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University of Idaho

Agricultural Experiment Station

Department of Chemistry.

THE COMPOSITION OF ARSENICAL INSECTICIDES.

BY

S. AVERY.

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The Composition of Arsenical Insecticides.

During the past year the Department of Chemistry has devoted considerable time to the study of Insecticides. Much of the work is too technical to be of immediate interest to the practical man. The details of the methods of study and analysis will be published in scientific journals. This bulletin is intended to convey to the intelligent horticulturist a brief statement of some of the results obtained. No attempt has been made to write a *Manual of Spraying*. It is hoped, however, that a perusal of these pages will give the orchardists of Idaho some practical information in regard to the composition and character of the insecticides that they are liable to use during the coming season.

The writer is indebted to Professor Huntley, Horticulturist of this Station, for valuable suggestions; to the State and District Inspectors for collecting samples; and, especially, to Mr. Thorn Smith, formerly of this Department, and to Mr. Hal Beans, Assistant Chemist, for devising methods and carrying on much of the analytical work.

Paris Green.

There is a wide-spread opinion that this insecticide is commonly adulterated. A bulletin issued during the past season by the Oregon State Board of Horticulture contains the following: "Paris green is one of our commercial articles which is shamefully adulterated. * * So far as we know but two adulterants are used—gypsum and Glauber's salts. The method generally given

for the detection of adulteration is to dissolve a small sample of the Paris green in ammonia. If there is any gypsum it will not dissolve, but forms a sediment. Glauber's salts can not be detected by this method, it being equally as soluble as Paris green; but if one has a strong microscope at hand the adulterant granules can be easily detected, they being white, while the pure article is green Ammonia, however, is generally a good test, gypsum being most commonly used as an adulterant. * * * Paris green being so much adulterated, its use has been pretty much discarded."

Bulletin 126 of the California Station gives in its summary: "Paris green as now found on the market is often unsatisfactory, occasionally a bogus article, sometimes adulterated, commonly low grade, and very often with much free arsenic, which is dangerous to foliage, especially in California, and the injury from which cannot always be prevented by the addition of lime."

Many orchardists in Idaho report that they have had poor results from spraying with Paris green and think that the green may have been adulterated.

In view of this uncertainty, it was determined to analyze as many samples of Paris green as could be found in the hands of the dealers or users in the State. No effort was made to ascertain the factories producing these samples. The question to be answered was simply this: "Is the Paris green sold in the State in most instances reasonably pure?"

Accordingly a circular letter was addressed to horticultural inspectors and prominent orchardists requesting that samples be sent to the Station for analysis. In most instances replies were received and considerable interest seemed to be felt in the work.

Composition and Standards of Purity.

Paris green is also known as Schweinfurt green and Emerald green. It was long used as a pigment before its use as an insecticide became common. According to Ehrmann and others, pure Paris green is copper aceto-arsenite; in 100 parts—oxide of copper 31.29; arsenious acid 58.65; acetic acid 10.06. Wagner states that this formula is only empirical because a portion of the copper is present as the suboxide, and a portion of the arsenic as

arsenic acid. This statement has been frequently quoted in station bulletins. The writer believes, however, that experiments conducted at the Idaho station show that in the samples examined during the past year this variation is very slight if it exists at all, and that Ehrmann's formula is essentially correct.

A commerical product could hardly be expected to be absolutely dry and free from occasional particles of foreign substances; hence the per cent in the best samples would be slightly below the figures given in the last paragraph. If we allow 3 per cent for moisture and dirt, the percentage of a commercial sample, otherwise pure, would run approximately—copper oxide 30.35; arsenious acid 56.89; acetic acid 9.76.

While the assumption of 3 per cent. of foreign matter is entirely arbitrary, it is interesting to note that the average of 19 samples analyzed in this laboratory shows: Copper oxide 30.49 per cent; arsenious acid 56.86 per cent.

Several of the states have now well enforced laws requiring that Paris green exposed for sale in the state shall contain not less than 50 per cent of arsenious acid. In such cases there is a margin of a little over 8 per cent between a pure sample and the minimum legal requirement. No laws as yet require that the arsenic shall be so chemically united as to form copper-aceto-arsenite or Paris green.

Paris Green Used in Idaho During the Past Season.

The following gives the per cents. of total arsenious acid, copper oxide, and "soluble arsenious acid." As will be shown later in this bulletin, soluble arsenic is an indefinite term. The figures here given represent the amount of arsenious acid rendered soluble by water under the following conditions: $\frac{1}{2}$ gram of Paris green was suspended in 50 cc. of distilled water in a stoppered cylinder; after allowing to stand for one week, with occasional shaking, the amount of arsenic in solution was determined.

