overcome or remedied by simply stirring the mixture. It is equally effective, as might be expected, as an insecticide with the lime-formed emulsion, and amongst other advantages that may be claimed for it there is no perceptible whitening of the tree or foliage; and, further, in some places it may be found cheaper and easier to make than the lime emulsion. Its use is suggested as an alternative where good lime is unobtainable and also for making the emulsion when intended for ornamental trees, shrubs, etc., where the whitening of the foliage is objectionable. The flour emulsion can be added to Bordeaux mixture, Bordeaux and Paris green, if desired."

*Soap Washes.**

"The most effective soap wash is made with whale-oil soap, one pound to from four to six gallons of water. The term whale-oil soap is merely a trade name for fish-oil soap, made with either potash or soda. The potash soaps, which are the best, because even stronger solutions remain liquid when they cool, are soft soaps. The soda soaps are hard. Of the two, the potash soaps are considered the best to use on vegetation, as well as being more convenient. Both kinds should always be dissolved in hot water.

"When bought at retail prices, these soaps cost from 15 to 20 cents per pound, according to the locality, but if obtained in large quantities, can be got at from 3 to 5 cents per pound. Fifty-pound kegs are supplied at 5 cents per pound. Two well-known brands of potash soft soaps which have been much used in Canada, and have given good satisfaction, are those made by W. H. Owen, of Port Clinton, Ohio, and by Good & Co., of Philadelphia, Pa. If thought desirable, these soaps can be made at home; but it is very unpleasant and dirty work, and it is, besides, doubtful whether such good or cheap results can be secured as by buying from firms which make a special business of manufacturing soaps with only the required amount of moisture and the proper grade and amount of potash. It has been found in experiments carried on at Washington that what is required for spraying purposes is a caustic potash and fish-oil soap, made with a fairly good quality of fish-oil, and from which water has been eliminated by boiling, so that it does not exceed 25 or 30 per cent. of the weight of the soap. Soaps made with caustic soda instead of caustic potash are unsuitable for spraying purposes. Dr. J. B. Smith (New Jersey Experiment Station), in his circular No. 5, "Whale Oil Soap and Its Uses," says: "Whale-oil, or fish-oil, soap is one of the most reliable materials for use against plant-lice, and generally against sucking insects which can be killed by contact insecticides. It kills by clogging the spiracles, or breathing pores, of the in-

*Central Experimental Farm, Ottawa, Bull. No. 52.

sects, and als . to some extent by its corrosive action. The advantages of fish-oil ove ordinary laundry soap lie in the greater penetrating power, in the fact that it remains liquid when cold, at much greater strengths, and that fish-oil itself seems to be more fatal to insect life than other animal fats. A good soap can be made as follows:

Concentrated potash lye	3½ pounds.
Water	7½ gallons.
Fish-oil	1 gallon.

Dissolve the lye in water, boil, and to the boiling solution add the fish-oil; continue to boil for two hours, and then allow to cool. Any grade of fish-oil will answer

"Whale-oil soap may be applied in the strength of one pound in four gallons of water for brown or black plant-lice, and one pound in six gallons for green plant-lice; warm water should always be used when dissolving it.

"Soaps of all kinds are very useful in adding adhesiveness to liquid mixtures when it is necessary to apply these to such vegetation as cabbages, turnips, peas, etc., which have their leaves covered with a waxy secretion which prevents water from lying upon them. Any kind of soap will answer for this purpose, and it may be remembered that one quart of soft soap is about equal to one pound of hard soap."

Another method for making home-made fish-oil soap is given by Van Slyke and Urner, and is as follows:*

Formula for Making Forty Pounds of Fish-oil Soap.

Caustic soda	6 pounds.
Water	1½ gallons.
Fish-oil	22 pounds.

"The caustic soda is completely dissolved in the given amount of water and the fish-oil is added gradually under constant and vigorous stirring. The combination occurs readily at ordinary summer temperatures and the operation is soon completed. The mixing may be done in any receptacle sufficiently large to contain the whole amount of material. It would probably not be desirable to attempt to make more than 20 to 40 pounds at a time, since the difficulty of thoroughly stirring a larger mass would tend to make a complete combination less sure, thus rendering liable the presence of too much free alkali. *Complete and thorough stirring is essential to success.* Caustic soda should be handled with precaution, since in concentrated form it easily injures the skin.

