
Oregon Agricultural College Experiment Station

THE ARSENATES OF LEAD

BY

R. H. ROBINSON and H. V. TARTAR.



CORVALLIS, OREGON

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INTRODUCTION.

In this bulletin are given the results of some chemical investigations on the arsenates of lead which are so widely used at present as insecticides. This work was begun early in 1913 and finished in October, 1914. It was undertaken as a part of one of the research projects now carried on by this department and supported by funds provided by the Adams Act of the United States Government. Sufficient data have been secured from which to draw certain conclusions. These are presented herewith.

Arsenate of lead is the arsenical now used for the successful control of the codling moth. A consideration of a few statistics will show the possible agricultural value of any advance in knowledge of the real nature of this material or of its insecticidal properties. According to the 1910 census, the apple crop of the United States which amounted to 147,522,000 bushels, was valued at \$83,231,492.00; the pear crop, which amounted to 8,840,733 bushels, was valued at \$8,000,000.00. It is deemed a conservative estimate that at the time these figures were taken the financial loss on ripened fruit due to the codling moth amounted to at least \$12,000,000.00 for apples, and \$750,000.00 for pears. Besides, these statements do not take into account the loss, caused by this insect, of fruit which had set and failed to ripen.

The 1910 census figures also show that there were in this country 151,322,840 apple trees and 15,171,524 pear trees of bearing age. Estimating on the basis that it requires 4 gallons of spray material containing arsenate worth 1-1/3 cents for one spraying of each tree, it would have required annually \$6,992,760.00 worth of arsenate of lead for the three necessary sprayings for the pear and apple trees of bearing age in this country.

In 1912 the State of Oregon produced about 3,750,000 boxes of apples valued at \$2,812,500.00, and 500,000 boxes of pears worth \$400,000.00. The estimated financial loss due to the codling moth is \$290,000 for apples and \$40,000 for pears. Careful estimates also show that at the present time there are in this state approximately 3,730,000 apple trees and 1,000,000 pear trees of bearing age. The estimated value of the lead arsenate required adequately to spray for one season this number of bearing apple and pear trees is \$203,390.00.

Arsenate of lead is also employed for the destruction of the cotton bollworm, the tobacco worm, and the Colorado potato beetle, but figures are not available to show the amount used for this purpose. This being true, complete estimates of the use of this insecticide cannot be made. It is common knowledge, however, that the demand for this arsenical has now reached such proportions that a number of manufacturing chemists in the United States are making arsenate of lead in large quantity.

The above data are amply sufficient to show that any extension of our knowledge of the constitution and important properties of the arsenates of lead, as well as the analytical methods necessary to the proper valuation of the same, may be of considerable practical importance to the fruit growers of this state and nation. The imperfectness of our present knowledge of these substances need not be taken up at this point; it will be brought out in the discussion which follows.

A good portion of the results here presented are technical in nature; too technical perhaps to be thoroughly understood by one unfamiliar with the fundamental principles of chemistry. The subject matter, however, can hardly be presented otherwise, and no apology need be made for this shortcoming.

Acknowledgment. The authors wish to express their hearty thanks to Professors H. F. Wilson and V. R. Gardner of this Station who have read the bulletin in manuscript and have offered valuable suggestions and corrections. Professor Wilson has also cooperated in the field tests, the results of which are herein reported.

CHAPTER I.

The Preparation and Nature of the Arsenates of Lead.

HISTORICAL.

But little attention was given to the chemistry of the arsenates of lead previous to their use as insecticides. Lead orthoarsenate (neutral or tri-plumbic), $\text{Pb}_3(\text{AsO}_4)_2$, is reported to have been prepared by Mitscherlich¹ by the use of the reaction of disodium hydrogen arsenate, Na_2HAsO_4 , with basic lead acetate, or with neutral lead salts. It is also stated that this substance was prepared by Berzelius⁷ by the reaction of ammonia on lead pyroarsenate, $\text{Pb}_2\text{As}_2\text{O}_7$. The substance obtained was a white amorphous powder.

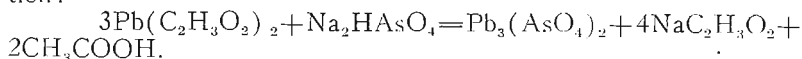
According to Mitscherlich and Berzelius¹, lead pyroarsenate is precipitated when lead chloride or lead nitrate react in aqueous solution with arsenic acid; also as a precipitate resulting from the reaction of di-ammonium hydrogen arsenate, di-potassium hydrogen arsenate, or di-sodium hydrogen arsenate with lead nitrate in excess. It is also stated by the authority cited that Salkowski prepared this substance by the use of the reaction of neutral lead acetate and disodium hydrogen arsenate and that it is a white, easily melted, amorphous powder. On the whole the work of these early investigators is very imperfect and is in some instances contradictory.

Moulton², chemist of the Massachusetts Gypsy Moth Commission, was the first to prepare lead arsenate for use as an insecticide. For this purpose he used lead acetate and di-sodium arsenate.

The work of Moulton was continued by Smith³, who studied the reactions involved and other matters pertaining to manufacture. "He stated that the ordinary spray material was not a single salt, but a mixture of neutral, $\text{Pb}_3(\text{AsO}_4)_2$, and acid, PbHAsO_4 , arsenates, and believed that the relative amount of each depended principally upon the source of the soluble lead salt, although temperature and concentration at the moment of precipitation affected the results; in other words, the acetate of lead has a tendency, other factors being equal, to yield the neutral salt and the nitrate, the acid salt."⁴

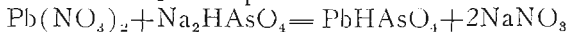
Smith also states that the specific gravity of arsenate of lead is 1.00668 (salt not specified).

Haywood⁵ claims that the reaction between lead acetate and disodium arsenate takes place as represented by the following equation:



(1). Figures refer to references given at the end of the chapter.

He also found that the reaction between lead nitrate and di-sodium arsenate takes place in the main as follows:



The slight variation in the resulting compound from the theoretical composition of lead hydrogen arsenate caused Haywood to suggest that some unknown secondary reaction took place to a small extent.

Haywood and McDonnell⁶ state that, when pure lead nitrate and di-sodium arsenate are used, the reaction represented by the second equation given in the preceding paragraph proceeds almost according to the theory, though a small amount of lead orthoarsenate is usually formed. They also hold that when lead acetate is used a product is obtained at times which is principally lead hydrogen arsenate. They corroborate Smith's³ statement that the reaction is affected by various conditions, such as concentration, temperature, etc.

Volck⁷ devised a qualitative method for the detection of lead hydrogen arsenate in the presence of the lead orthoarsenate. He also proposed the preparation of the orthoarsenate by the use of the reaction of lead hydrogen arsenate with ammonium hydroxide, although he admitted that the samples prepared in this manner contained somewhat less than the theoretical percentage of arsenic oxide. From his experiments, Volck further concluded that the lead hydrogen arsenate hydrolyzes easily to form the orthoarsenate, and that commercial lead arsenate might contain pyroarsenate as a component.

Holland and Reed¹ state that they prepared the orthoarsenate by precipitation, under certain conditions, from dilute solutions of lead acetate and di-sodium arsenate. In proof of this they showed that the amounts of lead and arsenic found in the precipitates corresponded closely to the theoretical composition of the lead salt. These investigators also state that lead hydrogen arsenate "is readily prepared from nitrate of lead and di-sodium hydrogen arsenate, provided dilute solutions are employed and the sodium salt is added carefully in excess (10%). By this method of procedure no difficulty was experienced in producing salts of theoretical composition."

