

Water Soluble Arsenic in Spray Material

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WATER SOLUBLE ARSENIC IN SPRAY MATERIALS

H. C. YOUNG

Injury to fruit and foliage from spray materials is becoming exceedingly common. Too frequently the loss incurred by such injury is as large or larger than could have been expected from the pests to be controlled. For many years bordeaux mixture was the standard spray for most types of fruit but, today, it is used only when absolutely necessary. Its disuse has been brought about, not because of a lack of efficiency in controlling diseases, but because of the injury it produces.

Upon demonstration of its usefulness lime-sulfur was promptly substituted for bordeaux and soon became the generally recommended spray. It held this position, seemed to control well, and gave but little injury for a period of nearly 20 years. Then rather suddenly, it began to injure, and today in many fruit sections it is regarded as dangerous as bordeaux mixture.

What has brought about this increasing injury by these two standard spray materials is difficult to answer. Possibly in former times much foliage injury was overlooked and a less exacting finish on fruit was demanded. Perhaps spraying was not so thoro. Many believe that trees gradually lose their tolerance to sprays, or that the injury becomes cumulative. Others think that the present-day cultural practices and, possibly, gradually changing weather conditions are factors. At any rate, the spraying schedule of the present with its recommended standard materials is resulting in too much injury and a change is imperative.

The margin of difference between tree tolerance to a fungicide or an insecticide and the killing concentration is small, making it difficult to develop materials which will be effective and yet will not injure. Possibly, this would not be so difficult if the weather did not exert its influence. In fact, a fungicide may be made up so that it will kill fungi and not injure the tree under normal temperature, say 18° C. (65° F.), but if the temperature be raised 10 degrees it may cause severe injury. On the other hand, if the temperature should drop 10 degrees the fungicide would be much less effective and no foliage injury would result. This is particularly true with sulfur sprays. The reverse occurs with bordeaux.

The perfect fungicide or insecticide is one that will not injure foliage under any condition and will control under all conditions. This may be impossible, or at least very difficult to find, especially in the case of fungicides, since the parasite is a plant somewhat similar in general relations and chemical composition to the higher plant, its host. This problem was foreseen several years ago, and work was begun in this laboratory to determine chemical differences between fungi and their host plants with the object in view of finding compounds that occur in the fungus and not in the higher plant which would react to fungicides. Considerable progress has been made, but as yet no working hypothesis developed.

Fruit growers, in an attempt to avoid spray injury, have used many types of substitutes. They have diluted both bordeaux and lime-sulfur. They have used many types of wettable sulfur sprays, as well as a great many proprietary remedies. Many so-called corrective materials such as lime, calcium caseinate, ferrous sulfate, aluminum sulfate, zinc sulfate, and a host of others, have been used. This has resulted as a rule in poor control, not much reduction in injury, general dissatisfaction, and a large number of confusing recommendations.

As far as the author is aware, there has been a somewhat limited amount of constructive study given to the problem of spray injury. Much of the work has been of the "cut and fit" nature, and little effort has been made to determine the underlying cause or causes. Part of the spraying schedule calls for a combination of some fungicide and an insecticide, and, for apples, this is usually lime-sulfur and arsenate of lead. When spray injury results, it is caused either by the fungicide or the insecticide, or a combination of both, brought about by an inter-reaction between the two. There are known cases where lime-sulfur alone has injured—Saffro (7), Wallace (13), Young and Walton (15), and others. There are also reports of arsenical injury—Fernald and Bourne (2), Smith (8), Swingle (10), Ginsburg (3), Haenseler and Martin (4), Stewart (9), and others. The combination sprays of wettable sulfur and arsenate of lead have been studied by Haenseler and Martin (4), and Ginsburg (3). They found the injury factor on peaches to be due to water soluble arsenic. Swingle (10) found that peaches sprayed with 0.01 percent solution of arsenic and arsenious acids were severely injured. He found that an arsenate of lead containing more than 0.5 percent water soluble arsenic would burn peach foliage, and that there was an accumulation of free arsenic in the leaf brought about by the gradual hydrolysis of the lead

arsenate and its continuous absorption. Consequently, a lead arsenate containing much more than 0.5 percent water soluble arsenic may be expected to burn peach foliage.



Fig. 1.—Spray injury on Jonathan apples sprayed in mid-July with 1-80 liquid lime-sulfur and $1\frac{1}{2}$ lbs. lead arsenate

The combination spray of lime-sulfur and arsenate of lead has received less study, especially after the spray has been applied. It is well known that acid lead arsenate alone does not often burn apple foliage. An examination of this spray mixture before it is applied does not show an excessive amount of water soluble arsenic. Consequently, most of the damage to apple foliage by this combination has been attributed to the lime-sulfur itself. This led to the idea that lime-sulfur should be diluted for the late sprays. However, when this was done injury was frequently even more severe, especially where lime was not added. A striking example of this

occurred during the season of 1929, where a grower used a 1 to 80 liquid lime-sulfur and $1\frac{1}{2}$ pounds of lead arsenate to 50 gallons of spray. The results were disastrous, as is shown by the photographs in Figure 1.

This spray was applied under moderate temperature and humidity conditions such as are considered safe for spraying, during late July. In the same locality 2 pounds dry lime-sulfur, 2 pounds lime, and $1\frac{1}{2}$ pounds lead arsenate to 50 gallons of water caused severe injury. Upon close examination it was found that the injury in both cases was typically arsenical and not due to the action of lime-sulfur as is generally supposed.

In this investigation an attempt was made to determine what happens when lime-sulfur and acid lead arsenate are mixed together before and after the material is sprayed on the tree; under what conditions arsenic becomes soluble in the mixture; also what effect is produced by such 'correctives' as calcium hydrate, calcium caseinate, ferrous sulfate, aluminum sulfate, and a large number of other materials that might be supposed to have corrective properties. The effects of temperature, length of time of drying, strength of material, and sulfur substitutes were tried. Manganese arsenate (Manganar) was tested as a substitute for lead arsenate.

