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CHEMICAL STUDIES OF THE COMBINED LEAD
ARSENATE AND LIME-SULFUR SPRAY

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CHEMICAL STUDIES OF THE COMBINED LEAD ARSENATE AND LIME-SULFUR SPRAY

R. W. THATCHER AND LEON R. STREETER

SUMMARY

There is very little, if any, chemical reaction between basic arsenates of lead and lime-sulfur solutions when these are mixed to form a combination insecticidal and fungicidal spray. But the use of basic arsenates of lead for this purpose is ruled out by the fact that they are less efficient as insecticides than are the acid arsenates of lead.

When acid lead arsenate is mixed with lime-sulfur solution, a definite chemical change takes place whereby the weight of insoluble solid matter in the mixture is nearly doubled. This solid matter contains some unchanged lead arsenate, a large proportion of lead sulfide and an equivalent amount of arsenate of lime, and about 20 per cent of free sulfur. There is also a slight increase in the amount of soluble arsenic in the mixture. These changes undoubtedly reduce the fungicidal efficiency of the mixture and increase the danger of foliage injury when it is applied in the orchard.

These changes can be prevented by adding hydrated lime to the mixture but the solid residue in the spray mixture is thereby correspondingly increased.

The undesirable reaction can be effectively prevented by the addition of casein-containing preparations, used in economical proportions. Skim-milk, with added lime, or commercial casein preparations may be used for this purpose.

The beneficial effect of casein preparations in preventing this undesirable chemical reaction is in addition to their so-called "spreader" effects.

Such evidence as there is so far available from orchard experiments indicates that there is little likelihood of reduction of the killing efficiency of combined lead arsenate and lime-sulfur sprays by the addition of casein preparations in order to prevent the undesirable chemical changes in the mixture.

Whether the addition of casein preparations to this combination spray will completely eliminate the danger of foliage burning from its application to trees in full leaf, can only be determined by further orchard experiments; but it seems probable that this danger may be at least greatly reduced, if not entirely overcome, in this way.

The addition of tobacco dust to the combined lead arsenate and lime-sulfur sprays, to increase their insecticidal action against certain types of insects, also effectively prevents the undesirable reaction between the arsenate and sulfur compounds, without the addition of any casein-containing materials.

INTRODUCTION

The economic advantage of applying combination sprays to control both insect pests and fungous diseases in a single operation is apparent. Several such possible combination sprays have been tried out by different investigators, with widely varying and sometimes conflicting results. A review of the reports of these experiments indicates that a part of the divergence of the results obtained is due to the failure of the experimenters to realize that there are often chemically different substances sold under the same trade name and that these give different results when mixed together to form combination sprays. Hence, it seemed to us to be desirable to undertake a series of studies of these matters, using in every case materials of which we knew the exact nature and composition; so that it would be possible to trace the observed effect to a definite known cause in each case.

We decided to investigate first the combination of lead arsenate with lime-sulfur for spraying purposes, since these are a widely used insecticide and fungicide, respectively, which it is desirable to combine into a single spray mixture if possible. The results of our studies of the chemical reactions which take place between the different arsenates of lead and lime-sulfur and of possible methods of preventing these in spray mixtures are presented in this bulletin.

There have been numerous studies by both entomologists in the orchard and chemists in the laboratory of the effect of combining these two materials for spray purposes. The orchard studies have given conflicting results, due apparently to the different kinds of arsenates of lead used in the combinations. The laboratory studies have shown clearly that there is an actual change in chemical com-

position which results when acid arsenate of lead and lime-sulfur solutions are mixed; that this change is much greater with acid arsenates than with neutral or basic arsenates; that it is greater with lead arsenates than with arsenates of lime; that it results in changing some of the soluble sulfur of the mixture into insoluble sulfur; and that it tends to increase the percentage of soluble arsenic in the mixture. The details of these studies and their relation to our investigations as reported herein will be discussed in appropriate sections of this report.

It is probable that these chemical changes tend to decrease the fungicidal properties of the mixture and to increase the danger of foliage injury when it is applied in the orchard. Our experiments have been planned to clear up the uncertain points concerning the reactions which take place in the mixture and to find a feasible method for preventing these, so as to increase the safety and efficiency of these mixtures for orchard use.