Space will not be taken at this time to go into any extensive criticism of the work that has been done; this will be brought out in the discussion of the results which follow. Taken as a whole, the literature indicates that there are at least two common lead arsenates, lead hydrogen arsenate and lead orthoarsenate; that these two compounds are the main components present in ordinary commercial lead arsenate; that lead pyroarsenate may possibly be present in the commercial salts; and that there is very little accurate knowledge of the preparation and the chemical and physical properties of the pure compounds.

EXPERIMENTAL.

Considering the information available, it seemed best to take up the study of the lead arsenates by first attempting to prepare the pure compounds themselves, because a knowledge of the nature of these substances is fundamental to any further scientific work which may be of permanent agricultural value. The preparation of three different arsenates of lead was studied: (1) lead hydrogen arsenate (lead acid arsenate or diplumbic arsenate), (2) lead orthoarsenate (neutral or triplumbic arsenate) and (3) lead pyroarsenate.

(1) Preparation of Lead Hydrogen Arsenate.

The preparation of this substance was first tried by using the reaction between lead nitrate and di-sodium hydrogen arsenate. Both concentrated and dilute solutions were employed, using the reacting equivalents of the different substances and also one or the other in excess. Many attempts were made and, in some instances, the salts obtained approximated the theoretical composition very closely but not within the experimental error of analysis. Our experiments showed that very slight changes of condition affect the nature of the reaction. After much work had been done it was decided that this method could not be used safely to prepare pure lead hydrogen arsenate, as has been claimed by Morse and Reed.⁴

The preparation of this compound was attempted in several other ways and the best results were obtained by using the following method: Fairly pure hydrogen arsenate is prepared by use of the reaction between lead nitrate and di-sodium arsenate. The precipitate is washed quite thoroughly with distilled water and then dissolved completely in nitric acid, using just enough of the acid to effect solution. To this solution dilute ammonium hydroxide is added slowly with constant stirring until approximately three-fourths of the nitric acid used has been neutralized. During the addition of the ammonium hydroxide the lead hydrogen arsenate will gradually be precipitated. The precipitate is then allowed to stand over night in contact with the solution (which is acid in reaction due to the presence of considerable amount of nitric acid). The supernatant liquid is then decanted through a filter and the precipitate washed first with distilled water slightly acidulated with nitric acid and then with water which has been recently boiled to remove carbon dioxide, until the washings no longer give a test for nitrates with diphenylamine. The precipitate is then dried at 110° C.

The salt obtained in this manner is free from nitrates and ammonium salts. It is pure lead hydrogen arsenate and is a white, amorphous, finely divided, fluffy powder. Analyses made of these samples gave results as follows:

Table I.

	Arsenic as As_2O_5 . Per cent.	Lead as PbO . Per cent.	Ratio As_2O_5 to PbO
Sample No. 1	32.99	63.92	1:1.937
Sample No. 2	32.98	63.92	1:1.937
Sample No. 3	32.88	63.70	1:1.937
Theoretical for $PbHAsO_4$	33.15	64.46	1:1.945

It will be noted that the percentages are somewhat lower than the theoretical for lead hydrogen arsenate. This is due to the presence of a small amount of water that can not be easily removed. Samples do not lose this water below $200^\circ C$. Experimental work has not been carried out to the point where the writers are able to state whether or not there is a definite temperature at which this moisture can be removed without changing some of the substance into the form of the pyroarsenate. It will also be noted that the ratio of arsenic oxide to lead oxide is a trifle lower than the theoretical. This is due to the fact that the method for determining lead which is now used by the Association of Official Agricultural Chemists is hardly as accurate as the method used for arsenic; there is a tendency for the results to be slightly low.

(2) *Results of Attempts to Prepare Lead Orthoarsenate.*

The preparation of this compound was first attempted by the use of the reaction between lead acetate and di-sodium arsenate. The results obtained showed that this reaction is easily affected by various conditions such as temperature, concentration, the rate in which the substances are brought together, and the amount of salt used in excess. Evidently, this reaction cannot be used to prepare pure orthoarsenate of lead. The insoluble precipitate obtained from the reaction referred to is really a mixture of two different compounds; this will be brought out in a later portion of this bulletin.

The preparation of the ortho-compound was further attempted by employing the reaction between ammonium hydroxide and lead hydrogen arsenate as has been suggested by Volck.⁷ The ammonium hydroxide used was freed from carbonate by redistillation from barium hydroxide. It was found that the reaction between ammonium hydroxide and lead hydrogen arsenate is complete after the mixture had been heated gently on a steam bath for three hours and that the reaction is the same whether only a slight or large excess of ammonium hydroxide is used. Four samples of the substance obtained in this manner were carefully washed free from soluble salts and then dried at $110^\circ C$. The analyses of the samples are as follows:

Table II.

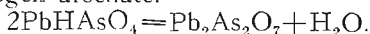
	Arsenic as As_2O_5 . Per cent.	Lead as PbO . Per cent.	Ratio As_2O_5 to PbO
Sample No. 1	23.42	74.72	1:3.190
Sample No. 2	23.43	74.68	1:3.189
Sample No. 3	23.42	74.86	1:3.196
Sample No. 4	23.46	74.61	1:3.180
Theoretical for $Pb_2(AsO_4)_2$	25.57	74.43	1:2.911

These results show that the substance obtained is not a pure orthoarsenate of lead. It contains more lead and less arsenic than the theoretical figures. At first, the authors thought that perhaps there was a small amount of free lead hydroxide present. To ascertain if this were true, the substance was heated in a drying oven to a temperature somewhat greater than 130° C. There was no change in color due to the formation of lead oxide nor was there any loss in weight. Even microscopic examination failed to show the presence of any lead oxide. A sample of freshly prepared lead hydroxide, when heated to a temperature a little above 130° C, gradually changed to an orange-yellow color with the formation of lead oxide and there was a gradual decrease in weight from loss of water. These results indicate clearly that there is no uncombined lead hydroxide present in the insoluble material resulting from the reaction of ammonium hydroxide with lead hydrogen arsenate. In fact, the tests, which have been tried *show that it is a definite chemical compound, a new basic lead arsenate of which there is no mention in literature.* The analyses indicate that its composition may be represented closely by the formula $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$. It is a white, amorphous granular powder; microscopical examination does not show any crystalline structure. There is no loss of water at temperatures below 200° C.

A number of attempts have been made to prepare a pure orthoarsenate of lead. In these experiments all of the reactions which are now used in the manufacture of lead arsenate have been tried in aqueous solution and also in non-aqueous solutions so far as conditions would permit. Other possible reactions have been investigated. Without going into any lengthy discussion of the reactions used, the authors will state that *lead orthoarsenate is not formed under the ordinary aqueous conditions employed in the manufacture of commercial lead arsenate, and that it is not a component of the commercial material as has been formerly supposed.* The compound present, which has been represented to be the orthoarsenate, is in reality the basic lead arsenate mentioned above. Further proof of this will be brought out in a later portion of this bulletin.

(3) *The Preparation of Lead Pyroarsenate.*

Since the presence of this substance in the ordinary commercial salts used for insecticidal purposes has been suggested, it was deemed advisable to undertake the preparation of the pure compound. It would seem, on theoretical grounds, that the simplest method would be by the removal of water by means of heat from lead hydrogen arsenate.



Samples of lead hydrogen arsenate were heated in a drying oven to a temperature somewhat higher than 200° C. without loss in weight. When this compound is fused at a dull red heat, however,

it loses water and a white, glassy, somewhat crystalline substance is left on cooling. Analyses made of this substance show it to be the pyroarsenate.