WATER SOLUBLE ARSENIC IN LIME-SULFUR AND ARSENATE OF LEAD MIXTURES

Method of procedure.—The lime-sulfur-lead arsenate mixtures were made up in the usual way, by adding the lead arsenate to the dilute lime-sulfur. In all this work 1000 cc quantities of the mixture were prepared and shaken until samples were taken. Preliminary tests showed that thoro shaking was necessary for uniform results. After shaking for the required time the mixtures were filtered and two 100 cc aliquots of the filtrate were used for each determination. The method adopted for the arsenic determinations was a slight modification of those generally used and, for that reason, will be given in detail here.

Aliquots of 100 cc of the filtrate were digested with 5 cc of superoxol for 30 minutes in an autoclave with 1 to 2 pounds pressure, then digested to fuming with 5 cc of concentrated sulfuric acid and filtered with as little water (30 cc) as possible. The filtrate was diluted again to 100 cc with water and 1 gram of KI added and evaporated to about 50 cc, or until practically clear. It was next cooled, 200 cc of water added and decolorized with 1 to 2 drops of one-tenth normal sodium thiosulfate. Sodium carbonate

was added to neutrality, then the mixture was slightly reacidified and made alkaline with an excess of sodium bicarbonate. It was then titrated with one-hundredth normal iodine, starch being used as an indicator.

The dilutions, time of shaking, and the percentage of As_2O_5 are given in Table 1. In all mixtures, unless otherwise stated, the acid lead arsenate, PbHAsO_4 , was used at the rate of $1\frac{1}{2}$ pounds to 50 gallons of the spray.

TABLE 1.—Soluble Arsenic in Lime-Sulfur and Arsenate of Lead Mixture not Dried

Lime-sulfur strengths in $1\frac{1}{2}$ lb. arsenate of lead to 50 gal.	Percent water soluble arsenic after shaking				
	30 min.	1 hour	12 hours	24 hours	36 hours
1-60.....	1.4	2.1	5.8	6.0	6.4
1-80.....	1.6	2.7	7.4	8.0	8.2
1-80.....	2.1	3.2	10.6	11.5	12.6
Filtrate from first wash of sludge.....	4.5	5.6	6.2	6.2	6.2

The results given in Table 1 are averages of six replications. This number of replications seemed to be necessary owing to a considerable fluctuation in results, these varying at times as much as 10 percent in the duplicates when run on separate days. An attempt will be made below to explain the cause of these variations.

The interesting and important point in this experiment is the extremely high percentage of water soluble arsenic in the 1-80 liquid lime-sulfur when compared with a 1-40 dilution. From a chemical standpoint it was also interesting that the water soluble arsenic did not increase much after 12 hours. The sludge was also very high in water soluble arsenic.

Since the water soluble arsenic was so high in the mixtures it was thought that possibly this would only occur when they stood or were shaken in solution. It seemed inconceivable that tree foliage or fruit could ever withstand without injury such concentrations of arsenic. Consequently, a determination was made under conditions as nearly comparable to those in the orchard as facilities would permit. The mixtures were prepared in the same way as described above and shaken for 30 minutes. Then 50 cc was spread evenly over a rubber mat 20 inches square. By the aid of an electric fan and bunsen burners placed so that the flames blew thru the fan and over the mat the spray was dried in 30 minutes at a temperature of 30°C . (84°F). When dry, the mat was thoroly washed in 300 cc of distilled water, the wash water was filtered first thru ordinary

filter paper and then thru a Gooch filter. Two 100-cc aliquots of the clear filtrate were used in making the determinations. The results of both liquid and dry lime-sulfur mixtures are given in Figure 2.

Each point on the curve represents the average of six replications. Again the results from day to day on duplicate runs varied considerably. However, the variations were small as compared with the large differences between dilutions. It might be expected that any spray containing such a large amount of free arsenic as the summer strengths of lime-sulfur when mixed with lead arsenate would burn almost any type of foliage. In fact, it is remarkable that such mixtures can be used at all.

The liquid lime-sulfur curve contains two high and two low points. The second rise in the curve may be explained by the increased hydrogen sulfide formed when lime-sulfurs are diluted. Hydrogen sulfide will break down acid lead arsenate forming lead sulfide, the reaction probably being $2\text{PbHAsO}_4 + 2\text{H}_2\text{S} = 2\text{PbS} + \text{As}_2\text{O}_3 + 2\text{H}_2\text{O}$. It might also be assumed that H_2S incites the reaction and, as arsenious acid is formed, that it reacts further on the lime-sulfur causing a release of more hydrogen sulfide. The speed of reaction between lime-sulfur and lead arsenate depends then, to a considerable extent, on the start it gets. Undoubtedly, these reactions are also somewhat reversible and the extent to which they will go, in any one direction, depends on how they start and the environmental factors affecting them. Consequently, in these tests, considerable variation might be expected unless all influencing factors were known and governed. Similar wide variations as to reactions occur under field conditions and such variations may account for the severe burning in one case and the lack of it in another.

The source of the initial production of hydrogen sulfide in lime-sulfur has been investigated but to date the author is aware only of theories concerning it. Martin (5) states that it is formed from the monosulfide present, which is the first to break up, possibly thru the action of the CO_2 which is present in the air and water. This problem is being investigated and will be reported upon later.

