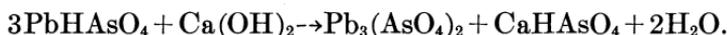


A STUDY OF LEAD ARSENATE AND LIME SPRAY MIXTURES¹

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INTRODUCTION

For several years the addition of slaked lime to lead arsenate sprays, for the purpose of decreasing or preventing injury to stone fruits, such as peach and plum, has been recommended by the United States Department of Agriculture. The chemical reactions which may take place in such a mixture have received the attention of at least two investigators. Robinson (8)² suggests that the reaction which takes place may be represented by the equation:



Campbell (2) on the basis of certain "semiquantitative experiments" proposes that "for the purpose of discussion" the reaction may be represented by the equation:



Experiments carried out in the summer of 1925 indicate that neither of the above reactions represents completely the change which takes place, and it appears desirable, therefore, to give an account of this work.

The first part of the present paper embodies the results obtained in laboratory studies of the chemical reactions which may occur in mixtures of acid lead arsenate and lime. The second part of the paper deals with the effectiveness of the mixture in preventing the arsenical injury which results when lead arsenate is used alone in spraying peach orchards.

LABORATORY EXPERIMENTS

EARLIER INVESTIGATIONS

The most comprehensive investigations of the arsenates of lead, carried out in recent years, are those of C. C. McDonnell and C. M. Smith (5) and of McDonnell and Graham (4). Tartar and Robinson (10) and G. E. Smith (9) have also made a study of these compounds.

If we confine our attention to the compounds which can be prepared by precipitation from solution, there are six arsenates of lead to be taken into account. Using the nomenclature of McDonnell and Smith (5), these are: (1) Monolead ortho arsenate, $\text{PbH}_4(\text{AsO}_4)_2$; (2) dilead ortho arsenate, PbHAsO_4 ; (3) trilead ortho arsenate $\text{Pb}_3(\text{AsO}_4)_2$; (4) 4, 1, 3, 1-lead-hydroxy arsenate (hydroxy mimetite),

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² Reference is made by number (italic) to "Literature cited," p. 321.

$Pb_4(PbOH)(AsO_4)_3 \cdot H_2O$; (5) 5, 2, 4-lead-hydroxy arsenate, $Pb_5(PbOH)_2(AsO_4)_4$; (6) octo-lead arsenate, $8PbO \cdot As_2O_5 \cdot \frac{1}{2}H_2O$.

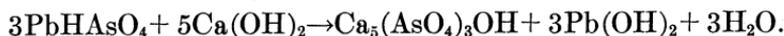
The first of these is obtained only in strongly acid solutions, and is therefore not of importance in the present discussion.

Four arsenates of calcium are described in the literature. These are: (1) Primary calcium arsenate, $CaH_4(AsO_4)_2$; (2) secondary calcium arsenate, $CaHAsO_4$; (3) tertiary (normal) calcium arsenate, $Ca_3(AsO_4)_2$; (4) basic calcium arsenate, $Ca_5(AsO_4)_3OH$.

The first three of these have been recognized for many years. The existence of the last one seems to have been suspected by several investigators. It has been prepared and studied by Tartar, Wood, and Hiner (11). These investigators have obtained evidence that an arsenate of calcium more basic than $Ca_5(AsO_4)_3OH$ is not formed by the action of calcium hydroxide solution on this compound at ordinary temperatures.

McDonnell, Smith, and Coad (6) studied the effect of atmospheric carbon dioxide on commercial calcium arsenate during storage. They found that carbonation increased the "water-soluble arsenic oxide," but that when the sample was sufficiently basic, the "soluble arsenic oxide" in the completely carbonated samples exceeded 1 per cent in only one case.

On the basis of the work just discussed, it becomes possible to state what reactions will probably occur in a mixture of acid lead arsenate ($PbHAsO_4$) and a large excess of calcium hydroxide, suspended in water. There will be formed basic calcium arsenate, as a result of the decomposition of the acid lead arsenate. The lead arsenate will probably go through several stages of basicity, using the term in the sense of ratio ($PbO:As_2O_5$), and may eventually be deprived of all arsenic oxide, leaving one of the hydrates of lead oxide as a final product. Assuming, for the moment, that lead hydroxide ($Pb(OH)_2$) is the final product we may represent the change which takes place, when the reaction goes to completion, as:



EXPERIMENTS IN 1925

ACTION OF CALCIUM HYDROXIDE ON ACID LEAD ARSENATE

The lead arsenate used in these experiments was a commercial product which was dried at $110^\circ C$. to constant weight. Its composition was found by analysis to be:

	Found	Calculated for $PbHAsO_4$
Lead oxide (PbO)-----per cent--	64.94	64.30
Arsenic oxide (As_2O_5)-----do--	31.50	33.11
Water (H_2O) (by difference)-----do--	3.56	2.59

The lead arsenate used was therefore slightly more basic and contained somewhat more water than corresponds to the formula $PbHAsO_4$.