We first prepared quantities of the different arsenates of lead in our own laboratory, so that we might know the nature and composition of the compounds with which we were working. We then mixed these with lime-sulfur solutions in different proportions, with and without the addition of various quantities of other materials which we believed might serve to prevent the undesirable changes from taking place, and allowed the mixtures to stand for different lengths of time and under different conditions. The precipitated solid material was then filtered off, its quantity determined in each case, the general character of the solid residue observed, and in some cases analyses to determine its composition have been made. In all, a total of nearly 120 different tests have been carried out, including a great variety of combinations and conditions.

EXPERIMENTAL WORK

MATERIALS USED

Lime-sulfur solutions.—A commercial concentrated lime-sulfur solution having a specific gravity of 1.283 (32° Baume) was used for most of these tests. In those tests in which tobacco dust was added, a home-made lime-sulfur solution, which was available at the time, was used. In some of the experiments this was diluted 1 to 10, "winter strength," and in other tests 1 to 30, "summer strength," with distilled water adding the other substances involved in the particular test which was under way.

Lead arsenates.—The various lead arsenates which were used in the different experiments were all made in our laboratory, according to methods which had been found by us to give compounds of known and definite composition (1)¹. As an additional check upon the composition, each particular lot of lead arsenate used was first analyzed; so that its exact composition and nature were known before its reaction with lime-sulfur under varying conditions was determined.

Pure casein.—This material was taken from a stock lot which had been prepared in the laboratory for the dairy chemistry research of this Station, under conditions which have been found satisfactory for the production of pure casein².

Calcium hydroxide or hydrated lime.—This was a fine white powder, free from carbonates, purchased from a chemical manufacturing firm, C. P. grade.

Distilled water.—Water, freshly boiled to free it from dissolved carbon dioxide, was used in making up all solutions and mixtures, in order to prevent the introduction of errors due to the action of carbonic acid on the alkaline materials used.

All other materials were the ordinary commercial products such as would be available in orchard practice.

MIXTURES OF ARSENATES OF LEAD WITH LIME-SULFUR SOLUTIONS ALONE

Our first experiments were designed to study the conditions under which the chemical reaction between lead arsenate and lime-sulfur takes place and to find a simple but satisfactory method of measuring the amount of the change under any given set of conditions. Different samples of arsenate of lead were mixed with lime-sulfur solutions of different concentrations and these mixtures were allowed to stand for varying lengths of time under different conditions. The mixtures always contained suspended solid matter, of course, inasmuch as the lead arsenate, even if unchanged in any way by contact with the other ingredients of the mixture, is insoluble in the lime-sulfur solution and settles down to the bottom of the mixture if the latter is not agitated. When the lead arsenate is affected by the lime-sulfur, it undergoes the familiar change in color from white to brown and finally to a deep black, due to the formation of black lead sulfide. At the same time, it changes from a flocculent, finely divided condition into a more flakey form and takes on a greasy appearance

¹Figures in parenthesis refer to Literature Cited, page 20.

²Carpenter, Dwight C, unpublished results.

with a decided tendency to gather into a rather compact mass and to stick to the walls of the containing vessel, so that it is not so easily distributed thru the mixture by shaking.

This change in appearance is characteristic and indicates that a reaction has taken place whereby at least a part of the lead arsenate is changed to lead sulfide. But the change in appearance alone cannot be used as a measure of the extent to which the chemical reaction has gone. We sought, therefore, to find some method of quantitatively measuring the extent to which this change takes place in various reacting mixtures. A large number of such mixtures were filtered thru ordinary quantitative filter paper, the residues washed with distilled water until the washings came thru colorless, then dried at 60°C. to constant weight, cooled in a dessicator, and weighed. In several cases, partial analyses of this dried material were made, in order to determine how it differed in composition from the original lead arsenate used. Also, analyses to show the amount of arsenic and of certain sulfur compounds which were in solution in the filtrate and washings were made in a considerable number of cases.

It soon became apparent that the total weight of the dried precipitated matter afforded a most convenient and satisfactory measure of the extent to which the reaction had proceeded in any given case. It was found that check determinations by this method at different times always gave concordant results, within reasonable limits, whenever the conditions of the experiment were uniform; that the addition of other insoluble solids to the mixture gave proportionate increments in the weight of residue obtained; and that the weights of residues found under different conditions were in accord with other analytical data from the same experiment. Accordingly, this means of measurement was used in all the studies which are reported in this bulletin.