The nature of the sludge formed in the lime-sulfur-arsenate of lead mixtures was also investigated. It was found that the percentage of lead sulfide formed, as determined by the method of Robinson (6), was in direct proportion to the amount of soluble arsenic formed. These proportions held in later tests made with calcium hydrate where the soluble arsenic content was decidedly reduced. They also held in the sludge formed both in the solution

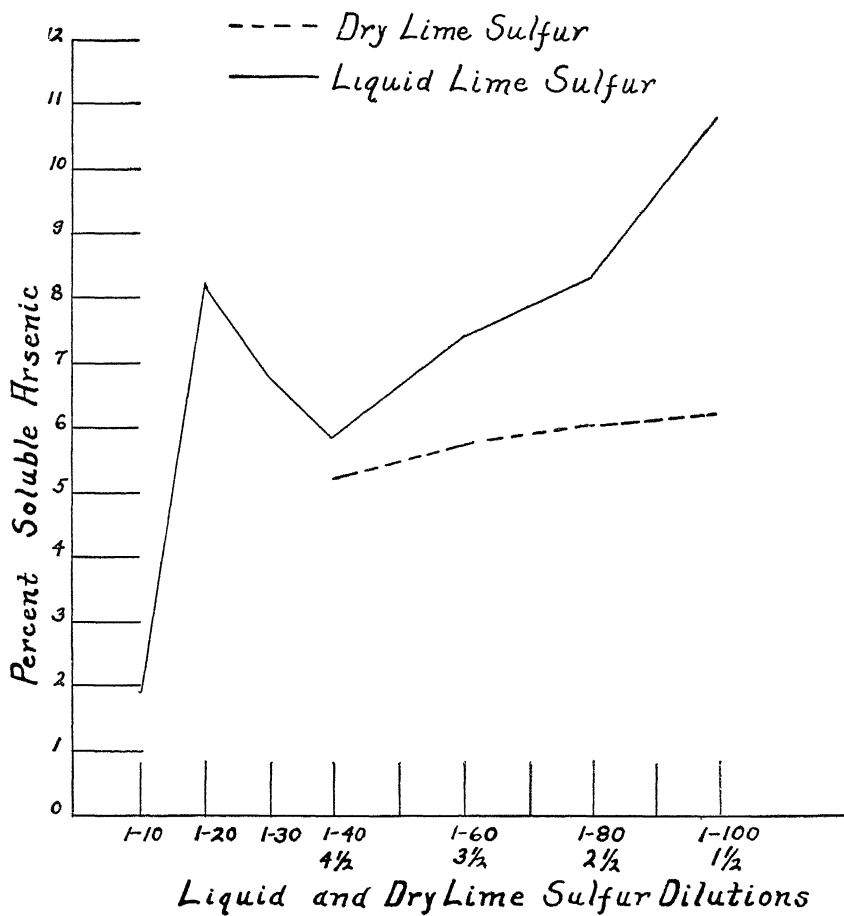


Fig. 2.—Soluble arsenic in liquid and dry lime-sulfur-lead arsenate mixture

and the dried material on the mat. It is evident from these tests that lead arsenate is broken down primarily by hydrogen sulfide or other sulfides and that a direct reaction takes place.

WATER SOLUBLE ARSENIC IN LIME-SULFUR AND LEAD ARSENATE MIXTURES TO WHICH CORRECTIVES WERE ADDED

The method used was exactly the same as in the previous experiment. In preparing the mixtures the corrective was added to the dilute lime-sulfur, the contents shaken thoroly and then the lead arsenate added. This method was used because of the protective action the corrective is supposed to have on the breakdown of lime-sulfur rather than on any action on the lead arsenates or on the formation of insoluble arsenates. The mixtures were dried and the determinations made in the same manner as before. The quantities of correctives, dilutions of the lime-sulfurs, and percent of soluble arsenic are given in Table 2. These are also shown graphically in Figures 3 and 4.

The high calcium lime used was freshly hydrated and contained less than 2 percent magnesium. This type of lime seemed to be very effective in reducing water soluble arsenic in lime-sulfur and lead arsenate mixtures. However, even where 5 pounds was used, the reduction was not sufficient to insure against injury on all types of foliage and under all conditions. This is especially true if a part of the arsenic is made insoluble by combining with the calcium. Calcium arsenate has been found unsafe for many types of foliage. On the other hand, if lime prevents the reaction by which soluble arsenic is usually formed, the spray should be quite safe, especially for apples.

Hydrated limes high in magnesium were inefficient in reducing soluble arsenic even when 5 pounds was added to the mixture. Likewise, hydrated lime that is old or partly carbonated or carbonates of any material tried, were wholly inefficient. This may explain the reason for many severe cases of burning with dry-mix sulfur-lime sprays on peaches.

Contrary to expectation, calcium caseinate did not reduce soluble arsenic in these sprays. These results are contrary to those obtained by Thatcher and Streeter (12) tho they did not dry the sprays, as was done in this case. Here again, care should be taken to use fresh calcium caseinate, because, if the lime in it is allowed to carbonate, soluble arsenic will be increased rather than decreased. Martin (5) states, in this connection, that colloidal

materials such as casein should have a tendency to retain the hydrogen sulfide, thus increasing the chance that water soluble arsenic will be formed.

TABLE 2.—Amount of Soluble Arsenic in Liquid Lime-Sulfur and Arsenate of Lead Mixtures With and Without Correctives