DEALER OR SENDER.	PER CCNT. OF ARSENIOUS ACID.	PER CENT. OF COPPER OXIDE.	PER CENT. OF SOLUBLE ARSENIOUS ACID.
Lumpkin Drug Co, Moscow.....	55.69	31.38	3.82
Hodgins Drug Store, Moscow,.....	55.08	31.54	2.44
Torson Drug Store, Moscow,.....	57.07	31.38	5.52
McCarter Drug Store, Moscow,.....	57.33	31.24	3.93
Prof. J. M. Aldrich, Moscow,... ...	60.49	30.53	3.92
Lee R. Carlton, Kendrick,.....	58.18	31.10	3.39
F. W. Neimann, Salmon,.....	56.17	29.59	2.86
S. G. Isaman, Lewiston,.....	55.56	30.77	3.52
Joy's Drug Store, Boise,.....	55.20	29.55	3.58
W. S. Whitehead, Boise,.....	56.84	31.16	3.30
Mr. Ketchum, Payette,.....	56.09	30.68	2.80
McCrum & Co., Boise,.....	55.68	31.11	3.11
McCrum & Deary, Boise,.....	56.84	30.14	3.33
Joy's Drug Store, Boise,.....	56.96	30.10	2.61
F. W. Galbraith, Boise,.....	56.72	29.09	2.72
W. S. Whitehead, Boise,.....	56.78	30.24	2.98
A. C. White, Kendrick,.....	56.48	30.72	3.21
H. A. Russell, Kendrick.....	61.05	28.50	4.32
Nick Broche, Kendrick,.....	56.23	30.58	2.41
Average	56.86	30.49	3.35

All of these samples are of good quality, and, with one or two exceptions, remarkably uniform.

The averages agree, almost exactly with the calculated per-centage composition of a sample of copper-aceto-arsenite containing 3 per cent. of moisture and foreign substances.

Samples of this character leave almost nothing to be desired in the way of purity. No evidence, whatever, of the reputed wide spread adulteration of Paris green was discovered in Idaho during the past season.

The Action of Water on Paris Green.

Nearly all authorities state that pure Paris Green is insoluble in distilled water, and assume that, in case Paris green gives off arsenic to distilled water, the cause is traceable to free or uncombined arsenious acid in the original sample. This assumption is incorrect. Pure Paris green is broken up, to a greater or less extent, by the prolonged action of water, and is resolved into soluble arsenic, soluble copper, and a residue containing a higher per cent. of copper than the original green. Pure Paris green usually consists of well defined microscopic

green balls which resist fairly well the disintegrating action of water. If these balls are broken by grinding, the decomposition is rapid. In this laboratory we have extracted, by means of distilled water alone, 55 per cent of the total arsenic in a sample that we have every reason to believe was perfectly pure. This sample was, however, finely pulverized.

Free arsenious acid is always soluble in water; combined arsenious acid is liable to be rendered soluble by water; soluble arsenic burns foliage. In ordinary spraying operations Paris green, free from uncombined arsenious acid, is not decomposed with sufficient rapidity to seriously burn the foliage of most forms of vegetation. Till better methods are devised for distinguishing between uncombined arsenious acid, and soluble arsenic, resulting from decomposition, this Station will adopt the following: All samples of Paris green will be recommended as safe for ordinary spraying purposes in Idaho which do not yield more than 6 per cent of soluble arsenious acid when suspended for one week, at ordinary temperature, in water, in ratio of 1000 parts water to one of the green.

Determination of the Quality of Paris Green.

Many tests have been proposed for the determination of adulterations in Paris green. A typical sample of this substance has a peculiarly characteristic bright green color; the particles have slight adhesion for each other. A person who is familiar with the color and physical properties is not likely to be greatly deceived. Still some off-colored samples are better and purer than other more brilliant ones.

Bulletin 49 of the Oregon Station contains the following: "The effect of the adulterants on the appearance of the Paris green is to render the color lighter, but if the adulterants have been added to a coarse grained sample there will be little difference between its appearance and that of a normal one of fine texture.

If one has a microscope capable of magnifying two hundred diameters it would be a comparatively easy matter to detect the admixture of these materials which could be present for no other purpose than adulteration.

There is really no *easy* and *sure* chemical method that can be applied by every one for the detection of the adulteration. It is often said that pure Paris green will dissolve perfectly in ammonia. This is true, but Paris green adulterated with sodium sulphate will dissolve equally well in that liquid, hence the test is not adequate unless the adulterant happens to be gypsum or some other substance insoluble in ammonia. After a little experience the streak left upon glass by causing a small pile of the green to slide over it may give some idea of the purity of the sample. To execute the test: with the point of a knife place a small pile of the Paris green on a piece of glass held slanting; tap the glass lightly with the knife and the pile will move across the glass leaving a streak on the glass. If the Paris green is pure this path will be a bright green, otherwise it will be more or less white."

While the tests above given are of some value in determining the quality of Paris green, they are not recommended by the Idaho Station. Even a person familiar with the work with a microscope at his disposal cannot always readily distinguish between powdered, arsenious acid added to bring up the per cent. of arsenic in a low grade sample, and broken balls of Paris green. The only satisfactory test is a chemical analysis. Samples sent to the Station by residents of Idaho will be analyzed free of charge.