A saturated solution of lime water was prepared from c. p. calcium hydroxide, and analyzed, for each series of experiments, by titration with N-100 hydrochloric acid solution, using phenolphthalein as indicator.

The experiment was carried out as follows: A portion of lead arsenate was weighed out accurately and placed in a jar provided with a glass top and rubber seal, to which was added a definite quantity of lime water and freshly distilled water to give the desired dilution. The jar was then sealed and placed in a motor-driven shaking machine. After shaking at room temperature (about 25° C.) for the required time, the contents of the jar were allowed to settle (usually over night) and 10 c. c. of the clear liquid was removed for titration with N-100 hydrochloric acid. The calcium hydroxide remaining in the solution was subtracted from the amount originally introduced. It was assumed that this difference gave the amount of the calcium hydroxide which had reacted with the lead arsenate. In all these experiments the effect of atmospheric carbon dioxide was reduced to a minimum by working rapidly and removing the tops of the reaction vessels just enough to permit the withdrawal of the samples.

In the first series of experiments the reacting substances were brought together and the shaking continued for a sufficiently long time to permit the reaction to go to completion. The results are summarized in Table 1.

TABLE 1.—Action of $\text{Ca}(\text{OH})_2$ solution on PbHAsO_4 , after long-continued shaking, at room temperature (25° C.)

Lead arsenate used	$\text{Ca}(\text{OH})_2$ added	$\text{Ca}(\text{OH})_2$ left	$\text{Ca}(\text{OH})_2$ used up	Total volume	Time of shaking	$\text{Ca}(\text{OH})_2$ used up	
						Per gram of lead arsenate	Per gram of As_2O_5
Grams	Grams	Grams	Grams	C. c.	Hours	Grams	Grams
0.50	0.3180	0.1440	0.1740	200	150	0.3480	1.105
.75	.3290	.0920	.2370	200	150	.3160	1.003
2.00	1.4927	.7945	.6982	1,000	290	.3491	1.108
3.00	1.4927	.5764	.9163	1,000	290	.3054	.969

For the production of $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, 1 gm. of As_2O_5 reacts with 1.072 gm. of $\text{Ca}(\text{OH})_2$. The other product of the reaction is one of the hydrates of lead oxide.

In two of the jars there was formed a greenish-yellow, flaky substance. This was separated from the white calcium arsenate by stirring, settling, and decantation. The greenish-yellow material, being much heavier, settled quickly. A quantity sufficient for analysis was collected and dried in the air. A determination of lead oxide in the air-dried sample showed it to contain 96.32 per cent PbO . This result corresponds closely to the hydrate $2\text{PbO}\cdot\text{H}_2\text{O}$ (96.12 per cent PbO) which has been described by Luedeking (3). Another hydrate, $3\text{PbO}\cdot\text{H}_2\text{O}$, has been described by Pleiszner (7), who obtained it by the action of barium hydroxide on warm solutions of lead salts, or cold solutions of PbO . The optical properties of the greenish-yellow crystals obtained in the writers' experiments do not agree well with those ascribed to the hydrate $2\text{PbO}\cdot\text{H}_2\text{O}$, and the composition does not agree with the hydrate $3\text{PbO}\cdot\text{H}_2\text{O}$.

The results leave no doubt, however, as to the fact that at ordinary temperatures the reaction between lead arsenate and calcium hydroxide, if given sufficient time, results in the complete decomposition of

the lead arsenate, with the formation of basic calcium arsenate and a hydrate of lead oxide.

RATE OF REACTION

To ascertain to what extent this reaction proceeds in the ordinary spraying operation a second series of experiments was undertaken, in which weighed quantities of lead arsenate were shaken with known quantities of calcium hydroxide for periods of time which were insufficient for the completion of the reaction. Preliminary experiments having shown that the reaction takes place rather slowly, analysis of the solution was made at the end of 21 and of 37 hours of shaking. The rate of disappearance of calcium hydroxide from the solution may be taken as a measure of the rate of the reaction. The results are given in Table 2.