The authors show that when caustic soda can be got for 4½ cents per pound and the fish-oil at 29 cents per gallon, the material for 40 pounds of soap costs $1.14, or 2.85 cents per pound.

* New York Experiment Station Bull. No. 257, 1904.

Hydrocyanic-Acid Gas, HCN.

This insecticide is used largely in the fumigation of nursery stock. It is also used for destroying scales on orchard trees and for ridding mills, stores, and elevators of grain pests and rodents. The applicability of it was first demonstrated in California, where it was found useful in combatting the cushiony scale affecting citrus trees, but it has since found a very extended use against other insect enemies.

The gas is not bought as such, but is prepared at the time of use from a substance known as potassium cyanide (KCN). The cyanide is a solid body and when treated with sulphuric acid (H_2SO_4), is decomposed or broken up and the gas liberated as:

KCN	+	H_2SO_4	=	$HKSO_4$	+	HCN
Pot. cyanide.		Sulphuric acid.		Pot. acid sulphate.		(Hydrocyanic acid gas).

The gas at low temperature is condensed to a liquid and is then called *prussic acid*. The liquid boils at 26.5° C., and thus is easily changed into the gas again. Being quite light, the gas rapidly diffuses and penetrates to every little nook and corner of the fumigating enclosure. For this reason it is very effective, and, when supplied in sufficient quantity, leaves nothing undone.

Fumigation of trees is best done while in the dormant state; if trees in foliage are treated, night should be chosen as the time of action, since the actinic or light-giving rays of the sun have a very damaging effect on leaves for some time after they have been surrounded by the gas.

As the gas is *extremely poisonous*, great care should be taken that it be not inhaled; and before a building or tent is entered after the operation, a thorough airing should be given.

For generating the gas, an open glazed vessel is used, an ordinary crock serving the purpose admirably. The water is first placed in the vessel, the sulphuric acid is then added, and last, the potassium cyanide is dropped in and the door quickly closed. All ventilators, cracks and openings should be tightly closed to prevent any leakage or waste of gas. The amounts of the different materials employed are as follows:

Potassium cyanide (98 per cent.)	1 ounce.
Sulphuric acid (1.83 specific gravity)	1 fluid ounce.
Water	3 fluid ounces.

Enough will be supplied by these quantities to fill 150 cubic feet of confined space. If there are 300 cubic feet of space, then twice the quantities given will have to be employed; if 450, then two and a half times; and so on up. The factor to be used can always be found by dividing the cubical contents by 150.

It is interesting to know that the residue left in the vessel after the action is completed is a valuable fertilizer, and should not be wasted. It should either be placed at some depth in the manure or compost heap or buried near the base of some tree or shrub. At any event, do not leave it lying around, as it is both acid and poisonous.

Carbon Bisulphide, CS_2.

As the formula indicates, this compound is made up of carbon and sulphur, one atom of the former and two of the latter. In the pure form it is a clear liquid with a pleasant odor, but when impure it is somewhat colored and possesses a highly disagreeable smell. It boils at 64.2° F., and thus volatilizes or changes to a vapor or gas very readily at ordinary temperatures. This gas ignites at a temperature of 297.5° F.

The vapors are very *poisonous*, and thus are very valuable in dealing with grain weevils, and the pea bug; and also for overcoming subterranean workers. Its use was first discovered in France, where it was and is employed against the grape phylloxera. The wine districts there were saved from complete annihilation by its introduction.

Since the vapor is 2.63 times heavier than air, it tends to work downward very rapidly, and will thus penetrate to some depth in the soil. In dealing with grain pests the liquid is placed in shallow dishes on top of the pile and then as the evaporation goes on, the vapor will work downward and penetrate the whole bulk.

Dosage: (1) For grain weevils, use one pint (1½ lbs.) for every 1,000 cubic feet of space. Place in shallow pans on top of the grain, using at least one pan in every 25 square feet of surface. Thus a bin of grain 25 feet long, by 5 feet wide, by 8 feet deep, would require 1 pint to be distributed in five pans. Larger quantities would not be harmful and would be more effective; the fluid is cheap, therefore employ an overdose rather than an insufficient quantity.