The results from the first series of tests of the action of various samples of lead arsenate with lime-sulfur solutions of different strengths and for varying periods of time are shown in Table 1. The determinations recorded as Series A are those made with different lots of acid arsenate on several different occasions as checks against other treatments and indicate the accuracy with which results can be duplicated by this method under varying laboratory conditions. Those designated as Series B show the effect of lengthening the period of standing of the mixture before filtering off the residue; and Series C, the effect of varying the concentration of the

lime-sulfur solution. Series D presents typical results from using basic arsenate of lead.

TABLE 1.—SHOWING WEIGHT AND CHARACTER OF RESIDUE OBTAINED BY MIXING VARIOUS ARSENATES OF LEAD WITH LIME-SULFUR SOLUTIONS UNDER DIFFERENT CONDITIONS.

TEST No.	ARSENATE	USED	LIME-SULFUR USED, DILU- TION	TIME OF STANDING HOURS	WEIGHT OF RESIDUE GRAMS	APPEAR- ANCE OF RESIDUE
	Kind	Amt. gr.				
Series A						
10	Acid arsenate No. 1	2.4	1 to 30	24	4.58	Black, heavy
11	Acid arsenate No. 2	2.4	1 to 30	24	4.62	Black, heavy
25	Acid arsenate No. 3	2.4	1 to 30	24	4.54	Black, heavy
55	Acid arsenate No. 4	2.4	1 to 30	24	4.40	Black, heavy
119	Acid arsenate No. 6	2.4	1 to 30	24	4.56	Black, heavy
Series B						
7	Acid arsenate No. 1	2.4	1 to 10	2	2.33	Gray, floccu- lent
2	Acid arsenate No. 1	2.4	1 to 10	24	4.04	Black, heavy
24	Acid arsenate No. 3	2.4	1 to 30	2	2.75	Brown, floc- culent
25	Acid arsenate No. 3	2.4	1 to 30	24	4.54	Black, heavy
26	Acid arsenate No. 3	2.4	1 to 30	48	4.64	Black, heavy
Series C						
2	Acid arsenate No. 1	2.4	1 to 10	24	4.04	Black, heavy
10	Acid arsenate No. 1	2.4	1 to 30	24	4.58	Black, heavy
43	Acid arsenate No. 4	2.4	1 to 10	24	4.14	Black, heavy
55	Acid arsenate No. 4	2.4	1 to 30	24	4.40	Black, heavy
Series D						
49	Basic arsenate No. 1	2.4	1 to 30	24	2.36	Gray, floc- culent
94	Basic arsenate No. 3	2.4	1 to 30	24	2.48	Gray, floc- culent

These data clearly lead to the following conclusions: (a) When acid arsenate of lead is mixed with lime-sulfur solutions, and the mixture allowed to stand for 24 hours or more (Series A and B), a definite chemical change takes place which produces a definite increase in weight and change in properties of the solid residue in the mixture. This is in accord with the findings of Ruth (2), Robinson and Tartar (3), and Cook and McIndoo (4). (b) This change takes place rather slowly. After 2 hours there is but slight increase in weight or discoloration of the residue, but at the end of 24 hours the reaction is practically complete (Series B). This is in accord with the results obtained by Cook and McIndoo (4), who found some change in the chemical composition of lime-sulfur solution to which lead arsenate had been added during the first hour with an increase in this change up to 19 hours, but no further change thereafter.

(c) The reaction appears to be influenced slightly by the concentration of the lime-sulfur solution (Series C), tending to go somewhat further in the more dilute solutions, but the differences observed as due to this cause are so slight as to make them negligible from the practical standpoint, and the results reported below may safely be considered as applicable to all mixtures of acid arsenate of lead and lime-sulfur in varying strengths. (d) Basic arsenates of lead are not changed to any appreciable extent by mixing with lime-sulfur solutions, even if the mixture be allowed to stand 24 hours or more. This fact has been previously noted by Robinson and Tartar (3) and Cook and McIndoo (4). Unfortunately, however, basic arsenates have been found to have so much less insecticidal properties than do the acid arsenates or other arsenicals that they have very little use in spray practice. Hence, the "compatibility" of the basic arsenates of lead with lime-sulfur solutions is of little practical importance.

In order to obtain some further evidence as to the constancy, or uniformity, of the chemical change which takes place when the acid arsenate is mixed with lime-sulfur solutions, several of the residues were partially analyzed to determine the percentage of lead sulfide which they contained. This was done by treating a weighed portion of the dried residue successively with dilute nitric acid and carbon bisulfide to dissolve out of it any unchanged lead arsenate, calcium arsenate and other calcium salts, and precipitated sulfur, respectively. The undissolved lead sulfide was then filtered off, washed, dried to constant weight, and weighed. The results obtained are shown in Table 2.