TABLE 2.—*Effect of shaking 1 gram of lead arsenate with 200 c. c. of a solution of calcium hydroxide (temperature about 25° C.)*

Quantities of Ca(OH) ₂ (in milligrams)—				
Originally present	Used up in 0 to 21 hour period	Used up per hour in 0 to 21 hour period	Used up in 21 to 37 hour period	Used up per hour in 21 to 37 hour period
110.9	29.4	1.40	32.5	2.03
126.7	30.2	1.44	28.5	1.78
129.8	31.0	1.47	24.5	1.53
133.0	30.2	1.44	24.1	1.50
136.0	28.8	1.37	25.1	1.57
142.3	27.8	1.32	23.0	1.44

It is evident that the rate of disappearance of calcium hydroxide does not vary greatly with time, and that it is exceedingly slow. The complete decomposition of 1 gm. of the lead arsenate used in these experiments requires about 338 mgm. of calcium hydroxide. The average hourly rate of 1.52 mgm. corresponds to the complete decomposition of less than one-half of 1 per cent of the lead arsenate.

On the basis of these results it seems reasonable to conclude that the spray which reaches the foliage consists essentially of unchanged lead arsenate particles, possibly altered superficially to basic calcium arsenate and either lead arsenate or lead hydroxide, and this is mixed with a considerable amount of slaked lime. After such a mixture is exposed to the air, carbonation takes place, so that a deposit of the composition mentioned will soon be altered completely to a mixture of calcium carbonate, acid lead arsenate, and a small amount of basic lead arsenate, or calcium arsenate.

RATE OF LIBERATION OF "SOLUBLE ARSENIC"

In a final series of experiments the question of whether the action of atmospheric carbon dioxide results in any large increase in "soluble arsenic" was taken up. The lead arsenate used in these experiments was somewhat basic to begin with, and had a low content of "soluble arsenic." If the chemical action of the lime, followed by atmospheric action, tended to increase the content of "soluble arsenic" appreciably, this should be readily apparent.

In these experiments 2 gm. of lead arsenate were accurately weighed, mixed into a paste with water, and then the cooled milk of lime resulting from the action of about 40 c. c. of water on 6 gm. of quicklime was added. The whole was intimately mixed on a watch glass and allowed to evaporate to dryness in the air. As soon as the material was dry it was powdered in a mortar and then returned to the watch glass, where it was exposed to the air of the laboratory. A number of such samples were prepared and a determination of "soluble arsenic" by the usual method (1, p. 50) was made at intervals of several days. The results are as follows:

Sample No.	Time of exposure (days)	Per cent of soluble arsenic, expressed as As_2O_5
1.....	1	0.27
2.....	3	.44
3.....	5	.60
4.....	8	.60
5.....	9	.68
6.....	16	.60
7.....	23	.64
8.....	154	.65
Lead arsenate without lime.....		.44

The solutions obtained by treating the above samples with water were tested with phenolphthalein to determine whether the lime had been completely carbonated. All samples gave an alkaline reaction, even the one which had been exposed to the air for 154 days.

In order to determine what the result would have been, had complete carbonation taken place, two additional experiments were carried out. In one of these the water suspension obtained from sample No. 8 was rendered just acid to phenolphthalein by bubbling carbon dioxide through it. The "soluble arsenic" was then determined in the usual manner. Since it was very difficult to avoid a slight excess of the gas, the second experiment consisted in adding 11 gms. of c. p. calcium carbonate powder to 2 gms. of the lead arsenate and 1 liter of carbon-dioxide-free water. The "soluble arsenic" was then determined as before, the results being as follows:

	Per cent soluble arsenic expressed as As_2O_5
Sample 8, acidified with CO_2 gas.....	4.15
Lead arsenate treated with c. p. $CaCO_3$	3.15

The results show that, under the conditions of the experiment, carbonation takes place very slowly, and that as long as there is any unchanged calcium hydroxide the amount of "soluble arsenic" is very low. As soon as all the lime has been converted to carbonate, however, there is a large increase in the "soluble arsenic."