It is well known that pyroarsenic acid does not exist in the presence of water, and consequently if lead pyroarsenate is a constituent of the ordinary commercial salts it must be due to the easy dehydration of lead hydrogen arsenate. The results given above show that this substance has to be heated to a fairly high temperature before loss of water occurs, and, evidently, *lead pyroarsenate is not a constituent of the commercial lead arsenate.*

REFERENCES.

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4. Twenty-fourth Ann. Report Mass. Agr. Exp. Sta.
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CHAPTER II.

Important Properties of Arsenates of Lead.

An essential phase in the study of the arsenates of lead is the consideration of their important properties. Not only is this of interest from a purely scientific standpoint, but, to the practical worker, it is of vital consequence. Such a knowledge may enable him to select the best type of arsenical and use it intelligently under special or peculiar conditions, without danger of obtaining dis-

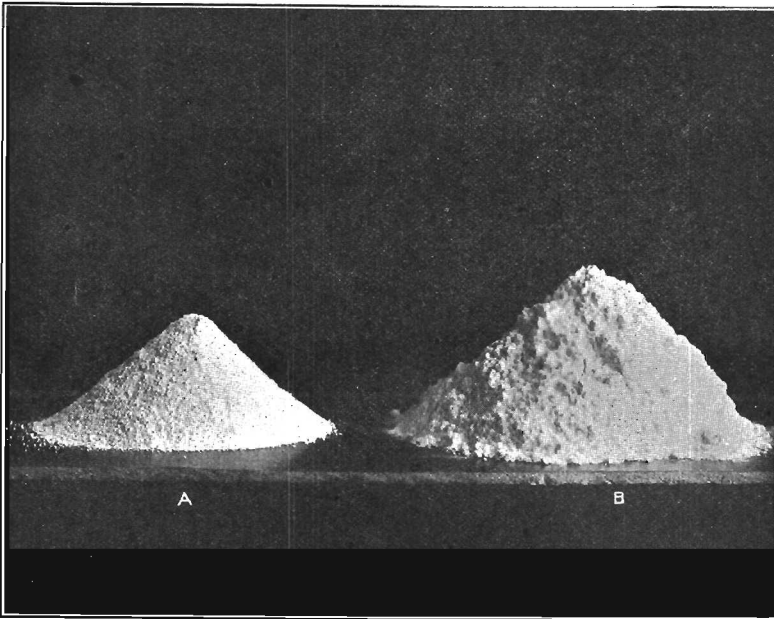


Fig. 1. The Comparative Bulkiness of the Arsenates of Lead.
(a) basic lead arsenate; (b) lead hydrogen arsenate.

astrous results. In this discussion, consideration will be given only to the two lead arsenates used for insecticidal purposes, namely, the hydrogen arsenate and the basic arsenate.

General Physical Appearance of the Arsenates of Lead.

There is a distinct difference in the general physical appearance of these two types of lead arsenates. The acid salt has a very fluffy appearance similar to that of wheat flour. It is usually an amorphous powder not showing to the eye any tendency to crystalline form. Under special conditions, however, it will crystallize in the

form of small irregular transparent plates. So far as the authors know, this can be done only in the laboratory where it is possible to exercise great care and special control when the salt is separating out. The basic arsenate is also an amorphous powder; it is very granular and compact, being much more dense than the acid salt. All efforts made to obtain it in crystalline form have failed.

Because of its fluffiness, the acid compound is much more bulky than the basic. Their comparative bulkiness is illustrated in Fig. 1, where a pound each of the different salts is depicted.

Microscopical examination shows that under the usual conditions of preparation, the ultimate particles of the two arsenates are about the same in size. Such examination of a limited number of samples also indicates that when suspended in water, the particles of the basic compound have more of a tendency to collect together, thus forming larger particles which settle out more rapidly. This property of this substance perhaps prevents its being spread so evenly over the foliage of fruit trees by the usual methods of spraying as can be accomplished with the lead hydrogen arsenate.

The Specific Gravity of Lead Hydrogen Arsenate and Lead Basic Arsenate.

The specific gravity of a spray material is, to the fruit grower, one of the most important physical properties. An insoluble insecticide should be in a fine state of subdivision and of a specific gravity sufficiently low, that it will remain in suspension in water for some length of time in order that it can be sprayed on trees in uniform strength and will spread evenly over the surface of the leaves. A review of the literature discloses the fact that no one has yet made a determination of this property of the arsenates of lead. In one instance, Smith places the specific gravity of lead arsenate, salt not specified, at 1.00668¹. It is plainly evident, however, that this figure is not the true specific gravity but simply a figure obtained by suspending an hydrometer in an aqueous suspension of the spray material.

The specific gravity of lead hydrogen arsenate and basic lead arsenate prepared as described in Chapter I, was found by determining the weight of the toluene displaced by a known quality of the salt. The toluene was first dried by means of solid sodium hydroxide and then distilled. Its specific gravity at 20° C. referred to water at 4° C. was found to be 0.8669. Care was taken to remove air from the arsenate when covered with toluene by placing the pycnometer in an exhausted desiccator.

The data obtained on the two salts are as follows:

Table III.

(a) LEAD HYDROGEN ARSENATE.		
Grams PbHAsO ₄	Grams toluene displaced.	Specific Gravity PbHAsO ₄ , 20°/4°
11.1070	1.6610	5.79
11.5724	1.6630	5.79
11.3230	1.6968	5.78
		Average 5.786
(b) BASIC LEAD ARSENATE.		
Grams Basic Lead Arsenate	Grams toluene displaced	Specific Gravity basic lead arsenate 20°/4°
14.5770	1.7794	7.10
20.5749	2.5083	7.11
		Average 7.105

The data in the above table show that the specific gravity of lead hydrogen arsenate at 20°/4° is 5.786 and of the basic arsenate 7.105. Inferring from specific gravity of the two arsenates the former salt would probably remain in suspension in water for a longer period of time than the basic salt.

This conclusion has been substantiated by settling experiments. The lead hydrogen arsenate settles much less rapidly from aqueous suspensions than does the basic salt. This is illustrated in Figs. 2 and 3, these plates showing graphically the variation in settling observed with the two compounds. As stated in the legend, tube *a* is a suspension of the basic salt and tube *b* of the acid salt. Each of the samples represents the same amount of actual lead arsenate and the column of water in each case is 14 inches high. The samples were thoroughly shaken and then photographed, Fig. 2, after standing two minutes, and Fig. 3, after standing one hour. It will be noted that after two minutes the material in tube *b* had settled very little, while in tube *a* nearly to the bottom. Even after an hour some of the finer particles still remain in suspension in tube *b* and the distinguishing line between the water and the main body of the precipitate is indistinct.

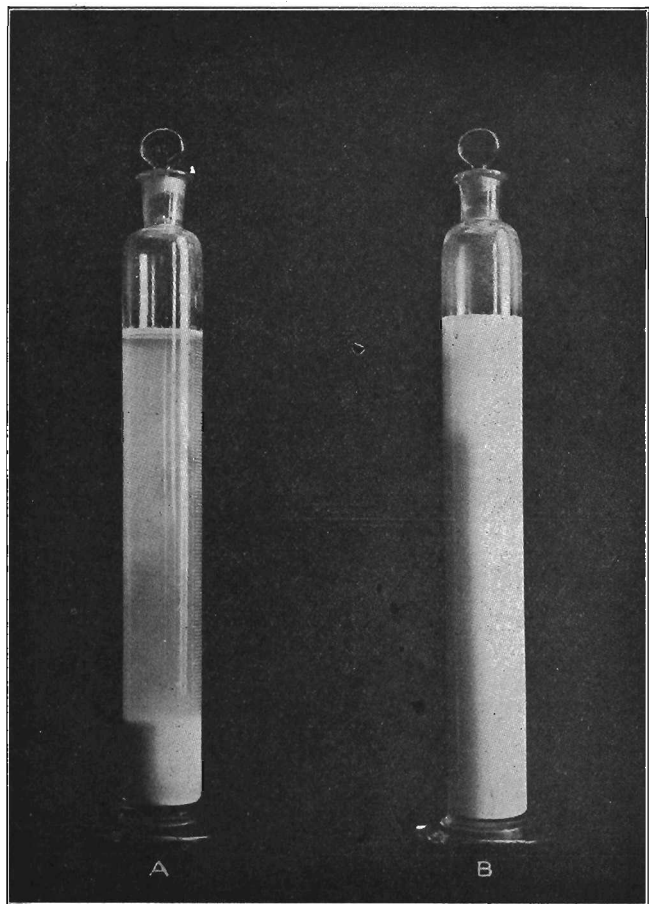


Fig. 2. After standing two minutes.