London Purple.

This insecticide is used in Idaho less frequently than Paris green. London purple is generally supposed to consist of arsenite of lime mixed with a small per cent. of arsenate of lime and a residue of an "aniline dye." According to an investigation just published*, the greater part of the arsenic is in the form of arsenate of lime. It has long been known that London purple is peculiarly liable to burn foliage and this tendency has been traced to its high per cent of soluble arsenic. Tests made in this laboratory show that in some samples considerable lime is present in the form of the carbonate. In such cases there is

*Haywood, Jour. Am. Chem. Soc. Dec. '00. p. 800.

present inert matter of no value whatever. Since the composition of London purple varies so greatly, and since the appearance of the article affords no means of judging of its composition, the prospective purchaser can protect himself only by means of a chemical analysis.

Other Arsenical Insecticides.

During the past year or two, several samples of "Arsenoids" have been sent by the manufacturers to this station for examination. These, apparently, represent honest efforts to produce good articles that can be sold at a lower price than Paris green. Most of them present efforts to neutralize and render insoluble arsenious or arsenic acid by means of lime, barium oxide, lead oxide or copper oxide. As these products have not been generally put on the market in Idaho, it seems unnecessary to study them closely. On the other hand a series of experiments was conducted to determine the relative capacity of the bases just mentioned to form stable and insoluble compounds with arsenious and arsenic acid.

Calcium Arsenite.

The normal arsenite of lime is decomposed by boiling water. The lime and arsenic do not go into solution in the same proportions in which they exist in the original compound. A solution of arsenious acid in water is not completely precipitated by adding an equivalent amount of lime water. Arsenite of lime suspended in water is entirely dissolved by passing in carbonic acid gas.

From the above it will be seen that lime forms unstable compounds with arsenious acid, and that these compounds readily give off soluble arsenic when exposed to the action of water or carbonic acid gas. In spite of these unfavorable properties, home-made arsenite of lime has been used with success in Michigan, Iowa, the states of the Pacific coast and elsewhere. The tendency of arsenite of lime to give off soluble arsenic is reduced or at least retarded as the excess of lime is increased. This fact is in harmony with the observation of Mr. Smith, of Hood River,

Oregon, that a large excess of lime prevents the burning of foliage.

Calcium arsenate shows about the same stability towards water and carbonic acid as the corresponding arsenite.

Copper Arsenite.

This is sometimes sold as "Green Arsenoid." It is a dull green color and shows about the same stability towards water and towards carbonic acid as Paris green does.

Barium Compounds.

Oxide of barium seems to have at best, only a slight tendency to form insoluble arsenites. There is no evidence to show that it can be used successfully in the manufacture of arsenical insecticides.

Lead Compounds.

Lead arsenite is a stable compound and is but slightly affected by boiling water or by the combined action of water and carbonic acid. Of all compounds studied, however, normal lead arsenate is the most stable. Water even on prolonged boiling does not liberate soluble arsenic. Carbonic acid is also without effect. Lead arsenate is the only arsenical insecticide studied in this laboratory that completely withstood the action of these two agencies. This is, of course, in harmony with the observations made by prominent horticulturists that arsenate of lead can be used with almost absolute safety on the most delicate vegetation.

Home-Made Arsenite of Lime.

The following directions by Professor Taft of Michigan have been widely circulated and apparently given good results: "Boil one pound of (white) arsenic and two pounds of lime in two gallons of water for forty minutes and then dilute as required. Use one pound of the arsenic, prepared as above, in every three hundred to four hundred gallons of water, to destroy the codling-moth. Unless used in Bordeaux mixture, it is best to add a small amount of lime when diluting.

The usual precautions to prevent poisoning should be observed. Especial care should be taken that well-burned and

fresh (i. e. not air-slaked) lime be procured. This product would probably be found by the orchardists of Idaho about one-fourth as expensive as Paris green.

The well known formula of Professor Kedzie of Michigan, as given in California bulletin No. 126, is as follows: Boil two pounds of white arsenic with eight pounds of sal-soda in two gallons of rain water. Boil these materials together in an iron pot not used for any other purposes; boil them fifteen minutes or until the arsenic dissolves, leaving only a small muddy sediment. Put the solution in a two-gallon jug and label *Poison, Stock Material for Spraying Mixture.* The spraying mixture can be prepared whenever required in the quantity needed at the time, by slaking two pounds of lime, and adding this to forty gallons of water; pour into this a pint of the arsenic stock solution; mix up, stirring thoroughly and the spraying mixture is ready for use The arsenic in this mixture is equivalent to four ounces of Paris green.

Prepared for spraying in this way, arsenic would cost in Idaho, pound for pound, about one-half as much as when purchased in the form of Paris green.