ORCHARD EXPERIMENTS

The results of the laboratory work just described would seem to indicate that the addition of lime to lead arsenate should be effective in preventing injury to peach foliage for a time at least. During the period from the time the spray application is made until the calcium

oxide, not combined as arsenate, is carbonated, the proportion of the "soluble arsenic" is low, and a corresponding freedom from injury may be expected. To determine this point, and also to obtain data on the efficiency of various spray combinations of acid lead arsenate and slaked lime against the Japanese beetle, a number of experiments were conducted in peach orchards in the vicinity of Riverton, N. J., in 1923, 1924, 1925, and 1926.

All of the orchards used for the experimental work consisted of bearing trees in a healthy condition, with a very good growth of foliage. The sprays were delivered by a power sprayer at a pressure of 200 pounds per square inch. Disc nozzles were used with rods. A thorough application was made. In the experiments reported for 1923, 1924, and 1926 the lead arsenate and lime were used in connection with orchard control measures against the Japanese beetle. The lead arsenate and lime were commercial products and no chemical analyses were made of their composition. In 1925, however, a special study was made of the effect of lime and lead arsenate mixtures on peach trees, and chemical analyses were made of the lime and lead arsenate used during that year.

Observations were made at intervals throughout the summer for injury to the fruit, foliage, and wood. The injury, expressed in percentage, is an estimate of the area injured as compared with the rest of the tree. The characteristics of arsenic injury were definite in every instance in which record was made as to the extent of injury.

The experiments made and the results obtained each year are given below.

EXPERIMENTS PERFORMED IN 1923

The orchard selected for these experiments consisted of the Rochester variety of peaches. Twenty-five trees were selected for each plot and these plots were sprayed June 29. The treatment of the plots was as follows:

- Plot 1. Lead arsenate, 3 pounds; water, 50 gallons.
- Plot 2. Lead arsenate, 2 pounds; water, 50 gallons.
- Plot 3. Lead arsenate, 1 pound; water, 50 gallons.
- Plot 4. Lead arsenate, 3 pounds; lime, 3 pounds; water, 50 gallons.
- Plot 5. Lead arsenate, 2 pounds; lime, 3 pounds; water, 50 gallons.
- Plot 6. Lead arsenate, 1 pound; lime, 3 pounds; water, 50 gallons.
- Plot 7. Control, lime, 3 pounds; water, 50 gallons.
- Plot 8. Control unsprayed.

RESULTS

Observations were made throughout the summer for fruit, wood, and foliage injury, the final results being recorded September 26. At this time heavy deposits of spray residue remained on the fruit and with the exception of plot 1 no foliage, fruit, or wood injury was evident. Plot 1, which had been treated with 3 pounds of lead arsenate to 50 gallons of water, showed foliage injury to the extent of approximately 10 per cent. Aside from this, the trees in all of the plots were vigorous and of good color.

EXPERIMENTS PERFORMED IN 1924

The orchard selected consisted of the following varieties: Hiley Belle, Carman, Old Nixom, and Elberta. The plots consisted of trees of each variety. The treatments were applied June 12, as follows:

- Plot 1. Lead arsenate, 1½ pounds; lime, 3 pounds; water, 50 gallons.
- Plot 2. Lead arsenate, 1½ pounds; water, 50 gallons.
- Plot 3. Control, unsprayed.
- Plot 4. Lead arsenate, 2 pounds; lime, 3 pounds; water, 50 gallons.
- Plot 5. Lead arsenate, 2 pounds; water, 50 gallons.
- Plot 6. Control, unsprayed.
- Plot 7. Lead arsenate, 1 pound; lime, 3 pounds; water, 50 gallons.
- Plot 8. Lead arsenate, 1 pound; water, 50 gallons.
- Plot 9. Control, unsprayed.
- Plot 10. Lead arsenate, ½ pound; lime, 3 pounds; water, 50 gallons.
- Plot 11. Lead arsenate, ½ pound; water, 50 gallons.

RESULTS

Observations were made at various periods during the season, final results being recorded August 31. Plot 2, treated with lead arsenate 1½ pounds, water 50 gallons, and plot 5 treated with lead arsenate 2 pounds, water 50 gallons, showed foliage injury to the extent of 10 per cent, and slight wood and fruit injury. All other plots were free from arsenical injury. Thus it is shown that the lime added to lead arsenate prevented injury to the foliage in plots 1 and 4.