(a) basic lead arsenate, (b) lead hydrogen arsenate.

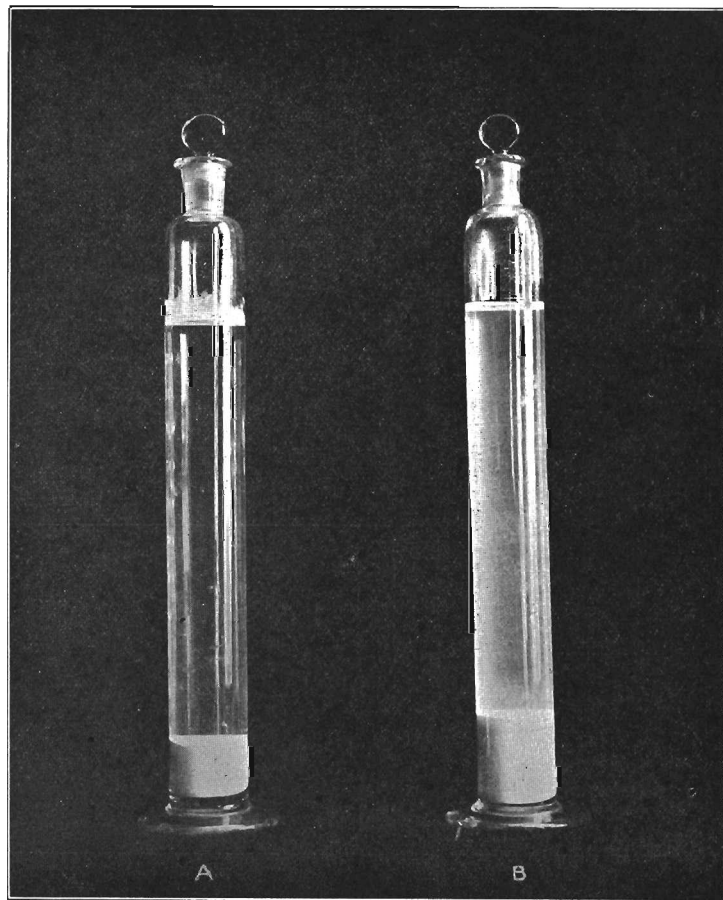


Fig. 3. After standing one hour.

*The Solubility of Lead Hydrogen Arsenate and
Lead Basic Arsenate.*

This property is of much importance in the consideration of the adaptability of arsenic containing compounds for use as insecticides because a very small amount of soluble arsenic compound is sufficient to cause injury to the foliage of fruit trees. Spraying practice during recent years has amply demonstrated, too, that internal insecticides insoluble in water give good results, probably by virtue of the solvent action of the juices of the digestive tract of the insect. The tendency of manufacturers at present is, therefore, to furnish the arsenic of insecticides in *insoluble form*; this tendency has been stimulated also by the passage of state and national laws restricting the amount of arsenic permissible in soluble form.

There are several things to be considered in making a determination of the solubility of lead hydrogen arsenate. Although one of the hydrogens of arsenic acid resembles the hydrogen of strong acids in its dissociating tendency, the other two hydrogens are those of weak acids. Hence perceptible hydrolysis takes place in solutions of this acid, even when the base combined is strong; that of tertiary salts being greatest in extent. It is difficult to predict the influence of this hydrolysis upon lead hydrogen arsenate. There is also the possibility of the formation of more insoluble normal or basic salts. In discussing the solubility of lead hydrogen arsenate Volck² states that "the liberation of the arsenic oxide (arsenic acid) from the acid arsenates depends on transposition to the ortho or neutral arsenate under neutral or alkaline conditions." He also infers that a given quantity of lead hydrogen arsenate can be completely changed to the orthoarsenate by bringing it in contact with water and then replacing the supernatant liquid from time to time with fresh water.

The writers have endeavored to verify Volck's statements. The experiments tried, however, show that arsenic acid is not formed in sufficient quantity by hydrolysis at room temperature to give the qualitative tests suggested by Volck nor can the composition of lead hydrogen arsenate be changed to any appreciable extent by bringing it in contact with an excess of pure water and removing the supernatant liquid from time to time, even though the operation be continued for several days. At temperatures near the boiling point there is evidence of only a slight hydrolysis. We feel safe in stating that if there is any hydrolysis of this substance it is slight and can only be determined by the use of refined physico-chemical methods.

Unfortunately, other pressing work in progress in this laboratory has prevented the taking up of a critical study of this hydrolysis. An idea of the solubility of the salt was obtained, however, by determining the amount of arsenic in solution when using the pro-

visional method of the Association of Official Agricultural Chemists for the determination of "water-soluble arsenic oxide" in commercial lead arsenate. Eight hundred cc. of the water extract did not contain sufficient arsenic in solution to be quantitatively estimated by making the final titration with fiftieth-normal iodine solution. This result indicates that lead hydrogen arsenate is a very insoluble substance.

In attempting to make a determination of the solubility of basic lead arsenate one meets with the numerous perplexing difficulties which are common with the basic salts. These difficulties are such as to preclude perhaps the securing of quantitative data by the usual methods. For getting an idea of the solubility of this substance, use was made of the method of the Association official Agricultural Chemists referred to in the preceding paragraph. There was not sufficient arsenic present in eight hundred cc. of the water extract to be estimated by titration with fiftieth-normal iodine.

When warm water was used there was no difference in the results obtained. Evidently this salt is also very insoluble.

The conclusions given in the preceding paragraph are reached from investigations upon pure samples prepared in the laboratory and indicate the solubility of a pure chemical compound in distilled water. The study of the solubility of commercial lead arsenate used as spray material presents, however, a different phase of the subject since this material does not usually contain pure compounds. In such samples the soluble substances are not the arsenates of lead but foreign ingredients which have not been removed during the process of manufacture and consequently may pass into solution directly or possibly react with the lead arsenate freeing arsenic in a soluble form which passes into solution when the solubility test is made. Since, as stated previously, a very small amount of arsenic in the soluble form may cause injury to the foliage of fruit trees, it is very essential that a solubility test be made to ascertain the extent of the presence of these substances in the spray material. This point will be brought out more thoroughly in Chapter IV.

Since it has been claimed that lead hydrogen arsenate is enough soluble or hydrolizes sufficiently under ordinary field conditions to cause foliage injury, it was thought advisable to carry out some experiments under the usual orchard conditions to ascertain the effect of the different arsenates in this regard. These experiments were undertaken in cooperation with Professor H. F. Wilson, Entomologist of this Station. Each of the arsenates was tried out in three different strengths, 2, 4, and 8 pounds respectively, to 100 gallons of water. In common practice the greatest strength of lead arsenate used is four pounds of the paste (containing approximately 50 per cent water) to 100 gallons, or, in other words, two pounds of the actual salt to this volume of water. The experiments, therefore,

represented the greatest strength in use by orchardists, as well as double and quadruple strengths. The spray was used on apple trees (Yellow Newtowns) two consecutive years, 1913 and 1914, under the usual damp weather conditions common to the Willamette Valley. In 1913 the trees had not been sprayed previously and were more or less affected with scab. The orchard had received but one cultivation and therefore seemed more liable to show foliage injury than if the trees had been faithfully cared for. The two days following the spraying were more or less cloudy, and during the next week the weather conditions varied from rain to sunshine, mostly rain. In 1914, the experiments were made at the same time of season and in the same orchard.