(2) For pea bugs use 1 pint for every 100 bushels of peas.*

(3) For subterranean workers (root maggots, etc.) inject small quantities into the soil around the base of the infested plant, 2 or 3 teaspoonsful in a place.

As with hydro-cyanic-acid gas, all openings should be well sealed to prevent escape and waste. Inhalation should also be avoided as much as possible, although small quantities breathed in will produce no harm except in cases of a weak heart. Fresh air is the cure, and when one begins to feel a dizziness, it is wise to seek at once the open atmosphere. Before entering a room where it has been used, thorough ventilation should be given.

Precaution:—As one volume of carbon bisulphide vapor mixed with 14.3 volumes of air forms a highly *inflammable* and *explosive* mixture, *never allow a light or even a spark*, or a lighted pipe or cigar to be brought near it.

Carbolic Acid, Phenol, C_6H_5OH.

This substance is an oxygen derivative of benzene, one of the members of the aromatic series of the carbon compounds. It has a permanent but characteristic and pleasant odor, which seems to be quite distasteful

* See Ontario Agri. College Bulletin No. 126, p.p. 26-27.

to many insects. In the undiluted form this acid is very active, and will burn and blister the flesh and cause much pain, but in the diluted form, as 1 part to 40 or 50 parts of water, it makes an important disinfectant that is extensively used in medicine. In the form of an emulsion with soap and water it is very useful in destroying the eggs and young maggots which infest onions, radishes, and similar garden crops.

The emulsion is made thus:

Carbolic acid	1 pint.
Hard soap	1 pound.
Water	1 gallon.

Dissolve the soap in the boiling water, and while boiling add the acid and continue the boiling for a few minutes, stirring thoroughly. Put the emulsion away in a tightly closed vessel and label *"Stock Solution of Carbolic Acid—Poison."* Before using, dilute 1 part of the stock solution with 50 parts of water.

Carbolic acid is also used in the form of what is known as "Carbolized Plaster," in which case the acid is mixed with land plaster (gypsum), road dust, air-slaked lime or some other diluting medium, and is then sprinkled or dusted on in the dry state.

Carbolic acid	1 pint.
Diluent (land plaster, etc.)	50 pounds.

This mixture is said to be very effective against flea beetles, cucumber beetles, etc.

Tobacco.

A strong decoction that is very obnoxious to insects and at the same time poisonous (nicotine) can be made from tobacco (stocks, refuse leaves, sweepings, etc.), by steeping in water for a prolonged period. This could be made a very valuable source of an insecticide by those people living in a tobacco district, or near a tobacco or cigar factory.

A good way to use the strong extract, although it can be sprayed as it is after it is diluted with water to about the color of strong tea, is as follows:

Hard soap	1 pound.
Water	8-10 gallons.
Strong tobacco extract	1 "

Dissolve the soap in boiling water, add the decoction, and then make up to 8-10 gallons.

White Hellebore.

This is a powder obtained by grinding up the dried roots of a plant known as Veratrum Album. The powder is of a light yellowish color and possesses a rather pleasant odor, and contains as its active principle a very powerful alkaloid called Jervine. It kills both by poisoning the insect and by stopping up the breathing pores, and can thus be classed as both a food poison, and a contact insecticide. Hellebore is much less poisonous than the arsenicals and soon loses its poisonous action when exposed in the air; thus it can be used on plants bearing fruit which is just about ready for market, with much more safety than can be the mineral poisons. This volatility of the alkaloid also shows the necessity of using a fresh article and one that has been kept away from the air in a tightly sealed receptacle.

Use either the dry powder or with water, 1 oz. to 2 gallons warm water.

Pyrethrum (Insect Powder, Buhach).

This powder is also called Dalmatian Insect Powder and Persian Insect Powder. It is also, like hellebore, obtained from plants, being the pulverized flowers of the botanical genus Pyrethrum. Value as an insecticide is due to the presence in it of an oil which is exceedingly poisonous to most insects, but practically harmless to human beings and the higher animals. It can be used with impunity, therefore, and on account of this fact is of special value.