EXPERIMENTS PERFORMED IN 1925

A 4-year-old peach orchard, planted especially for experimental work by the Japanese Beetle Laboratory, in 1921, consisting of Carman, Hiley Belle, Georgia Bell, and Elberta, was selected. Stone lime⁴ from three different manufacturers was used. Three applications of lead arsenate and lime were made May 12, June 12, and July 13, respectively, as follows:

- Plot 1. Lead arsenate, 1½ pounds; lime from Bellefonte, Pa., 3 pounds; water, 50 gallons.
- Plot 2. Lead arsenate 1½ pounds; lime from Norristown, Pa., 3 pounds; water, 50 gallons.
- Plot 3. Lead arsenate, 1½ pounds; lime from Sherwood, Tenn., 3 pounds; water, 50 gallons.
- Plot 4. Lead arsenate, 1½ pounds; water, 50 gallons.
- Plot 5. Control, unsprayed.

The composition of the lime used in these experiments is as follows:⁵

	Lime from Bellefonte	Lime from Norristown	Lime from Sherwood
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
SiO ₂	0.72	0.29	0.43
Al ₂ O ₃ , Fe ₂ O ₃61	.59	2.50
CaO.....	95.37	97.07	55.46
MgO.....	.24	.26	35.18
Loss on ignition.....	2.48	1.13	6.49

⁴ The authors are indebted to G. J. Fink, chemical director of the National Lime Association, Washington, D. C., through whose courtesy the lime was furnished.

⁵ The composition of the lead arsenate used is given on page 2.

RESULTS

The results from the applications of sprays were very definite. Although a treatment consisting of three applications of lead arsenate at the rate of $1\frac{1}{2}$ pounds to 50 gallons of water is somewhat in excess of the usual recommendations, the writers used this in order to be sure that the effect upon the trees of adding the lime to the lead arsenate would be pronounced. The trees in plot 4, which had been treated with $1\frac{1}{2}$ pounds of lead arsenate to 50 gallons of water, were 90 per cent defoliated August 31, when the final results were recorded. The wood on these trees was so severely injured that only 2 trees of the 24 in the plot were living in 1926. The foliage in plot 3 was injured 5 per cent. All other plots were free from arsenical injury. Apparently a lime high in magnesia is as satisfactory for this purpose as one low in magnesia.

EXPERIMENTS PERFORMED IN 1926

The same orchard that was used in 1924 was again used in 1926 for conducting these studies. Four plots were used to determine the effect on the foliage of adding lime to lead arsenate, and the treatment was as follows:

- Plot 1. Lead arsenate, $1\frac{1}{2}$ pounds; lime, 3 pounds; water, 50 gallons.
- Plot 2. Lead arsenate, $1\frac{1}{2}$ pounds; lime, 6 pounds; water, 50 gallons.
- Plot 3. Lead arsenate, $1\frac{1}{2}$ pounds; water, 50 gallons.
- Plot 4. Control, unsprayed.

RESULTS

In plot 3, where lead arsenate had been applied without the lime, 10 per cent injury resulted to the foliage, whereas no foliage injury resulted in the plots treated with the lime and the lead arsenate. The results are similar to the results from experiments conducted during previous years, as described above.

The influence of the weather conditions on the physical and chemical action of the lime and lead arsenate mixture is not considered here, but will be discussed in another paper.

SUMMARY

The action of a solution of calcium hydroxide on acid lead arsenate has been studied in the laboratory.

Under the conditions of the experiments, long-continued action of an excess of calcium hydroxide on acid lead arsenate resulted in decomposition of the lead arsenate, with the formation of basic calcium arsenate and a hydrate of lead oxide.

The reaction takes place slowly, and, under the conditions usually met with in spraying operations, probably less than 1 per cent of the acid lead arsenate is decomposed.

The action of carbon dioxide of the air on the mixture of calcium hydroxide and lead arsenate does not produce an appreciable increase in "soluble arsenic" until after all the lime has been carbonated. Thereafter the amount of "soluble arsenic" increases very materially. In the particular case studied, the increase was from 0.65 per cent to 3.15 per cent of As_2O_5 .

Orchard experiments with lead arsenate, with and without the addition of slaked lime, have been conducted during the seasons of 1923 to 1926, inclusive, at Riverton, N. J.

It is definitely shown that slaked lime added to lead arsenate prevents peach foliage injury by "soluble arsenic." In one series of experiments, in which a lime high in magnesia was used, no injury resulted.

There is a practical advantage in combining 3 pounds of slaked lime with 1½ pounds of acid lead arsenate in 50 gallons of water.

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