TABLE 2.—SHOWING PROPORTION OF ACID ARSENATE OF LEAD WHICH IS CONVERTED INTO LEAD SULFIDE BY THE ACTION OF LIME-SULFUR SOLUTION.

TEST NO.	WEIGHT OF ACID ARSE-NATE	WEIGHT OF RESI-DUE	LEAD SULFIDE IN RESIDUE	PROPORTION OF ARSEN-NATE USED CHANGED TO LEAD SULFIDE
	<i>Grams</i>	<i>Grams</i>	<i>Per cent</i>	<i>Per cent</i>
10	2.4	4.58	20.80	57.9
11	2.4	4.62	21.39	59.7
12	2.4	4.42	20.46	54.9
18	2.4	4.66	20.00	56.3
19	2.4	4.63	20.05	56.3

These results show a remarkable uniformity in the percentage of lead sulfide found in these residues, when the limitations of the method of analysis which are available for use on such mixtures are considered. Furthermore, Ruth (2) reports that he found a uniform

content of 22.5 per cent of free sulfur in similar residues which he obtained by mixing acid arsenate of lead with lime-sulfur solutions.

These observations would seem to establish clearly the fact that the reaction between acid arsenate of lead and lime-sulfur is a definite one, which results in a definite change of a certain proportion of the lead arsenate into lead sulfide.

As to the nature of the other compounds which are formed during this change, Bradley and Tartar (5) state that they found the solid residue to contain lead arsenate, calcium arsenate, lead sulfide, and free sulfur and that the weight of the residue in the mixture increases by continued standing in the open air, due to continued deposition of free sulfur, as is the case of lime-sulfur alone if exposed to the action of the carbon dioxide in the air. Cook and McIndoo (4) found lead sulfide in their residues, but only a little calcium arsenate. They assume that "probably" calcium sulf-arsenate is the principal product resulting from the action of the arsenious acid group, which is liberated by the decomposition of the lead arsenate, upon the lime-sulfur solution; but give no experimental evidence in support of this assumption. They state that 5.2 per cent of the arsenic oxide of the acid lead arsenate used in their experiments were rendered soluble by the reaction between it and lime-sulfur. We have no evidence in support of, or opposed to, the assumption of Cook and McIndoo with reference to the presence in the residue of calcium sulf-arsenate, but we did find proportions of soluble arsenic in some of our filtrates similar to those reported by them.

In fact, there is nearly always some soluble arsenic in the mixture as soon as the reaction begins to take place. Also, the arsenate of lime which the mixture now contains is likely to be more or less decomposed by the carbonic acid of the air, either while in the spray tank or after spraying onto foliage, so as to liberate soluble arsenic in the spray solution, with consequent danger of burning foliage. Further, there is some evidence to show that precipitated sulfur, such as is present in this mixture, may produce burning of the foliage. Hence, the mixture, after the changes take place, not only has probably considerably less fungicidal value, because its sulfur is converted into forms which certainly are not as efficient as is lime-sulfur in killing effects, but also is more dangerous to use on orchard foliage.

MIXTURES OF ACID LEAD ARSENATE WITH LIME-SULFUR SOLUTIONS WITH ADDED LIME

Our further experiments were directed toward the finding of an effective and economical preventive for the undesirable reaction between acid arsenate of lead and lime-sulfur solutions.

We first investigated the effect of adding hydrated lime to the mixture. In some cases, the lime was added to the lime-sulfur solution before adding the lead arsenate to the latter. In others, the lime was weighed out and mixed with the lead arsenate before adding the latter to the lime-sulfur solution. As would be anticipated from the fact that the reaction between the lead arsenate and lime sulfur begins very slowly, it was found that it made no difference in the effect of the added lime on the reaction whether it was added to the one or the other material before mixing them. Table 3 shows the effect of adding hydrated lime to the mixture in the proportions of 10, 5, 3, 2, and 1 pounds of lime, respectively, to 100 gallons of mixture.

TABLE 3.—SHOWING THE EFFECT OF ADDED HYDRATE OF LIME UPON THE WEIGHT AND CHARACTER OF RESIDUE WHEN ACID LEAD ARSENATE AND LIME-SULFUR SOLUTIONS ARE MIXED.