The oil which imparts the killing power (largely by contact with the body of the insect) is very easily disseminated into the surrounding atmosphere and thus lost. For this reason these powders must be fresh and have been kept in tightly sealed receptacles, else they will be ineffective.

Application can be made in a number of ways:

1. *In solution*: 1 oz. to 3 gallons of water.
2. *Dry*: Apply while dew is on in the morning or after a rain.
3. *Dry, with dilution*: Mix with some flour or other light powder to any extent desired. Apply as 2.
4. *In fumigation*: Dust over live coals; for dealing with mosquitoes and flies.

FUNGICIDES.

It has long been known that chemical compounds are useful in combatting fungous diseases. As early as 1807 it was found in France that copper sulphate would prevent the germination of the spores of corn smut, but this discovery, one of a very important nature, was not appreciated or made known till a much later date. Sulphur was long used in the same country, but was not nearly so energetic as desired. No advances were made, however, till 1882, when the value of the compounds of copper became known. Since then great strides have been made in improved methods.

As indicated above, copper is a very important ingredient in fungicides. Nearly all the leading remedies contain it in some form or other; and so widely are its compounds used that we have come to term the combinations in which it occurs as "The Copper-Salt Fungicides."

Copper-Salt Fungicides.

Bordeaux Mixture.

This substance derives its name from the city of Bordeaux, in France, as it was in the vineyard district surrounding this place that it was first found useful. Therefore the name gives no indication as to what ingredients are present.

The source of the copper in this fungicide is copper sulphate, or what is commonly known as "bluestone." Now copper sulphate is an "acid salt," i.e., it is a salt which shows an acid reaction and will turn blue litmus ~~er red. This property of blue stone is due to the fact that it is a compound formed by the combination of a weak alkali ($Cu(OH)_2$) with a very strong acid (H_2SO_4), the outcome being that of a salt in which the acid property predominates. Being acid, therefore, copper sulphate cannot be applied to foliage, because it exerts a burning or destroying influence. Like white arsenic, it must be changed to some other form, a form which will not be injurious. Bluestone can be applied to foliage without doing harm, but in such a dilute form that it is not very effective.

The material used to overcome the acid property just mentioned is slaked lime or milk of lime. A good sample of lime is secured and slaked with a minimum quantity of water, thus changing it into the hydrate, as:

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{Ca(OH)_2}.$$

This slaked lime is then added to the bluestone, which has been dissolved in water, whereupon the following theoretical reaction takes place:

$$\underset{\text{Copper sulphate.}}{CuSO_4} + Ca(OH)_2 = \underset{\text{Copper hydrate.}}{Cu(OH)_2} + \underset{\text{Gypsum.}}{Ca(SO)_4}.$$

Providing enough lime has been used to act on all the copper, the latter will now all be present as copper hydrate, a precipitate or sediment of a beautiful sky-blue color, and which is practically insoluble in water. In this form, as a solid in suspension in water, it is sprayed on to the foliage.

Being in a solid form, copper hydrate, or Bordeaux, as it is called, is inert and will not act on the fungus. It must be changed to some form on the leaf which will be soluble in water. This change is brought about by carbon dioxide of the air and by that contained in dew and rain, or even by that which comes from the leaf itself.

How to make the Bordeaux Mixture. The first thing to do in the manufacture of the Bordeaux mixture is to decide on some recommended formula. The formula which has long been advocated in Ontario is known as the 4-4-40 formula. It is as follows:

$CuSO_4$ (crystallized copper sulphate)	4 pounds.
CaO (quick lime)	4 "
Water	40 gallons.

With good lime it only needs about one pound to act on all the copper; the excess given, three pounds, covers all danger which might arise from the use of a poor article. A large excess of lime is a disadvantage,—it causes the Bordeaux mixture to exert a slow fungicidal action, it is apt to cause the machinery to clog and to cause an uneven application, and the particles of lime offering more resistance to rain, will cause the mixture to be more rapidly washed from the trees. It may be an advantage, however, in a very wet season, by causing the Bordeaux to retain its efficiency longer and by allowing less injury to be done to foliage. Orchardists are inclined to use a less proportion of lime, and the following formula is recommended:

$CuSO_4$ (crystallized copper sulphate)	6 pounds.
CaO (quick lime)	4 "
Water	40 gallons.