Correctives added to 1½ lb. arsenate of lead in 50 gal. of spray mixture	Portion water soluble arsenic in lime-sulfur dilution of			
	1-40	1-60	1-80	1-100
	<i>Pct.</i>	<i>Pct.</i>	<i>Pct.</i>	<i>Pct.</i>
Nothing	5.8	7.4	8.3	10.8
1 lb. high Ca. lime.....	5.0	6.8	5.8	5.2
2 lb. high Ca. lime.....	4.2	4.5	4.3	4.2
3 lb. high Ca. lime.....	3.1	3.8	3.0	3.0
4 lb. high Ca. lime.....	1.8	1.8	1.3	1.1
5 lb. high Ca. lime.....	1.3	1.4	1.2	1.0
1 lb. high Mg.-lime.....	5.8	6.9	5.9	5.4
2 lb. high Mg.-lime.....	5.1	6.4	5.5	4.9
3 lb. high Mg.-lime.....	5.0	4.4	4.6	4.4
4 lb. high Mg.-lime.....	4.3	3.8	3.8	3.6
5 lb. high Mg.-lime.....	4.2	3.6	3.5	3.5
¾ lb. ferrous sulfate.....	6.5	5.0	3.5	3.5
½ lb. ferrous sulfate.....	4.8	3.2	3.8	3.0
1 lb. ferrous sulfate.....	4.3	2.8	2.7	1.8
2 lb. ferrous sulfate.....	3.2	2.0	2.0	1.4
¾ lb. zinc hydrate.....	7.5	7.5	7.6	7.8
1 lb. zinc hydrate.....	7.7	7.8	7.3	7.6
1½ lb. zinc hydrate.....	5.1	6.9	6.2	7.0
2 lb. zinc hydrate.....	4.2	6.9	6.3	6.4
¾ lb. Ca. caseinate.....	9.3	8.3	6.4	6.0
½ lb. Ca. caseinate.....	7.8	7.3	6.0	5.2
¼ lb. Ca. caseinate.....	6.4	6.4	6.0	5.0
1 lb. zinc sulfate.....	9.4	8.0	7.7	7.2
1 lb. aluminum hydrate.....	6.1	7.4	8.4	9.6
1 lb. aluminum sulfate.....	9.5	10.6	11.4	12.6
½ lb. tri sodium phosphate.....	9.0
2 lb. tri sodium phosphate.....	11.1
.....	11.4	12.8
2 lb. calcium chloride.....	11.2	12.2	12.4
3 lb. calcium chloride.....	11.2	12.2	12.4
1 lb. calcium carbonate.....
3 lb. calcium carbonate.....	16.5
1 lb. barium carbonate.....	16.8
3 lb. barium carbonate.....	17.4
5 lb. barium carbonate.....	11.2
1 lb. barium chloride.....	7.3
2 lb. barium chloride.....	7.4
3 lb. barium chloride.....	6.3
1 lb. barium hydrate.....	5.5
2 lb. barium hydrate.....	4.3
3 lb. barium hydrate.....	5.2
¼ lb. calcium chlorate.....	8.0
½ lb. calcium chlorate.....	7.8
1 lb. calcium chlorate.....

Ferrous sulfate, a corrective used by Dutton (1) to reduce spray injury, was somewhat effective in reducing the water soluble arsenic content, altho, at his recommended quantity of one-half pound, it was much less effective than high calcium lime. It would be scarcely advisable to use it in greater concentration because of the heavy precipitate formed. Undoubtedly the reduction in injury by the use of either ferrous sulfate or aluminum sulfate in

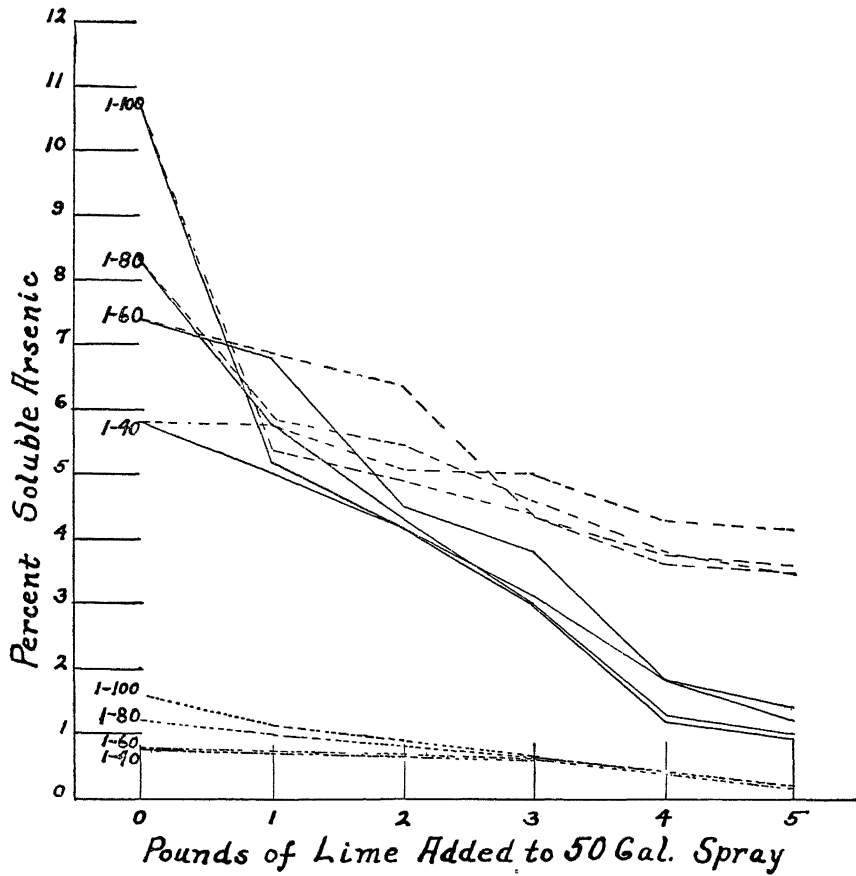


Fig. 3.—Water soluble arsenic in lime-sulfur and arsenate of lead mixture to which lime has been added

- High magnesium lime
- High Ca. lime and Manganar substituted for arsenate of lead
- _____ High calcium lime