TEST NO.	ACID LEAD ARSENATE USED	LIME-SULFUR USED	HYDRATE OF LIME USED	TIME OF STANDING	WEIGHT OF RESIDUE		CHARACTER OF RESIDUE
					Pound	Corrected for lime used	
80	<i>Grams</i> 2.4	<i>Grams</i> 1:30	<i>Grams</i> 5.50	<i>Hours</i> 24	<i>Grams</i> 7.88	<i>Grams</i> 2.38	Gray, flocculent
81	2.4	1:30	2.75	24	5.18	2.43	Brown, flocculent
82	2.4	1:30	1.65	24	4.20	2.55	Dark, flocculent
117	2.4	1:30	1.10	24	3.98	2.88	Dark, flocculent
118	2.4	1:30	0.55	24	3.89	3.34	Black, heavy

These results show that lime, if used in large enough quantities, will effectively prevent the reaction between acid lead arsenate and lime-sulfur. In tests Nos. 80 and 81 the solid material in the mixture was only slightly discolored even after standing 24 hours and the weight of the residue, after deducting the weight of lime added, was not appreciably increased. But when amounts of lime corresponding

to 3 pounds per 100 gallons of mixture (Test No. 82) or less were added, the residue was darkened in color and increased in weight, thus showing that the reaction between the acid lead arsenate and lime-sulfur had taken place, the extent of the change increasing as the proportion of lime used was decreased.

To prevent effectively the undesirable change, it is necessary to use the lime in the proportions of at least 5 pounds per 100 gallons of spray mixture, and this very materially increases the solid matter in the mixture as well as the cost of its preparation. For this reason, we determined to test various other materials which, from their chemical nature, might possibly serve as protective agents against the undesirable change without materially increasing the insoluble solid matter in the mixture or increasing its cost to a prohibitive extent.

MIXTURES OF ACID LEAD ARSENATE WITH LIME-SULFUR SOLUTIONS WITH ADDED ORGANIC COLLOIDAL MATERIALS

We first investigated the effect of adding to the mixture varying amounts of various organic colloidal substances which, from their chemical nature, might possibly serve to protect against, or retard, the chemical change between acid arsenate of lead and lime-sulfur solutions. These different organic colloidal substances were first used without any added lime in order to ascertain whether they possessed any specific protective effect of their own. Later, each of them was used with varying amounts of added hydrate of lime, in order to determine whether the mixture of the organic colloid with lime would exert a greater protective effect against the undesirable reaction than did either the colloid or the lime when used alone. These experiments were undertaken in several successive series, with the conditions varied as suggested by progressing experience and results obtained. But, for convenience, typical results from each of the several series are brought together in Table 4 to show the effect of adding these different organic substances to the mixture under different conditions.

These results clearly showed that casein is an efficient protective agent against the reaction between acid lead arsenate and lime-sulfur. When used in proportions as small as 2.8 ounces of the dry casein to 100 gallons of spray mixture (Test No. 69), it gave almost perfect protection against the undesired change; while with 4 ounces per 100 gallons (Test No. 67) there was no significant change in the mixture

TABLE 4.—SHOWING THE EFFECT OF ADDING VARIOUS COLLOIDAL SUBSTANCES, WITH AND WITHOUT ADDED LIME, UPON THE WEIGHT AND CHARACTER OF RESIDUE WHEN ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS ARE MIXED.