In no case was any injury to fruit or foliage caused by either of the arsenates, even when used at the rate of eight pounds of the salt to 100 gallons of water. These results, the writers believe, show that neither of the arsenates is soluble enough nor hydrolyzes sufficiently to burn apple foliage when used in the usual manner.

The Reactivity of the Arsenates of Lead.

Experiments with several reagents upon these substances show that the hydrogen arsenate, like most acid salts, is a very reactive compound, while the basic arsenate is quite inert. When the former was added to solutions containing various amounts of sodium chloride, sodium carbonate, and sodium sulfate, respectively, arsenic was rendered soluble in liberal quantities. Furthermore, this substance reacts readily with ammonia, and the other alkalies, a considerable quantity of the arsenic being changed to soluble form. The reactions of the acid arsenate with other alkaline substances will be discussed in Chapter IV. The basic arsenate, on the other hand, is not affected perceptibly by alkaline substances and only to a slight extent by the above mentioned salts; it is evidently a rather inert substance.

The greater tendency of the acid arsenate to react with common substances may account for the results obtained from experiments conducted to ascertain the comparative toxicity of these compounds to insects. This work was carried out in cooperation with Professor H. F. Wilson, Entomologist of this Station. Suspensions of lead arsenate in water in the proportions used in spraying were made up and sprayed on twigs from fruit trees. Other twigs were sprayed with suspensions which contained equal amounts of arsenic in the form of the different arsenates. The larvae of tent caterpillars were placed on the sprayed twigs in the open part of the insectary. Each experiment was kept separate from the rest and papers were placed under the twigs to catch the dead larvae.

The acid arsenate was found to be a quicker acting poison than the basic arsenate. The latter substance was slow in its action but was satisfactory in that it finally killed the caterpillars. *The re-*

sults of the experiments indicated that, in ordinary spraying practice, the arsenates of lead are perhaps used in greater quantity than is necessary. Further experiments using smaller quantities of these poisons are required accurately to ascertain their actual comparative toxic values.

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1. Twenty-fourth Ann. Report Mass. Agr. Exp. Sta.
2. Science, Vol. 33, p. 868 (1911).

CHAPTER III.

The Valuation of Commercial Arsenate of Lead.

In the analysis of the commercial brands of lead arsenates, the specific determinations usually required, as evidence that the product is not a violation of the Federal Insecticide Law, consist of an estimation of total arsenic oxide, total lead oxide, water soluble arsenic oxide, and moisture. This is sufficient to ascertain whether the sample fulfills the requirements as demanded by law, but it does not give evidence of the exact nature of the sample.

For the true valuation of these commercial samples, however, methods for their complete analysis are necessary. It is not enough to know the total arsenic or lead content to ascertain the value of the spray material as an insecticide but it is equally important to understand the forms in which these elements are combined, and to what extent they exist as such. For example, if a sample is found to contain lead combined in the form of the basic or hydrogen arsenate, the carbonate and the chloride, the proportion and the extent to which each compound is present is an important consideration and the estimation of each of these forms is essential in the valuation of the insecticide. Any other substance or impurity that would also depreciate the value of the sample is a factor in its valuation. These impurities, such as carbonates, chlorides, acetates, other water-soluble substances, etc., besides being adulterants may have an injurious effect upon foliage and hence depreciate the value of the material as a spray.

It has been brought out in Chapter II that the chlorides, sulfates, and carbonates of the alkali metals render the arsenic more soluble in certain varieties of commercial lead arsenate, and hence increase the liability to foliage injury. In order to make these estimations, new methods have been devised at this Station and submitted in some cases where the old ones were found to be inaccurate. Comparisons of the methods employed are given in the table of results.

It can be understood, after a consideration of the possibilities for the introduction of impurities and the existence of both arsenic and lead in different proportions to form several compounds, that the insecticidal value of various commercial arsenates are appreciably different. Results reported in the preceding chapter show that the arsenates of lead have different insecticidal properties. The pure lead hydrogen arsenate, specially prepared in this laboratory, was found to kill more quickly, to remain in suspension longer and to be more easily applied. From what has been stated regarding impurities and the difference in the constitution of the lead arsenates it is evidently important to ascertain, as far as possible, the true nature of the commercial arsenates.

Methods.

Because of the possibilities of the presence of impurities and adulterations and the existence of the two arsenates in one product, a number of commercial samples were selected, and a system for their total analysis devised. The following determinations were made: Moisture, total arsenic oxide, total lead oxide, lead hydrogen arsenate, water soluble arsenic oxide and lead oxide, lead carbonate, water soluble impurities, chlorides, sulfates, acetates, and acid insoluble impurities.

For the purpose of determination of moisture, total arsenic oxide, and total lead oxide, the official methods as outlined in Bulletin 107, Bureau of Chemistry, p. 239, were found to be satisfactory.

Water soluble arsenic oxide and lead oxide were determined by two different methods, one being the regular official method as given in Bulletin 107, Bureau of Chemistry, p. 240, and the other being one devised at this Station which for convenience is designated here as the "Oregon Station Method." This latter method is based upon the extreme insolubility of both the hydrogen and the basic arsenate. It is carried out as follows: a convenient amount—4 to 6 grams—of the sample is accurately weighed out and transferred to a 590 S. & S. filter paper, first macerating it in a mortar with a little water until it has a consistency that permits pouring onto the filter. Distilled water is used to extract the soluble arsenic oxide and lead oxide. (It is imperative that no carbonic acid nor ammonia be present in the water as they may react with the lead arsenate, liberating arsenic in a soluble form.) The water soluble impurities are extracted from the sample by washing with hot water until about a liter of filtrate is obtained. It is then cooled, made up to 1000 cc. and an aliquot taken and titrated with standard iodine solution after reduction with potassium iodide according to modified Gooch and Browning method. Should the filtrate come through cloudy it may be clarified by filtering through a Gooch, having a thin layer of pure carbon black over the asbestos pad.

At the present time there is no method for estimating the amount of lead hydrogen arsenate in commercial arsenate of lead. It has been shown that when lead hydrogen arsenate is treated with ammonium hydroxide (free from carbon dioxide) under ordinary conditions a basic arsenate of lead of constant composition is formed. The amount of arsenic passing into solution from a given quantity of lead hydrogen arsenate has also been found to be constant. Since the basic arsenate may be considered as insoluble from the usual analytical standpoint, lead hydrogen arsenate in mixtures with the basic arsenate can be easily determined by the following described method:

Take a convenient amount of the finely powdered sample (3-10 grams), depending upon the amount of the acid salt present, which

has been dried at 100° C., and add 200 cc. of a 5% solution of carbon dioxide-free ammonium hydroxide. Allow to digest with occasional shaking for a few hours at room temperature, when the reaction should be complete. The supernatant liquid is then filtered by suction from the insoluble basic salt by using a Buchner funnel prepared with a pad made of two sheets of filter paper with a layer of asbestos between. The upper paper should be a hardened filter. The filter is finally washed thoroughly with recently boiled distilled water until free from soluble salts. The final washings may be tested with lead nitrate solution to ascertain the completeness of the removal of the ammonium arsenate. The filtrate should be perfectly clear. In case there is difficulty in obtaining a clear solution, it may be overcome by refiltering through a Gooch crucible having a thin layer of carbon black on an asbestos pad. The final filtrate obtained is made up to convenient volume and an aliquot taken for the determination of arsenic.