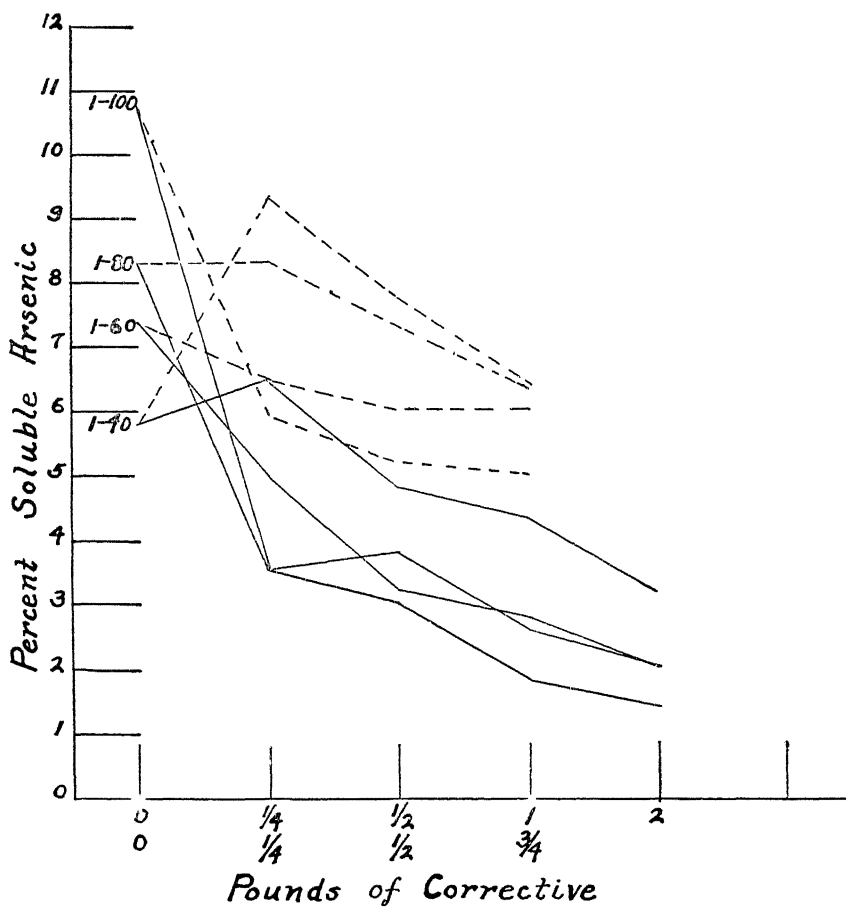


Fig. 4.—Water soluble arsenic in lime-sulfur and arsenate of lead mixture to which ferrous sulfate and calcium caseinate was added

————— Ferrous sulfate
 - - - - - Calcium caseinate

lime-sulfur-lead arsenate sprays is due to their action on the polysulfide, and not to their effect upon arsenic. In fact, aluminum sulfate in such mixtures increases water soluble arsenic. All other materials used either had no effect, or increased the soluble arsenic content in the lime-sulfur-lead arsenate mixtures.

WATER SOLUBLE ARSENIC IN DRY LIME-SULFUR-LEAD ARSENATE MIXTURES TO WHICH HIGH CALCIUM LIME WAS ADDED

These mixtures were prepared and the determinations made in the same manner as in the previous tests. The results are given in Table 3, and graphically shown in Figure 5.

TABLE 3.—Amount of Soluble Arsenic in Dry Lime-Sulfur and Arsenate of Lead Mixture With and Without Correctives

Correctives added to 1½ lb. arsenate of lead in 50 gal. spray mixture	Portion of water soluble arsenic in dry lime-sulfur dilutions of			
	4½ lb. to 50	3½ lb. to 50	2½ lb. to 50	1½ lb. to 50
Nothing	<i>Pct.</i> 5.2	<i>Pct.</i> 5.7	<i>Pct.</i> 6.0	<i>Pct.</i> 6.2
1 lb. high Ca. lime.....	4.6	5.7	5.4	5.4
2 lb. high Ca. lime.....	4.0	5.6	5.4	5.2
3 lb. high Ca. lime.....	4.0	4.3	4.3	4.3
4 lb. high Ca. lime.....	2.0	2.0	2.1	2.8
5 lb. high Ca. lime.....	1.0	1.2	1.3	1.6

The amount of soluble arsenic formed in dry lime-sulfur and lead arsenate mixture was high but showed far less increase as the mixture was diluted than was the case with liquid lime-sulfur. The addition of calcium hydrate brought about practically the same reduction as was found with liquid lime-sulfur. Again, the amount of soluble arsenic could not be reduced below 1 percent, even with 5 pounds of lime.

WATER SOLUBLE ARSENIC IN LIME-SULFUR-MANGANAR MIXTURE

Manganar is the trade name for manganese arsenate. It has been used as a substitute for arsenate of lead and one of its advantages is that it does not produce a black sludge when mixed with lime-sulfur. In fact, no visible change seems to take place in the mixture.

These mixtures were prepared and the determinations made in the same way as in the previous case, the only change being that 1½ pounds of Manganar was substituted for the same amount of lead arsenate. The results are given in Table 4, and shown graphically in Figure 3.