Test No.	ORGANIC SUBSTANCE USED		HYDRATE OF LIME USED	LEAD ARSENATE USED	LIME-SULFUR USED	WEIGHT OF RESIDUE		CHARACTER OF RESIDUE
	Kind	Amount				Found	Corrected for lime used	
3	Glue	<i>Grams</i> 0.044	—	<i>Grams</i> 2.40	1.10	<i>Grams</i> 3.96	<i>Grams</i> 3.96	Black, heavy
12	Glue	0.22	—	2.40	1.30	4.50	4.50	Black, heavy
14	Glue	0.44	—	2.40	1.30	4.46	4.46	Black, heavy
31	Glue	0.66	—	2.40	1.30	4.59	4.59	Black, heavy
96	Glue	0.55	1.65	2.40	1.30	3.63	1.98*	White, flocculent
114	Glue	0.55	0.55	2.40	1.30	2.72	2.17*	Brown, flocculent
53	Gelatine	1.12	—	2.40	1.30	4.62	4.62	Black, heavy
97	Gelatine	0.55	1.65	2.40	1.30	3.92	2.27*	White, flocculent
115	Gelatine	0.55	0.55	2.40	1.30	2.49	1.94*	White, flocculent
65	Egg albumin	0.37	—	2.40	1.30	4.46	4.46	Black, heavy
104	Egg albumin	0.55	—	2.40	1.30	4.52	4.52	Black, heavy
103	Egg albumin	0.37	0.55	2.40	1.30	2.65	2.10*	Brown, flocculent
102	Egg albumin	0.55	0.55	2.40	1.30	2.73	2.18*	Brown, flocculent
101	Egg albumin	0.55	1.12	2.40	1.30	3.05	1.95*	White, flocculent
128	Saponin	0.55	—	2.40	1.30	4.46	4.46	Black, heavy
129	Saponin	0.55	1.10	2.40	1.30	2.82	1.72*	White, flocculent
16	Casein	0.55	—	2.40	1.30	2.72	2.72**	White, flocculent
22	Casein	0.37	—	2.40	1.30	2.62	2.62**	White, flocculent
27	Casein	0.25	—	2.40	1.30	2.57	2.57**	White, flocculent
67	Casein	0.15	—	2.40	1.30	2.66	2.58**	White, flocculent
69	Casein	0.10	—	2.40	1.30	2.43	2.43**	Brown, flocculent

* A part of the hydrate of lime dissolved in the lime-sulfur solution used, hence weight of residue is less than total weight of lead arsenate and hydrate of lime used.

**Impossible to wash residue completely free from casein, increase in weight due to contamination with casein.

even after standing as long as 48 hours in some test cases. No experiments were conducted using lime in addition to the pure casein, as the latter was found to be perfectly effective without the addition of lime. Apparently, Regan of Montana has observed this same effect, since he states (6) that "calcium caseinate entirely prevents the reaction between lead arsenate and lime-sulfur," altho he does not present any experimental data in support of his statement.

On the other hand, none of the other organic colloidal materials which we tried, including glue, gelatine, egg albumin, and saponin, were at all effective in preventing the reaction when used alone, even in amounts as large as 1 or 2 pounds per 100 gallons of spray mixture. Mixtures of these with hydrate of lime gave more effective protection than did the same amount of lime when used alone; but in no case did the additional effect secured from the organic colloid seem to be sufficient to justify any hope of practical utilization, especially in view of the very successful applications of casein-containing materials which are reported below.

MIXTURES OF ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS WITH VARIOUS CASEIN-CONTAINING MATERIALS

Having discovered that casein is an effective protective colloid to use for preventing the reaction between acid arsenate of lead and lime-sulfur solutions, our next experiments were directed toward the finding of a cheap and convenient form of casein to use for this purpose. We first tried certain commercial preparations containing casein which are sold on the market under different trade names for use as a "spreader" in spray mixtures. These proved to be perfectly effective in preventing the reaction. We then tried buttermilk, whole milk, and skim-milk in varying proportions. In each case, except with milk which had been freshly drawn from the udder, there was enough acid in these milk products to cause a decomposition of some of the lime-sulfur, setting free considerable of the sulfur; also there was a marked tendency of the casein in the several milk products to curdle and form undesirable lumpy masses in the mixture. The latter difficulty was experienced even with fresh, sweet, whole milk.

We next tried the same milk products with added hydrate of lime, with altogether satisfactory results in every case. Having thus demonstrated that the casein of common milk products which have been made alkaline with lime is an effective protective agent against

TABLE 5.—SHOWING THE EFFECT OF VARIOUS CASEIN-CONTAINING MATERIALS, WITH AND WITHOUT ADDED LIME, UPON THE WEIGHT AND CHARACTER OF RESIDUE WHEN ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS ARE MIXED.