After free ammonium hydroxide is removed by boiling, the arsenic is determined by the modified Gooch and Browning method. The amount of arsenic in the total filtrate calculated as As_2O_3 and then multiplied by the factor 7.6034 gives the amount in grams of lead hydrogen arsenate present in the original mixture.

This method has been tried out on a number of mixtures of known composition and in each case has given good results.

In determining lead hydrogen arsenate in commercial samples, it is first necessary to remove any water-soluble arsenic oxide that may be present. Consequently, the residue obtained by leaching the sample with warm water, in the Oregon Station method described above, was used.

It may be stated parenthetically at this point that the nature of the insoluble salts formed by the reaction of lead acetate and lead nitrate with di-sodium hydrogen arsenate, reactions which have been widely used in the manufacture of the commercial product used as an insecticide, has been studied in a limited way by using the above described method in conjunction with the usual analytical methods.

The results obtained are given in Table IV.

These results show that the precipitates obtained were, in each instance, mixtures containing various amounts of the acid salt. It will be noted also that the ratio of the As_2O_3 , other than that combined as $PbHASO_3$, to PbO , other than that combined as $PbHASO_3$, approximates within experimental error that found in the basic arsenate already described. These results, considered with the work which has already been presented in Chapter I, seem to leave little doubt that the substance present other than lead hydrogen arsenate is the basic arsenate of lead.

Water-soluble solids or impurities were also determined by two different methods. In one case the official method as outlined in Bulletin 107, Bureau of Chemistry, p. 240, was applied. In the

Table IV. The Composition of Precipitates Obtained by Reactions of Lead Acetate and Lead Nitrate with Di-sodium Hydrogen Arsenate.

MATERIAL	Total lead as PbO Per cent.	Total arsenic as As ₂ O ₃ Per cent.	Total PbHAsO ₄ Per cent.	Ratio as As ₂ O ₃ other than that combined as PbHAsO ₄ to PbO other than that combined as PbHAsO ₄
1. Sample prepared by using Pb(C ₂ H ₃ O ₂) ₂ and Na ₂ HAsO ₄ in the theoretical proportion suggested by Haywood	73.21	24.93	14.96	1:3.189
2. Sample prepared by using Na ₂ HAsO ₄ with Pb(C ₂ H ₃ O ₂) ₂ in excess	74.10	24.28	7.42	1:3.179
3. Sample made using Pb(C ₂ H ₃ O ₂) ₂ with Na ₂ HAsO ₄ in excess	72.96	24.72	10.48	1:3.12
4. Sample made using Na ₂ HAsO ₄ with Pb(NO ₃) ₂ in excess	64.73	32.26	93.16	1:3.30

other, 200 cc. of the clear filtrate, obtained in the Oregon Station method for the water soluble oxide and lead oxide, was evaporated to dryness in a platinum dish upon a steam bath, dried at 110° C. and weighed. This gave the amount of water-soluble solids including foreign impurities and the soluble arsenic oxide.

Lead carbonate was calculated from the amount of carbon dioxide found in the sample, the Bowser¹ method being used as a basis for the determination of the carbon dioxide. The procedure, revised and made applicable for lead arsenate, is briefly as follows: an apparatus similar to that described by Bowser is used. About ten grams of the sample is introduced into an Erlenmeyer flask of 200 cc. capacity, and 50 cc. of water added, and, after inserting a rubber stopper through which a thistle tube passes, about 5 cc. of concentrated hydrochloric acid is allowed to run in. The absorbing tower contains 5 cc. of a 50% solution of potassium hydroxide. When all connections are secure a low flame is applied and about 25 cc. distilled over, titrated with normal acid to disappearance of the pink color of the indicator phenolphthalein, and finally with tenth-normal acid to neutrality with methyl orange indicator. Each cc. of tenth-normal acid used in the final titration is equivalent to 0.0267 grams of lead carbonate, PbCO₃. (Note--The lead may be otherwise combined than the normal carbonate but since the exact form was not ascertained it is reported as PbCO₃.)

The acid insoluble substances were estimated by dissolving 10 grams of the dry material in warm dilute nitric acid, 10% strength.

The insoluble matter was collected upon a Gooch, washed free of acidity, dried at 110° C. and weighed.

Chlorine was determined as follows: a convenient amount of the sample, usually 4 grams, is dissolved in warm dilute nitric acid and the insoluble impurities filtered off. Excess of standard silver nitrate is added to the filtrate, and titration completed as in the Vollhard method² for determining chlorine.

Acetates, when present, were tested for, qualitatively, by converting them into ethyl acetate and observing the characteristic odor. This was performed as follows: a convenient amount of sample is added to a hot solution of 5 cc. of sulfuric acid and 5 cc. of 95% alcohol. This is then brought to a boil, when in the presence of an acetate the characteristic odor of ethyl acetate is obtained. Should there be any free acetic acid in the sample, it may be leached out with hot water, and the acidity titrated against standard sodium hydroxide solution using phenolphthalein as indicator. Free acetic acid has been found in two samples of arsenate of lead recently analyzed in this laboratory.

The different commercial samples used as exemplary specimens were selected in such a manner that representative products as manufactured by various firms were secured. Two of the six samples obtained were of the dry powdered type recently placed upon the market, and the other four were of the usual paste variety.

The results of the total analyses of the several brands are given in Table V.

Table V. Analyses of Samples of Commercial Lead Arsenate.

Sample No.	Moisture Per Cent.	Total As ₂ O ₃ Per Ct.	Total PbO Per. C.	Total PbHAsO ₄ Per Cent.	WATER SOLUBLE As ₂ O ₃	
					Official Method Per Cent.	Oreg. Sta. Method Per Cent.
1.	0.15	32.53	63.50	99.38	0.08	0.12
2.	47.08	15.07	34.71	30.17	0.08	0.15
3.	0.19	31.47	64.02	92.01	trace	trace
4.	36.69	12.34	45.53	trace	trace	trace
5.	53.78	12.01	30.55	18.01	0.77	1.12
6.	41.35	16.19	31.64	55.97	trace	trace

TABLE V—(Continued).

Lead Carbonate Per Cent.	Insoluble Substance Per Cent.	Chlorine Per Cent	WATER SOL. IMPURITIES		Water Soluble PbO
			Official Method Per Cent.	Oreg. Sta. Method Per Cent.	
None	0.08	None	0.25	0.55	None
0.30	0.04	0.22	0.35	4.28	None
0.48	0.13	None	0.55	0.93	None
16.57	0.02	0.06	0.52	0.71	None
9.90	0.22	0.10	3.66	0.94	None
None	0.04	None	0.25	0.40	None

An examination of the table as a whole shows that the commercial arsenates of lead differ to a considerable extent in their chemical composition. By the analyses, samples No. 1 and No. 6 show the highest degree of purity, the former being almost a pure hydrogen arsenate. Furthermore, since the ratio of total arsenic oxide to total lead oxide in the pure basic arsenate is 1:3.19, this sample shows a large excess of lead oxide. This excess could not be accounted for were it not for the detection and quantitative estimation of the lead carbonate in the sample. Note also the absence of water soluble arsenic oxide. Obviously this might be expected from a mixture of basic lead arsenate and lead carbonate, for the presence of lead in the above form would perhaps combine with free arsenic acid, resulting in the formation of an insoluble arsenate. In fact, the absence of water soluble arsenic oxide in neutral arsenates generally, has been demonstrated by analysis of many samples received in this laboratory. Sample No. 5 on the other hand, is not a lead hydrogen arsenate since the ratio of total arsenic oxide to lead oxide is greater than that in the pure salt which is 1:1.9. Analysis shows, furthermore, that this excess of lead oxide is present in the form of the carbonate. Unlike Sample No. 4, it has an extraordinary amount of water soluble arsenic oxide.

