THESIS

THE ARSENIC INSECTICIDES

BY

Clarence B. Smith.

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Prapared for the degree of Master of Science.

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The Michigan Legislature of 1895, passed a law which is of considerable importance to the farmers and fruit growers of the state. In substance, it is as follows: The fruit growers of each township are compelled by law to spray their orchards with insecticides of known value when five fruit growers of the township so petition.

One result of the law is the large increase in the demand for the arsenic compounds as poisons. Paris Green (Aceto-arsenite of copper) and London Purple (Calcium arsenite) have in the past supplied this demand. But, these preparations have lately become the subjects of a monopolist's concern, in consequence of which, the price has been constantly rising. It was to find some material which has poisoning qualities equal to that of Paris Green and which costs only a nominal sum for its manufacture, that the work recorded in the following pages was performed. Arsenic is taken as the basis for this work, because, at the present time, arsenic in its compounds, is the cheapest and most effective of all known insecticides.

Arsenic in form of arsenious acid (As_2O_3) can be bought in the drug stores at from ten to fifteen cents per pound; but it is impossible to use the arsenic in this form as it not only kills all the insects, but also entirely destroys the foliage. And this is true not only of the pure arsenic, but also of all soluble compounds of arsenic. In fact, it has been conclusively proven by the experiment stations in both North Carolina and Iowa that the amount of injury done to foliage by the use of arsenite compounds is in exact ratio to the amount of soluble arsenic found in them. So, in experimenting with arsenical compounds as insecticides, this fact has been kept constantly in mind. It is also to be remembered in advocating any special form of insecticides for general use, that the great majority of those who use them have little knowledge of the chemical properties of the substances they are using; hence, the form-

ula must be a concise, exact, and never-failing one. In this connection it may be well to state that as long as the price of Paris Green remains at twenty cents per pound, it will be advisable for most small fruit growers to use it; first, because it is always ready for use; second, because it is always effective; then third, it is small in bulk and , fourth, it has been so long in use that every one is acquanted with its properties. But, when the price rises to thirty or forty cents a pound, as it has during the past spring and summer, it will pay in dollars and cents for th e horticulturist to use something cheaper.

White arsenic is a substance exceedingly difficult of solubility in water, yet in alkaline solutions it is readly soluble. It easily forms salts with the metals; and the arsanic salts with the exception of potasium and sodium, are mostly insoluble in water. This is especially true of the arsenites of lead, calcium, and copper; and it is with these metals in combination with arsenic that has made the foundation for my work during the summer. The ideal worked for in each case was an insecticide which should be cheap, easily prepared, harmless to the foliage, and possessing good sticking qualities.

My first work was with the water-soluble compounds, nitrate and acetate of lead, as a basis. I dissolved white arsenic in sodium carbonate and water forming the soluble arsenite of lime (Na_2CO_3 plus H_2O equals $2NaOH$ plus CO_2. $4NaOH$ plus As_2O_3 equals $2\ Na_2HAsO_3$ plus H_2O) This added to either the nitrate or the acetate of lead gives a very fine, white, flocculent precipiatate of the arsenite of lead leaving sodium nitrate or acetate in the solution. (Na_2HAsO_3 plus $Pb(NO_3)_2$ equals $PbHAsO_3$ plus $2NaCH_3CO_2$). The supernatant fluid, however, when the arsenite of soda is used, contains free arsenic. To get rid of this a small quantity of lime must be added; and, indeed, it may be said that with all arsenites, the addition of lime is requisite to insure the complete precipitation in the insoluble form of the free arsenic. When, however, the commercial arsenate of

soda is used with either the nitrate or acetate of lead, an insoluble precipitate of the arsenate of lead is formed, the supernalent fluid of which is entirely free from uncombined arsenic as is clearly proven by Marsh's test for arsenic. But both these compounds of lead are expensive, the nitrate costing 16 and the acetate 18 cents per pound. The commercial arsenate now in the laboratory cost about 15 cents per pound and the arsenate of soda, made by boiling sal soda and white arsenic, cost about the same. This would make a total cost of something like 25 or 30 cents a pound which is altogether too expensive for practical purposes. This being true, a much cheaper substance than lead must be obtained; this is found in the sulphate of copper ($CuSO_4.5H_2O$). When the arsenite of soda, made by boiling $Na_2CO_3.10aq.$ and As_2O_3 together is added to a solution of copper sulphate, a precipitate of the arsenite and hydrate of copper is formed.(The hydrate is formed because of the slight excess of Na_2CO_3 taken to dissolve the arsenic) with reactions as follows: Na_2HAsO_3 plus $CuSO_4$ equals $Cu HAsO_3$ plus Na_2SO_4 and NaOH plus $CuSO_4$ equals Na_2SO_4 plus $CuOH_2$. If now we add a little lime to this, free arsenic in the supernatant fluid will be found to be entirely absent, making the mixture acceptable as an insecticide as the copper sulphate costs only four cents a pound, hence making the total cost of an amount equivalent to a pound of Paris Green, twenty cents,---a price very reasonable.