As both copper sulphate and lime dissolve and slake, respectively, much quicker in hot water than cold, it is better to use heated water in order to save time. The very best lime obtainable is used, and if freshly burned, all the better. In slaking do not use an excess of water, but just enough to keep the lime moist. When the action is completed enough water is added to make a thin whitewash and then the whole is strained through coarse sacking to remove any lumps which would clog the nozzle of the spray pump. This done, enough water is added to make the volume up to one-half of what the final mixture will amount to. The copper sulphate solution is diluted to the same extent. The two are now mixed, the operation being best performed by two men, each with a bucket, one handling the lime and the other the copper sulphate. They are poured into the spray tank, two bucketsful at a time, until the whole is brought together. In this way a precipitate is obtained which will remain in suspension with only occasional agitation. If mixing is done before dilution, a very coarse precipitate is formed which settles rapidly to the bottom of the spray tank and requires almost constant stirring.

If large quantities of spray mixture are going to be used, it is an excellent plan to make up "stock" solutions of the copper and lime. This can be done by dissolving, say, one pound of copper sulphate in each gallon of water and making up a barrel full of it. Each gallon of the solution taken then represents one pound of the bluestone. The salt can be conveniently dissolved by filling the barrel with water and then suspending it therein, enclosed in a canvas sack. The lime can be handled in the same way, being sure, of course, that the contents of the barrel are thoroughly stirred up before dipping out any portion. Keep the barrels covered when not in use.

Precautions to be Used in Making. Before Bordeaux mixture is sprayed, it is absolutely necessary that all copper should be in the form of the sky-blue precipitate, i.e., enough lime must be used to act on all the bluestone. Formulæ advocated by the experiment stations always contain enough lime to precipitate all the copper, but it may sometimes happen that such a very poor quality is used that there will be some of the sulphate left unchanged. There are several simple ways by which one can tell when enough lime is present. Those who are very familiar with the reaction which occurs can tell by the color of the precipitate, it having a greenish* tinge when an insufficiency of lime is present instead of the deep sky-blue color. However those who are not familiar with the process must use more decided tests. Three simple ones can be employed, as follows:

1. Take some of the clear solution which is left on top when the sediment settles and place in a white saucer. Add a few drops of a solution of potassium ferrocyanide to it. If a reddish-brown precipitate or coloration appears, more lime is needed.

2. Take a portion of the clear fluid as before, and blow the breath gently over the surface. If a thin white pellicle or covering forms over the top, enough lime has been added.

3. Take a bright piece of steel, such as a knife blade, and hold it in the mixture for a minute or more. If it becomes coated with copper, more lime is required.

Test number one is the most reliable and is the one recommended.

In handling copper solutions use only wooden, brass, and copper vessels; all other receptacles would be corroded and destroyed by them; besides, the fungicide itself would be injured.

Copper compounds are *poisonous* and therefore should not be left lying around where children or animals can get at them.

Combined with an Insecticide. Bordeaux mixture is quite often combined with Paris green to impart to it an insecticidal value. In this case the mixture takes the place of water for holding the green in suspension. Other recommended arsenicals can be used for this also, such as lead arsenate and calcium arsenite. But if soluble compounds of arsenic are used, such as sodium arsenite, it would be necessary to slightly increase the amount of lime used in making the original Bordeaux mixture.

Soda Bordeaux.

This fungicide is made from copper sulphate just as the ordinary Bordeaux mixture. It differs, however, in that caustic soda is used to neutralize the acid property of the blue stone instead of lime; and that the final mixture contains sodium sulphate instead of calcium sulphate (gypsum). The resulting form of the copper, copper hydrate, is exactly the same, and exerts the same fungicidal power. The reaction which occurs may be represented by the following equation:

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$

Caustic soda. Copper hydrate. Sodium sulphate.