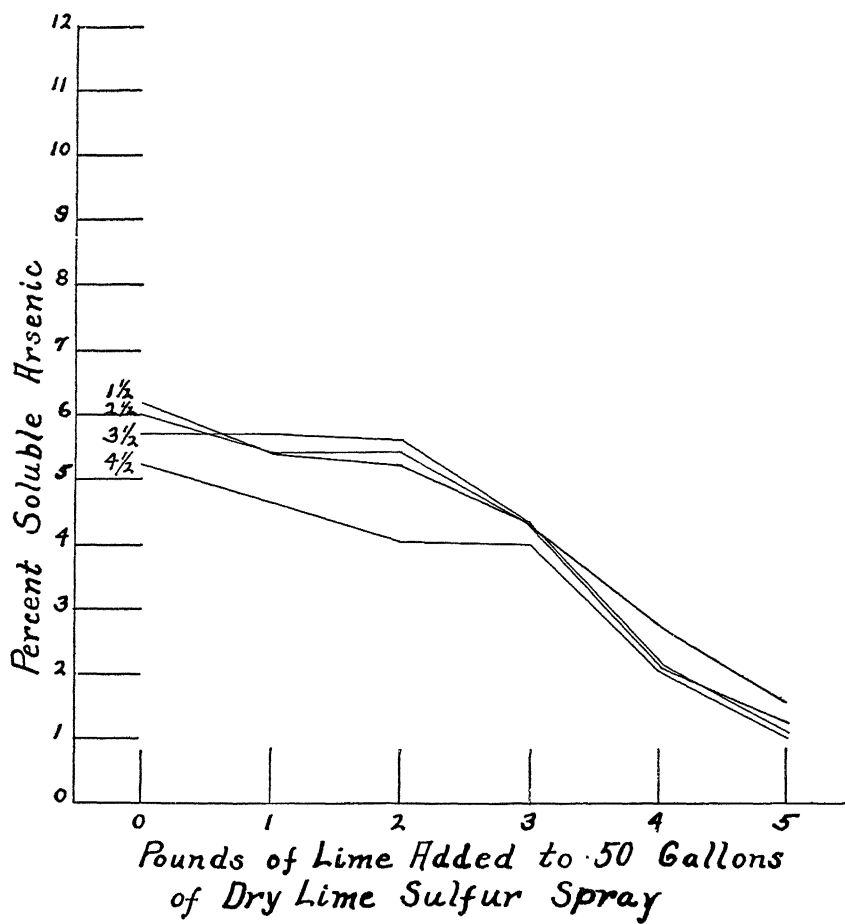


Fig. 5.—Water soluble arsenic in dry lime-sulfur and lead arsenate mixture and with lime added

Very little water soluble arsenic was found in the lime-sulfur-Manganar mixtures. This combination should be safe on almost any type of foliage in so far as the arsenic is concerned.

TABLE 4.—Soluble Arsenic in Liquid Lime-Sulfur and Manganar Mixtures With and Without Lime

Materials added to 1½ lb. manganar in 50 gal. spray mixture	Portion water soluble arsenic in lime-sulfur dilutions of			
	1-40	1-60	1-80	1-100
Nothing	0.8	0.8	1.2	1.6
1 lb. high Ca. lime6	.8	1.0	1.1
3 lb. high Ca. lime6	.6	.6	.6
5 lb. high Ca. lime2	.2	.2	.2

This material was tested in combination with many correctives and the results together with those obtained with lead arsenate are compared in Table 5.

TABLE 5.—Comparison Between Soluble Arsenic in Arsenate of Lead and Manganar When Added to Lime-Sulfur With and Without Correctives

Spray materials used in 50 gal. water and 1½ lb. arsenical	Portion water soluble arsenic in		
	Arsenate of lead	Manganar fresh	Manganar 6 mo. old
	<i>Pct.</i>	<i>Pct.</i>	<i>Pct.</i>
Alone	1.1	0.2	0.2
Lime-sulfur 1-40	5.8	.8	.8
Lime-sulfur 1-60	7.4	.8	.8
Lime-sulfur 1-80	8.3	1.2	1.2
Lime-sulfur 1-100	10.3	1.6	1.6
Lime-sulfur 1-60+½ lb. Ca. caseinate	7.3	.4
Lime-sulfur 1-80+½ lb. Ca. caseinate	6.0	.4
Lime-sulfur 1-60+½ lb. zinc hydrate	6.9	.2
Lime-sulfur 1-80+½ lb. zinc hydrate	6.2	.2
Lime-sulfur 1-60+1 lb. zinc sulfate	8.0	.2
Lime-sulfur 1-80+1 lb. zinc sulfate	8.0	.2
Lime-sulfur 1-60+1 lb. Al hydrate	7.4	.8
Lime-sulfur 1-80+1 lb. Al hydrate	8.4	1.2
Lime-sulfur 1-60+1 lb. Al sulfate	10.6	1.2
Lime-sulfur 1-80+1 lb. Al sulfate	11.4	1.4

In every case the Manganar mixtures contained much less soluble arsenic than was found when lead arsenate was used. The addition of correctives had little effect one way or another in the Manganar mixtures.

SOLUBLE ARSENIC IN MILD SULFUR SPRAYS WITH LEAD ARSENATE AND MANGANAR

The dry-mix sulfur-lime was prepared in the proportion of 6 pounds of 300 mesh ground sulfur and 3 pounds of fresh hydrated lime and 2 ounces of calcium caseinate. The mixtures used, the proportions concerned, and the percentages of soluble arsenic formed are given in Table 6.

TABLE 6.—Soluble Arsenic in Mild Sulfur Sprays in Combination With Arsenate of Lead and Manganar

Materials added to 1½ lb. of arsenical in 50 gal. spray	Portion of water soluble arsenic in	
	Arsenate of lead	Manganar
2 lb. dry mix sulfur lime.....	1.3	0.6
3 lb. dry mix sulfur lime.....	2.0	.6
4 lb. dry mix sulfur lime.....	3.2	.4
12 lb. dry mix sulfur lime.....	2.6	.3
2 lb. sulfuron.....	1.6	.3
3 lb. sulfuron.....	2.4	.6
4 lb. sulfuron.....	2.0	.6
4 lb. mist brand sulfur.....	1.4	.4
6 lb. mist brand sulfur.....	1.4	.4

The amount of soluble arsenic obtained for 12 pounds of dry-mix and lead arsenate was slightly lower than that obtained by Ginsburg (3), but high enough to burn peach foliage, Swingle (10). The Manganar again showed little perceptible change when used with these wettable sulfur sprays.

EFFECT OF WETTING AND DRYING ON FORMATION OF SOLUBLE ARSENIC IN VARIOUS SPRAY MIXTURES

Certain changes might be expected to take place when such complex mixtures were dried and re-wet several times. Accordingly mixtures were prepared in the usual way and spread on the rubber mats. The first drying was completed in 30 minutes, the mixture allowed to remain about an hour, and then re-wet with 50 cc water. The subsequent wetting and drying was done at varying lengths of time. The mixtures used, the duration and number of dryings, and the amounts of water soluble arsenic obtained are given in Table 7.