TEST No.	CASEIN-CONTAINING MATERIAL USED		HYDRATE OF LIME USED	LEAD ARSENATE USED	WEIGHT OF RESIDUE		CHARACTER OF RESIDUE
	Kind	Amount			Found	Corrected for lime used	
		<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	
5	Dried buttermilk	1.50	—	2.40	4.56	4.56	Black, heavy
27	Casein No. 3	0.25	—	2.40	2.50	—	White, flocculent
29	Casein No. 2	0.37	—	2.40	2.56	—	White, flocculent
66	Casein No. 2	0.25	—	2.40	2.72	—	Brown, flocculent
67	Casein No. 2	0.15	—	2.40	2.63	—	Brown, slightly heavy
69	Casein No. 2	0.10	—	2.40	2.43	—	Brown, flocculent
33	"Kayso"	1.10	—	2.40	2.70	—	White, flocculent
70	"Kayso"	0.55	—	2.40	2.64	—	White, flocculent
71	"Kayso"	0.37	—	2.40	2.62	—	Light brown, flocculent
72	"Kayso"	0.25	—	2.40	2.55	—	Light brown, flocculent
73	Whole milk	10.00	5.7	2.40	7.48	1.78	White, flocculent
74	Whole milk	10.00	2.8	2.40	4.60	1.80	White, flocculent
75	Whole milk	5.00	2.8	2.40	4.42	1.62	White, flocculent
84	None (check)	—	—	2.40	4.16	4.16	Black, heavy
85	Skim-milk	5.00	5.7	2.40	7.42	1.72	White, flocculent
86	Skim-milk	5.00	2.8	2.40	4.53	1.73	White, flocculent
87	Skim-milk	5.00	1.7	2.40	3.42	1.73	White, flocculent

TABLE 5.—CONCLUDED.

TEST No.	CASEIN-CONTAINING MATERIAL USED		HYDRATE OF LIME USED	LEAD ARSE-NATE USED	WEIGHT OF RESIDUE		CHARACTER OF RESIDUE
	Kind	Amount			Found	Corrected for lime used	
		<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	
88	Skim-milk	5.00	1.1	2.40	2.85	1.74	White, flocculent
89	Skim-milk	5.00	0.5	2.40	2.82	2.32	Brown, flocculent
90	Skim-milk	2.50	2.8	2.40	4.51	1.71	White, flocculent
106	Skim-milk	2.50	1.7	2.40	3.36	1.66	White, flocculent
107	Skim-milk	2.50	1.1	2.40	2.89	1.79	Brown, flocculent
108	Skim-milk	2.50	0.57	2.40	2.54	1.97	Brown, flocculent
109	Skim-milk	1.25	2.8	2.40	4.36	1.56	White, flocculent
110	Skim-milk	1.25	1.7	2.40	3.33	1.63	White, flocculent
111	Skim-milk	1.25	1.1	2.40	2.85	1.73	Brown, flocculent
112	Skim-milk	1.25	0.57	2.40	2.52	1.95	Brown, flocculent

the undesirable reaction, we conducted a considerable series of trials using varying quantities of skim-milk and lime in the mixture to determine the minimum amounts of these materials which might be effectively and economically used in preparing spray mixtures of this kind. Numerous determinations were made. To illustrate the results obtained, certain typical results are presented in Table 5.

These results show clearly that very small proportions of casein with added lime are fully effective in preventing the reaction between acid lead arsenate and lime-sulfur solutions. In Test No. 112, as little as 1 quart of skim-milk and 1 pound of hydrated lime per 100 gallons of mixture were used, and the residue was only slightly discolored and only very slightly increased in weight after making

allowance for the added lime and the proportion of the latter which dissolves in the lime-sulfur solution.

As a further confirmation of the efficiency of alkaline casein-containing materials in preventing the undesirable reaction and so reducing the possibility of foliage injury from the mixed spray when so treated, the quantity of soluble arsenic in the mixture was determined in the case of a considerable number of the tests reported above. The results of these determinations are shown in Table 6.

TABLE 6.—SHOWING THE EFFECT OF THE ADDITION OF SKIM-MILK AND LIME UPON THE QUANTITY OF SOLUBLE ARSENIC PRODUCED WHEN ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS ARE MIXED.

TEST No.	SKIM-MILK USED	HYDRATE OF LIME USED	LEAD ARSENATE USED	WEIGHT OF RESIDUE		SOLUBLE As_2O_5 FOUND	
				Found	Corrected for lime used	Weight	Percentage of total
	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Per cent</i>
95	None (check)	—	2.40	4.08	4.08	0.0216	2.56
85	5.00	5.7	2.40	7.42	1.72	0.0056	0.65
86	5.00	2.8	2.40	4.52	1.72	0.0041	0.48
87	5.00	1.7	2.40	3.43	1.73	0.0042	0.49
88	5.00	1.1	2.40	2.85	1.74	0.0046	0.53
91	5.00	2.8	3.60	5.59	2.79	0.0056	0.43

These results clearly show that the proportion of the arsenic in the lead arsenate which is rendered soluble by the action of lime-sulfur on it in the presence of skim-milk and added lime is practically nil, as the quantities of soluble As_2O_5 found in all of the mixtures to which the milk and lime were added (Tests Nos. 85 to 91) are as low as are generally found when lead arsenate is suspended in water alone and are within the limits of tolerance of water-soluble arsenic in lead arsenate allowed by official regulations (4).