The main point in connection with this mixture is that caustic soda is an extremely active alkali and any amount of it added over and above

*The green precipitate is basic copper sulphate, $CuSO_4\ Cu(OH)_2$, which would break up on the leaf under the influence of CO_2 and leave free copper sulphate.

that required to combine with all the copper will destroy foliage. Therefore, in making Soda Bordeaux, it is ***important to add just the exact quantity of the soda required to change all the bluestone to copper hydrate.*** This is done by adding the soda solution slowly to the copper solution, mixing thoroughly after each addition, and testing for the neutral point with litmus pape.. The moment the litmus paper takes on a faintly blue tinge is the time to stop adding. The copper is then all in the form of a sediment and any more alkali added will be left in the free state.

The following tentative formula can be given:

Soda	2 pounds.
Copper sulphate	6 "
Lime	5 ounces.
Water	40 gallons.

In making, add three-quarters of the soda solution at once, mix thoroughly and then add the rest gradually, mixing and testing until the proper quantity is present. It may not require the whole amount recommended, and it may require more, depending upon the quality of the soda. When the alkaline value of a sample of soda is once ascertained, then one can proceed with much more rapidity. The small amount of lime is added to make the mixture decidedly alkaline, and, therefore, safe, and to cause the precipitate to remain blue instead of changing to dark brown or black, which it does after standing some time where an excess of soda is used.

Caustic soda can be bought retail or in drums of one hundred pounds, from or through any chemist, while Gillett's lye, which is familiar to everyone, is a convenient form of soda for use in making Soda Bordeaux.

Soda Bordeaux has an advantage over the ordinary Bordeaux in that it is just as good a fungicide, and, at the same time is made without the labor of slaking and preparing of lime. There are disadvantages, however:

1. Great care is necessary in the addition of the caustic soda. Any added in excess is dangerous to foliage; an excess of lime is not harmful, although not advisable.

2. Unless exactly neutral, the addition of an arsenical to Soda Bordeaux to impart to it an insecticidal power, is dangerous. Any free alkali will act upon the arsenic compound and form sodium arsenite, which, being soluble, will scorch foliage.

This last difficulty has already been experienced by orchardists in the Niagara fruit district, and for this reason they may be prone to condemn Soda Bordeaux. However, if care enough be exercised, no harm can result from this source.

Copper Carbonate.

This valuable fungicide can be readily and easily made at home at much less cost than for what it can be bought on the market. The following method of making is recommended: A barrel is partly filled with water and 25 pounds of copper sulphate are dissolved in it and into this is poured a solution of 30 pounds of sodium carbonate (common washing soda) when the copper is thrown down as a pale green precipitate of "basic" copper carbonate. This precipitate rapidly settles to the bottom and after a time the clear solution above can be siphoned off. The barrel is filled with water again, the precipitate stirred up and allowed to settle, and the clear solution again drawn off. This washing removes the greater part of the impurities (sodium sulphate) and leaves behind about 12 pounds of basic copper carbonate. This can be removed from the barrel and dried in the air, after which it is ready for use.

The following quantities can be used for spraying:

Copper carbonate .... 1 pound.
Water .... 40 gallons.

Ammonical Copper Carbonate.

This spray is made from basic copper carbonate the preparation of which has just been outlined under "copper carbonate." When ammonia is added to this material, it dissolves to form a deep blue solution, and this solution diluted with the requisite quantity of water forms the well-known spraying compound.

This fungicide is of use in that it can be applied to trees when the fruit is well advanced in the stage of maturity without causing any disfigurement, such as would result from the employment of Bordeaux. This last material leaves a coating if sprayed just a short time before the fruit is picked, which does not enhance marketing qualities, and which, further, might cause poisoning.

Following are the quantities of material to use:

Copper carbonate .... 5 ounces.
Ammonia (sp. gr. 26° Beaume) .... 3 pints.
Water .... 45 gallons.

Eau Celeste.

The name of this material indicates that it was originated in France, and it was there, in 1885, it first came into use. It has decided action against fungi, but it exerts quite a caustic action on foliage, and for this reason cannot be much recommended. It is made in the following way:

Copper sulphate .... 1 pound.
Hot water .... 2 gallons.