TABLE 7.—Soluble Arsenic in Sprays That Were Dried and Re-wet Several Times

Materials added to 1½ lb. arsenical in 50 gal. spray	Portion water soluble arsenic after			
	First drying	12 hr. 6 dryings	24 hr. 8 dryings	48 hr. 12 dryings
	<i>Pct.</i>	<i>Pct.</i>	<i>Pct.</i>	<i>Pct.</i>
4 lb. dry mix + manganar.....	0.4	0.4	0.3	0.3
8 lb. dry mix + manganar.....	.3	.4	.3	.3
12 lb. dry mix + manganar.....	.3	.3	.3	.3
4 lb. dry mix + arsenate of lead.....	3.2	3.0	2.8	2.6
8 lb. dry mix + arsenate of lead.....	2.6	2.6	2.4	2.0
12 lb. dry mix + arsenate of lead.....	1.6	1.6	1.6	1.4
1-60 lime-sulfur + arsenate of lead.....	7.4	6.8	6.2
1-60 lime-sulfur + manganar.....	.86	.6
Arsenate of lead alone.....	1.1	1.4	1.6
Manganar alone.....	.24	.4

The number of dryings seemed to have very little effect on the increase or decrease of the soluble arsenic. The slight decrease (where occurring) was undoubtedly brought about by the formation of small amounts of calcium arsenate. These results might be anticipated when it is realized that the only calcium compounds remaining after a few hours are the carbonate and sulfate, neither of which is very reactive.

EFFECT OF TEMPERATURE DURING DRYING ON FORMATION OF SOLUBLE ARSENIC IN LIME-SULFUR AND ARSENATE OF LEAD MIXTURES

In this experiment distilled water at 24° C. (75° F.) was used in preparing the mixtures, which were then dried on mats for 30 minutes at varying air temperatures. The results are shown graphically in Figure 6.

Low temperatures increased the water soluble arsenic, a result which was unexpected. No attempt will be made to explain why this happened, tho the fact that it did happen undoubtedly explains why such variable results are obtained in relation to spraying and spray injury.

EFFECT OF PERIOD OF DRYING ON FORMATION OF SOLUBLE ARSENIC IN LIME-SULFUR AND LEAD ARSENATE MIXTURE

This experiment was conducted at a room temperature of 26° C. (79° F.). Different periods of drying were obtained by placing the mats at varying distances from the fan. The periods thus obtained and the results are shown in Figure 6.

The results given in the curve are averages of four replications. Quickly drying the mixture resulted in increased soluble arsenic. Sprays dried in 30 to 45 minutes yielded the smaller amount.

DISCUSSION OF RESULTS

When lime-sulfur and lead arsenate are mixed together in the proportions and dilutions usually employed for spraying, a black sludge or precipitate is formed. Chemical analysis has shown this to contain lead sulfide. In order that the lead sulfide be formed there must be a decomposition of the lead arsenate. Consequently, as the lead unites with sulfide the arsenic is liberated. It might be expected that in this reaction calcium would also be free to react but in the breakdown of lime-sulfur calcium is at no time free or in a very reactive state in so far as combining with arsenic. Lime-sulfur, according to Tarter and Bradley (11), is composed of

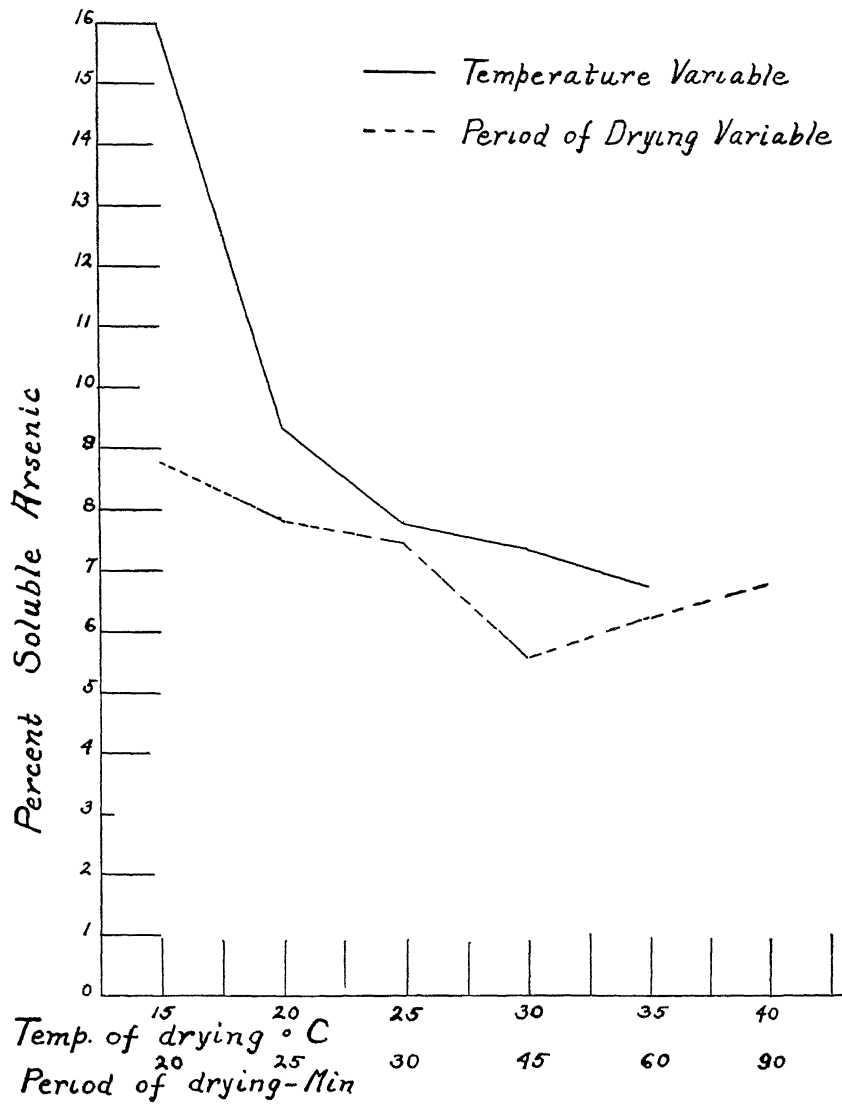


Fig. 6.—Water soluble arsenic in 1-60 liquid lime-sulfur and lead arsenate mixtures