At this point, it is well perhaps to comment upon the requirements of the Federal Insecticide Law with reference to the requirements for the arsenates of lead unless otherwise designated upon the label. In brief, the requirements are: "First, it must not contain more than fifty per centum of water; second, not less than twelve and one-half per centum of arsenic oxid, As_2O_5 ; third, not more than seventy-five one-hundredths per centum of water-soluble arsenic-oxid, As_2O_5 ." As stated, in Chapter I, the pure hydrogen arsenate as prepared in the laboratory, contains 32.98 per cent of total arsenic oxide, and in the basic or neutral salt there is 23.42 per cent of arsenic oxide, these being the highest percentages possible in a pure sample. On a 50 per cent water basis therefore, the maximum amount of arsenic oxide possible in a hydrogen arsenate is 16.49 per cent, and in the basic compound 11.71 per cent. Hence, it is evident that the law was made without a sufficient knowledge of the exact composition of the two types of lead arsenates, for no manufacturer could make a neutral arsenate that contains 12.5 per cent total arsenic oxide on a 50 per cent water basis when the pure product as prepared in the laboratory could contain at the most only 11.71 per cent. In order to abide by the law, therefore, it would be necessary to reduce the moisture or increase the arsenic oxide by some means. It would seem better to specify a maximum per cent of total arsenic oxide for hydrogen or acid arsenate and another amount for the neutral or basic arsenate.

A comparison of the amount of water soluble arsenic obtained by each method shows that the greater percentage is always found by the Oregon Station method. From these figures it is obvious that all the water soluble arsenic oxide is not obtained by the official method. Nor are the results obtained by the Oregon Station method too high, due to possible hydrolysis or other chemical action upon the sample, for in the three cases, Samples No. 3, 4, and 6, where only a trace is reported present by the official method, identical results are obtained by the Oregon Station method. These latter results further substantiate the claim made in a previous chapter that the pure arsenates of lead are extremely insoluble, and when there is any free arsenic oxide found it is due to the arsenic being in the form of a soluble salt and not in the form of either the hydrogen or basic arsenate. Note also that no soluble lead oxide was found by either method, which is further proof that the water soluble arsenic oxide was not in the form of a soluble lead salt.

As a further evidence that all the water soluble arsenic oxide is not obtained by the official method, a glance at the two columns depicting the quantity of water soluble solids or impurities found shows that the greater amount is consistently obtained by the Oregon Station method, indicating that all soluble material is not taken out by the ordinary official method as outlined in Bulletin 107, Bureau of Chemistry. In all cases here cited, the amount obtained by the Oregon Station method is nearly double that obtained by the official method. It is possible that the low results obtained by this method are due to the fact that the soluble substances present remained occluded or adsorbed by the arsenate of lead and consequently were not removed by water at room temperature. If, however, successive portions of hot water are used as in the Oregon Station method, this difficulty is overcome and the soluble salts go into solution. In the samples listed in this table, soluble impurities, in all probability, are composed chiefly of sodium and potassium arsenates since qualitative tests show the presence of these two bases. Other impurities than those found are probably due to impurities of the materials used in the preparation of the commercial arsenates.

Chlorides were found in three of the samples examined. In two of these cases the quantity present was in amounts worthy of note.

The per cent of acid insoluble impurities in all of the six samples cited is a negligible amount but these impurities should not, however, be considered an unimportant constituent, as other samples received in this laboratory have shown as high as 5 per cent acid insoluble material. When present to this extent it is an adulterant of no small consideration.

The tests for the presence of acetates, and sulfates likewise gave negative results in these six samples. Other arsenates, analyzed previously in this laboratory, have shown that these substances are

sometimes present to an extent that might depreciate the value of the arsenate as an insecticide. The detection and estimation of these impurities may be valuable because their presence with the arsenates of lead results in the liberation of water soluble arsenic oxide.

REFERENCES.

1. Journal Industrial & Engineering Chem., Vol. 4, p. 203.
2. Sutton, Volumetric Analysis, Tenth Ed., p. 145.

CHAPTER IV.

The Reactions of Lime-Sulfur with the Arsenates of Lead.

It is a prevalent custom among horticulturists throughout the country to use combination sprays; that is, mix two spray materials and make the application as a unit. This system is used in order to save the extra expense of making two sprayings. If, however, when two such sprays are so combined, there is a chemical reaction that renders soluble any substance that would cause burning of foliage or other injury, the practice, in that case, might be impracticable. In view of the possibilities for destroying to any extent, or wholly, the insecticidal or fungicidal powers of a spray material by mixing with another, a study of any reaction that occurs warrants special consideration.

By mixing lime-sulfur and lead arsenate, we have one of our most important combination sprays, and since there are two arsenates that may be used for this purpose, the question immediately arises as to which would be preferable to use with the lime-sulfur. It was shown by Bradley and Tartar¹ that small quantities of arsenic oxide were rendered soluble in mixing commercial lime-sulfur and neutral lead arsenate. Later it was noticed that the residue from the mixture of commercial acid arsenate and lime-sulfur was much darker than that obtained from the neutral sample, indicating that considerable decomposition or inter-reaction had taken place in the former instance. Investigations of commercial samples further substantiated this inference.

In order to ascertain, therefore, which type of lead arsenate might be preferable to combine with lime-sulfur, a study of the reactions taking place and the nature of the products formed was made. The lime-sulfur employed in this investigation was made in the laboratory from sulfur, J. T. Baker's recrystallized from carbon bisulphide, and the calcium oxide prepared by igniting pure calcium carbonate until all of the carbon dioxide had been driven off. The lime-sulfur was prepared in the ordinary way by boiling the materials in water until solution was effected. A solution having the specific gravity 1.2587 was obtained. The lead hydrogen arsenate and the lead basic arsenate were prepared by methods outlined in preceding pages of this bulletin, so that the pure products were secured. The analyses of the samples used are as follows:

Lead Hydrogen Arsenate.....	Total PbO, 63.86%
	Total As_2O_5 , 32.90%
Basic Arsenate.....	Total PbO, 74.70%
	Total As_2O_5 , 23.41%

The arsenates were added in each instance in the proportion of two pounds of the dry powder, which is equivalent to four pounds powdered hydrogen arsenate while the latter is the same kind in the

paste form. These samples contain very small amounts of impurities. Samples No. 2 and No. 3 are mixtures of the hydrogen and basic salt, the hydrogen arsenate predominating in the former sample, and the basic arsenate in the latter. Although both of these brands contain small amounts of lead carbonate, free arsenic oxide, and water soluble impurities, the small extent to which these substances are present are indications of a fair product. Attention is called especially to samples No. 4 and No. 5 which demonstrate the value and applicability of the methods devised at this Station. Both of these arsenates contain a high percentage of lead carbonate and of soluble impurities. No. 4 contains no lead combined as the of the paste lead arsenate, to 100 gallons of lime-sulfur solution diluted 1-30. As 1000 cc. of the dilute lime-sulfur solution was taken, the required amount of the lead arsenate was 4.8 grams. These proportions are the same as ordinarily employed in practical work. The mixtures were agitated occasionally during three days, allowed to settle, and as much as possible of the clear supernatant liquid poured off. The residue was then transferred to a filter paper, washed thoroughly with as small an amount of cold water as possible, dried first at 50° to 60° C. and finally in vacuo over sulfuric acid.