When the crystals are dissolved and the liquid has cooled, add:

Ammonia (sp. gr. 22° Beaume) .... 1½ pints.
Water, to make .... 25 gallons.

When the ammonia is first added a precipitation occurs, but on the addition of the excess this precipitate disappears and a deep blue solution results.

Copper Sulphate.

As was stated when dealing with Bordeaux mixture, this compound can be used to combat fungous diseases on plants, but if used in a solution concentrated enough to be of material benefit would destroy the foliage. Nevertheless, for dormant wood it can be used quite freely, and is recommended in the following strength:

Water	15-25 gallons.
Copper sulphate	1 pound.

In dealing with grain smuts, however, where the strength of the solution is not so necessarily guarded, this substance has been found to be decidedly beneficial. The Experiment Department of this College has done some extended work in dealing with smutted grain, and report the following results in connection with bluestone treatment with oats:*

(*a*) Copper sulphate	1 pound.
Water	25 gallons.
(*b*) Copper sulphate	1 pound.
Water	1 gallon.

In solution (*a*) smut affected grain was immersed for a period of 12 hours; and in (*b*) for a period of 5 minutes. After treatment the grain was dried and sown in test plots, along with a check plot of some left untreated. An average of three years' trial gave these data:

	Percentage of smutted heads.
(*a*) treatment	0.2
(*b*) treatment	1.1
Untreated	7.0

These results show that bluestone has a very decided action in checking smut, and this is especially marked with treatment (*a*).

Formalin.

Formaldehyde is derived from marsh gas (Methane, CH_4), the same gas which everyone has seen emanating from all swamps and low places where there is stagnant water, in the form of air bubbles. The formaldehyde is a gas, which under the influence of cold condenses to a clear mobile liquid that boils at — 21° C., and has the formula CH_2O. If this liquid be mixed with water until it forms 40 per cent. of the volume, we have a commercial article known as "formalin," and which is used and is valuable as a fungicide. It is especially useful as a treatment for grain smuts and potato scab.

Using the following strengths of formalin and method of treatment:

(*a*) Formalin	½ pint,
Water	21 gallons,
(Immersing for 20 minutes),	
(*b*) Formalin	½ pint.
Water	5 gallons,

*Ont. Agri. College Bulletin 140, pp. 14-15.

(sprinkling and stirring till thoroughly moistened), Prof. C. A. Zavitz (Bull. 140, pp. 14-15) obtained the following results with oats, the figures giving the percentage of smutted heads in the crop obtained from sowing the treated grain:

(*a*)	.0 per cent.
(*b*)	.0 per cent.
Untreated	7.0 "

These results show that both treatments with formalin entirely destroy the smut spores adhering to seed grain. These formulæ will also serve for the treatment of wheat.

Corrosive Sublimate.

This chemical is made up of mercury and chlorine, one atom of mercury in combination with two atoms of chlorine, represented by chemists as $HgCl_2$. It is medicinal in small doses, but large doses are ***extremely poisonous***; and its solution in water sprayed onto plants would, for this reason, make a very deadly food for biting insects. As an insecticide, however, it is not much used, on account of its corrosive action, but as a remedy for potato scab it is very valuable when used in the following quantities (handle in a wooden vessel):

Corrosive sublimate	1 ounce.
Water	7 to 8 gallons.

The solution and treated potatoes are both highly poisonous.

Liver of Sulphur, Potassium Sulphide.

This substance is a compound of the elements potassium and sulphur (K_2S) and its solution possesses considerable value as a treatment for certain fungous diseases, such as the gooseberry mildew; but it is not nearly so energetic as are the copper compounds. It is used to some extent in treating grains for smut, for which the following quanities are recommended:

Potassium sulphide	1 pound.
Water	24 gallons.

This solution should be used in a wooden vessel, and must be applied soon after making, since on standing in contact with air the sulphide becomes oxidized to the sulphate and thus loses in strength.

Acknowledgments.

The reports, bulletins, etc., of the Dominion and Provincial Departments of Agriculture, as well as those of the United States Department of Agriculture and the Experiment Stations of the various States of the Union, have been freely used in gathering the data embodied in this bulletin. Where possible, reference has been made to the source of the information, but in all cases the original source of the data could not be obtained.