————— Temperature variable and time of drying 30 min.
 - - - - - Time of drying variable, temp. constant at 30° C.

approximately 75 percent calcium polysulfides, 20 percent calcium mono-sulfide, 4.9 percent calcium thiosulfate, and a trace of calcium sulfite and sulfate. Just what calcium compounds are formed during the breakdown is not known but the end products according to Young (14) are sulfur, calcium thio-sulfate, calcium sulfate, and sulfite, with practically all of the calcium accounted for. The only element left that might possibly react with the free arsenic is the sulfur and this does not occur except as a trace. There can be expected, therefore, varying quantities of soluble arsenic when lime-sulfur and acid lead arsenate are mixed together.

The results of the foregoing experiments explain, at least in part, the reason for the spasmodic occurrence of spray injury. The temperature at time of spraying, length of time of drying on the leaves, type of water used (whether carbonates are present or not), the nature of the corrective agent, and a host of other factors account for variations in the final yield of soluble arsenic. In addition there is the degree of tolerance of the tree to arsenic, which unquestionably varies with variations in physiological and environmental conditions. There are undoubtedly climatic conditions under which a small amount of free arsenic will burn foliage, as well as other conditions in which much larger amounts cause no injury.

It would seem that the problem of spray injury resulting from arsenic is solved by the addition of high-calcium hydrated lime. But, while this reduces injury, it also reduces the efficiency of the fungicide and, according to unpublished preliminary results of Dr. Cutright, of the Department of Entomology, Ohio Experiment Station, 2 pounds of lime to 50 gallons of spray material appreciably reduces the efficiency of lead arsenate against codling moth. The fact remains, that anything which reduces injury from fungicides and insecticides also lowers their efficiency.

Manganar does not react with lime-sulfur to yield soluble arsenic, and is at present under extensive field experimentation, both as regards its effect upon sulfur and its control of insects. Until definite substitutes are developed the fruit grower will have to decide which he can best afford, loss from injury or loss from pests. Possibly he can use lime in his late summer sprays and still get control of diseases and insects, or he may be able to successfully substitute mild sulfur-lead arsenate sprays at this period.

SUMMARY

1. Mixtures of lime-sulfur and lead arsenate in summer spraying strength contain a dangerous amount of water soluble arsenic. The more dilute the lime-sulfur up to at least 1-100, the greater the amount of water soluble arsenic.

2. Freshly made high calcium hydrated lime is effective in reducing the water soluble arsenic in lime-sulfur-lead arsenate mixture. High magnesium hydrated lime is not so effective.

3. Carbonate of lime, calcium caseinate, and iron, aluminum, barium, and zinc compounds are valueless as correctives.

4. Manganar does not react with lime-sulfur to produce water soluble arsenic.

5. The wettable sulfur sprays react only slightly with lead arsenate and Manganar.

6. Temperature, period of drying, and a host of other factors regulate the production of water soluble arsenic in lime-sulfur-arsenate of lead mixture.

LITERATURE CITED

1. Dutton, W. C. Sulphate of iron reduces spray injury. *Am. Fruit Grower* 49: No. 2, p. 1, 1929.
2. Fernald, H. T. and A. I. Bourne. Injury to foliage by arsenical sprays. *Mass. Agr. Exp. Sta. Bul.* 40: 89-98, 1922.
3. Ginsburg, J. M. Studies of arsenical injuries and correctives. *N. J. Agr. Exp. Sta. Bul.* 468: 1-16, 1929.
4. Haenseler, C. M. and W. H. Martin. Arsenical injury on peach. *Phytopath* 15: 321-331, 1925.
5. Martin, Hubert. The scientific principles of plant protection. Chapters 4 and 5, p. 316, London, 1928.
6. Robinson, R. H. and H. V. Tartar. The arsenate of lead. *Oregon Agr. Exp. Sta. Bul.* 128: 1-32, 1915.
7. Saffro, V. I. An investigation of lime-sulfur injury; its causes and prevention. *Oregon Agr. Exp. Sta. Bul.* 2: 1-32, p. 64, 1913.
8. Smith, C. M. Excretions from leaves as a factor in arsenical injury to plants. *Jour. Agr. Res.* 26: 191-194, 1923.
9. Stewart, J. P. Some relations of arsenic to plant growth: Part I. *Soil Sci.* 14: 111-...., 1922.
10. Swingle, H. S. Composition of commercial lead arsenate and its relation to arsenical injury. *Jour. Agr. Res.* 39: 393-401, 1929.
11. Tartar, H. V. and C. E. Bradley. On the composition of lime-sulfur spray. *Jour. of Ind. & Eng. Chem.* II: 271-277, 1910.
12. Thatcher, R. W. and L. R. Streeter. Chemical studies of the combined lead arsenate and lime-sulfur spray. *N. Y. State Agr. Exp. Sta. (Geneva) Bul.* 521: 1-20, 1924.
13. Wallace, Errett. Spray injury induced by lime-sulfur preparations. *Cornell Agr. Exp. Sta. Bul.* 288: 103-137, 1910.
14. Young, H. C. The toxic property of sulfur. *Ann. Mo. Bot. Gard.* 9: 403-435, 1922.
15. Young, H. C. and R. C. Walton. Spray injury to apples. *Phytopath.* 15: 405-416, Pl. 1, 1925.