An analysis of the filtrate from each arsenate is given in Table VI, also that of a blank consisting of an equal amount of the untreated lime-sulfur, for comparison. The results are expressed in grams per 1000 cc. of solution.

Table VI. Composition of Lime-sulfur Solution before and after Addition of Lead Arsenate.

	Grams per 1000 cc.			
	Solution of lime-sulfur blank	Solution lime-sulfur and lead acid arsenate	Solution lime-sulfur blank	Solution lime-sulfur and basic lead arsenate
Total lime, CaO.....	4.2280	3.1880	4.2440	4.0880
Total Sulfur	8.8004	5.8367	8.8088	8.7496
Total Arsenic Oxide, As ₂ O ₅	None	.07367	None	.0014
Total Lead Oxide, PbO....	None	None	None	None

The determination of arsenic oxide was made by oxidizing with hydrogen peroxide, according to the method of Avery, running down with sulfuric acid, rendering alkaline with sodium bicarbonate and titrating with iodine, as in the modified Gooch and Brown-ing method².

The results of the analyses indicate that there is little chemical change in a basic arsenate-lime-sulfur mixture, while in the case of the acid arsenate there is evidence of a considerable amount of reaction. There is fifty-two times as much arsenic oxide (As₂O₅)

rendered soluble from the acid arsenate as from the basic, or, calculated from the amount of original material used, about 5% of the arsenic oxide, (As_2O_3), from the lead acid arsenate passed into solution. Furthermore, excessive losses of both lime and sulfur from solution took place; the amount of calcium oxide in solution was reduced from 4.228 grams to 3.188 grams or over 25 per cent; and the sulfur content from 8.8004 grams to 5.8367 grams or over 35 per cent. In the solution from the basic arsenate-lime-sulfur mixture, on the other hand, there is but very little loss of either lime or sulfur. The results indicate, however, that there is a very slight chemical action between these two materials.

A comparison of the composition of the dried, insoluble residue gives further evidence of the decomposition of the acid arsenate when mixed with the lime-sulfur. The residue obtained from the use of these substances was very dark in color, due, perhaps, to the presence of lead sulfide, while that obtained from using the basic arsenate was gray, indicating but slight decomposition. In making the analyses determinations were made of free sulfur, lead sulfide, lime, lead oxide, and sulfur combined as sulfate. Free sulfur was estimated by extracting the dried residue with pure carbon disulfide, evaporating the solvent, and weighing the sulfur direct.

The determination of lead sulfide was effected by digesting the sulfur-free residue in warm 3.50 per cent hydrochloride acid (1 to 10) until no lead was further dissolved. It was assumed that this strength of acid dissolved everything present excepting the lead sulfide. Tests made on the two arsenates of lead showed them to be soluble in this strength of warm hydrochloric acid. The lead sulfide was finally collected on a Gooch filter, washed thoroughly, dried at a moderate temperature, and weighed.

The total lime was determined by extracting the residue with concentrated hydrochloric acid and then, after removing the lead and arsenic by the use of hydrogen sulfide, precipitating as the oxalate, igniting, and weighing as calcium oxide.

The estimation of the other constituents was made by the methods usually employed.

The results of the analyses are given in Table VII.

Table VII. Analyses of Residues from Mixtures of Lime-sulfur and Lead Arsenates.

	Residue from Acid Arsenate plus lime-sulfur.		Residue from Basic Arsenate plus lime-sulfur.	
	per cent	grams	per cent	grams
Total Lime, CaO	12.97	1.1676	2.42	0.1029
Lead Sulfide, PbS	25.25	2.0780	0.44	0.0219
Sulfur combined as sulfate.....	0.77	0.0634	0.46	0.0230
Sulfur soluble in carbon disulfide.....	26.50	2.1806	0.13	0.0064
Total Arsenic oxide, As_2O_3	18.11	1.4978	22.71	1.1230
Total Lead Oxide, PbO	34.83	2.8701	72.13	3.5677
Weight of total residue.....		8.2286		4.9462

Considering that primarily this residue consisted only of lead arsenate, it is seen that considerable chemical change has occurred in the case of the acid arsenate especially. The basic arsenate is shown also to have been reacted upon slightly but not to an extent that would probably prove of any importance. After mixing with lime-sulfur the insoluble residue in the case of the acid arsenate was increased in weight to 8.2880 grams or nearly 100 per cent, while in the case of the basic salt the increase was very slight. The study of the reaction involved indicates a partial interchange of calcium and lead forming calcium arsenate and lead sulfide respectively, free sulfur being deposited at the same time. The soluble arsenic is then derived from partial solution of the calcium arsenate thus formed. The increase in the residue from the acid arsenate is due chiefly to the sulfur freed from the lime-sulfur, being, as the table shows, 26.50 per cent of the total residue. Sulfides of arsenic were not formed as these compounds are soluble in the alkaline lime-sulfur forming sulfo salts, and sulfo salts were not present in the solution.

From the work here reported, it is plainly evident that the reaction between the lead hydrogen arsenate and lime-sulfur is much more pronounced than the reaction between the basic arsenate and lime-sulfur. Some field tests have been made using these combinations of spray materials but further experimental work is necessary definitely to prove if the products from the reactions taking place are, under ordinary orchard practice, more liable to burn foliage than the lead arsenates themselves.

REFERENCES.

1. Journal Industrial and Engineering Chemistry, Vol. 2, p. 328 (1910).
2. Bull. 107 (Revised), Bureau of Chemistry.

SUMMARY.

1. A reliable method has been devised for the preparation of pure lead hydrogen arsenate.

2. All attempts to prepare pure lead orthoarsenate have been unsuccessful.

3. Lead pyroarsenate has been prepared.

4. A new basic lead arsenate of apparently constant composition has been obtained.

5. The general physical appearance of the pure lead hydrogen arsenate and the pure basic arsenate has been described.

6. The specific gravity of each of these arsenates has been determined.

7. The difficulties attending the accurate determination of the solubility of the pure compounds prepared have been pointed out. The tests made, however, show these compounds to be very insoluble.

8. Field tests made by using the pure arsenates at strengths as high as eight pounds to each hundred gallons of water, were tried for two consecutive seasons with no injury to foliage.

9. The lead hydrogen arsenate was found to react very easily with a number of different substances, especially those of an alkaline nature. On the other hand, the basic arsenate is a comparatively inert material.

10. Tests made with tent caterpillars showed the acid salt to be a much quicker-acting poison.

11. The necessity of more complete methods for the true valuation of commercial lead arsenates has been pointed out.

12. Satisfactory methods have been devised for, and applied to, commercial samples as follows:

(a) The estimation of lead hydrogen arsenate in the presence of mixed salts.

(b) The determination of lead carbonate.

(c) New methods for water-soluble arsenic oxide and water-soluble impurities.

(d) A method for acid insoluble impurities.

(e) The detection of acetates and the quantitative estimation of chlorine.

13. The application of these methods shows a wide variation in the composition of the commercial arsenates and gives a better valuation of them than the methods now in use.

14. The precipitates obtained from the reactions of lead acetate and lead nitrate with di-sodium hydrogen arsenate under certain

conditions are mixtures of lead hydrogen arsenate and the basic lead arsenate.

15. The inconsistencies of the federal insecticide law have been commented upon.

16. When lead hydrogen arsenate is mixed with lime-sulfur in the proportions used in field practice, a reaction takes place in which considerable quantities of lead sulfide and calcium arsenate are formed, accompanied by the deposition of free sulfur. Appreciable quantities of arsenic pass into solution due to the solubility of the calcium arsenate. The reaction between lime-sulfur and the basic arsenate is comparatively slight.