During the spring and summer, Dr. Kedzie and Professor Taft have been working with the arsenite of soda mixed with lime as a basis,---a much cheaper substance than either lead or copper. Their methods of preparation differ slightly but both are dependent upon the same principle. Dr. Kedzie makes a solution of the arsenite of soda by boiling the white arsenic with carbonate of soda for half an hour. This solution is then added as needed to a little lime and boiled in an iron kettle. This forms the insoluble arsenite of lime. (Na_2HAsO_3 plus $Ca(OH)_2$ equals $CaHAsO_3$ plus $2NaOH$). As lime coats practically

nothing, this makes a very cheap insecticide. Professor Taft however, boils the arsenic with the lime direct. The alkalinity of the lime dissolves the arsenic and at the same time it enters into combination with it forming the insoluble arsenite of lime. (AsO_2 plus $2Ca(OH)_2$ equals $2CaHAsO_3$ plus H_2O). I performed a number of experiments as to the time required for boiling the arsenic and lime before the whole was converted into the insoluble salt, and found that to be perfectly sure the supernatant fluid is devoid of free arsenic requires at least thirty minutes steady boiling. The disadvantage in this method is at once apparent. Every time one wishes to use a solution for spraying, no matter how small the quantity, he must stop and boil the ingredients for a half an hour. I prefe a modification of Dr. Kedzie's method. Make a solution of the arsenite of soda by boiling three parts of soda and one of arsenic. Now I find by repeated experiments that fresh lime, slaked with this arsenite of soda solution enters at once into chemical combination with it and that when the lime is afterwards diluted with water, the supernatent fluid does not give the slightest deposition of arsenic with Marsh's test. The advantage of this method over that of boiling with the lime direct, is considerable,,because a solution of the arsenite of soda can be made at one time sufficient to last during an entire season and kept in jugs or other vessels. It can then be used from time to time as occasion demands by simply using the solution to slake the lime with. The strength of the liquid being known(Na_2AsO_3), about three pounds of fresh lime should be taken for slaking a solution containing a pound of Na_2HAsO_3. In skilled hands two pounds of lime is an abundance but three pounds makes its use absolutely safe in the hands of amateurs. The same thing is true when the arsenate of soda is used. A solution used in slaking lime gives the insoluble compound of the arsenate of ~~soda~~ lime. Now the arsenate of soda is quoted in the chemical journals at thirteen cents a pound. The greater

part of it, however, consists of the arsenate of lime and other impurities. But should there be a large demand made for the pure arsenite of soda, some enterprising firm would soon commence its manufacture. In that case we could take at our convenience, our arsenite of soda, dissolve it in a little water and slake the lime with it, and thus do away with the boiling which is certainly an inconvenience of no small importance.

As compared with the precipitate obtained when the arsenite of soda and sulphate of copper are used, the arsenite of calcium is not as good for spraying purposes. First because in the coppere arsenite, CuHAsO3, we have not only the poison of the arsenic but also the poison of the copper, thus making the whole a more potent poison: second the hydrate of copper, Cu(OH)2, formed, is a good fungicide in itself while calcium is devoid of such properties; and thatd, the bulk of the depositdd material is much smaller and more floculent than is that of the araenite of lime; thus making it easier to spray and requiring less agitation to keep it thoroughly mixed.

A working formula of the copper sulphate solution, derived from the molecular weights of the substances and proved by actual tests is as follows:

Carbonate of soda	Na2CO3,10H2O	3parts.
White arsenic	As2O3	1part
Sulphate of copper	CuSO4,5 H2O	4 parts.
Lime	CaO	2 parts.

The copper sulphate solution is added to the soda arsenite solution and then added to the lime. If the above formula is taken in pounds, the whole, to be made equivalent to Paris green should be reduced to 600 gallons which makes an actual cost, estimated with the pride of carbonate of soda at 3 cants copper sulphate at 4 cents, and white arsenic at 12 cents, per pound respectively, at a little less than two cents per barrel.

The sqme formula without the copper sulphate makes ab abo one and one-half pounds of the arsenite of calcium which ca be diluted to about 350 gallons; this makew a cost of a

more than 1.5 cents per barrel, so there is not much difference in the relative costs of the two mixtures.

In briefly summarizing, I would say: Lead salts are too expensive for present use. Copper sulphate with the arsenite of soda and with lime is the most general and effective insecticide of those worked with.

Calcium arsenite is the cheapest of all known valuable insecticides and can be best made by slaking lime with an an arsenite of soda solution.