Hence, it is clear that skim-milk and lime, used in economical proportions, are an effective preventive of the undesirable reaction between acid arsenate of lead and lime-sulfur solutions. Commercial preparations of casein, such as "Kayso" and "calcium caseinate," are equally effective in preventing the reaction. The effects of these materials in preventing this undesirable reaction are in addition to their so-called "spreader," or adhesive effects, for which they have commonly been used in spray mixtures.

The minimum amounts of these casein-containing materials which may be used in common orchard practice will have to be determined

by field experiments. But from the laboratory results reported above, it appears probable that as little as 1 gallon of skim-milk, to which has been added 1 pound of hydrate of lime, when added to 100 gallons of spray mixture will certainly be a safe quantity to use. Even smaller proportions than these proved fully effective in laboratory tests. If commercial casein-containing materials are used, as little as 0.5 pound of the dry material to 100 gallons of spray mixture will undoubtedly be sufficient to insure the protective effect, altho somewhat larger proportions than this are generally recommended for the purpose of securing the "spreader" effect.

Whether the use of these casein-containing materials in the combination lead-arsenate-lime-sulfur spray mixture will in any degree reduce the insecticidal and fungicidal properties of the principal ingredients of the mixture, can only be determined by orchard experiments. But the rather common use of such materials as "spreaders," without any apparent diminution in the killing efficiency of the materials to which they are added, argues against the probability of such an effect.

Whether the addition of these materials to the combined lead-arsenate-lime-sulfur spray mixtures will completely remove the possibility of foliage injury from this spray can only be determined by orchard experiments. However, it seems probable that this danger will be very greatly reduced, if not wholly eliminated, by the prevention of the reaction between the principal ingredients of the mixture in this way.

INFLUENCE OF TOBACCO DUST UPON THE REACTION BETWEEN ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS

After the investigations reported above had been completed, an investigation of the possibility of adding nicotine-containing materials to the combined lead-arsenate-lime-sulfur spray, in order to increase the insecticidal properties of the mixture, was undertaken by the entomologists of this Station. The writers were asked to investigate the effect upon the volatility of the nicotine contained in this triple mixture by the methods discussed in Bulletin No. 501 of this Station, and the possible effect of the presence of the nicotine-containing materials upon the reaction between acid lead arsenate and lime-sulfur solutions as discussed in this bulletin. The results of the investigations of the first phase of the problem will be reserved for

publication elsewhere, but the latter phase may properly be discussed here.

The first preparation which was studied was made by adding tobacco dust to a home-boiled, concentrated lime-sulfur solution to which was then added lead arsenate as usual in the preparation of mixed sprays. Later, tests were made also with "Blackleaf Forty," with and without added lime. The results of the tests are shown in Table 7.

TABLE 7.—SHOWING THE EFFECT OF ADDED NICOTINE-CARRYING MATERIALS UPON THE REACTION BETWEEN ACID ARSENATE OF LEAD AND LIME-SULFUR SOLUTIONS WHEN MIXED.

TEST No.	SUBSTANCE USED		HYDRATE OF LIME USED	LEAD ARSENATE USED	WEIGHT OF RESIDUE		CHARACTER OF RESIDUE
	Kind	Amount			Found	Corrected for lime used	
		<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	
7	None (check)	—	—	2.40	4.56	—	Black, heavy
8	Tobacco dust	—	—	2.40	2.58	—	Brown, flocculent
3	Blackleaf Forty	1.00	—	2.40	4.69	—	Black, heavy
4	Blackleaf Forty	1.00	1.10	2.40	2.82	1.72	Brown, flocculent
6	None	—	1.10	2.40	2.89	1.79	White, flocculent

These results show that tobacco dust is an effective agent for preventing the undesirable reaction between acid lead arsenate and lime-sulfur. Hence when this triple combination spray is made, it is not necessary to add casein-containing materials or lime to stabilize the mixture. Blackleaf Forty alone is an acid preparation and increases rather than tends to prevent this reaction, but when used with sufficient amount of lime to make the mixture alkaline there is no increase in the amount of residue formed.

Whether these triple combination sprays will be useful in orchard practice, will have to be studied from that standpoint; but there is no doubt that they are chemically "compatible" and, hence, worthy of further study.

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