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A Chemical Investigation of Some Standard Spray Mixtures

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THE TUTTLE, MOREHOUSE & TAYLOR COMPANY

A Chemical Investigation of Some Standard Spray Mixtures

R. E. Andrew* and Philip Garman

Modern spray practices have become complicated procedures. The necessity of attaining maximum efficiency with a minimum of labor has led in the case of fruit growing to the use of high powered outfits which apply spray mixtures at a rapid rate and to the combination of sprays in order to avoid separate applications. In the combination of sprays there has been much uncertainty of results and failure to explain certain phenomena which have not been well understood, at least from a chemical standpoint. For instance, we know that the ingredients of a certain spray formula mixed in a certain order give a definitely colored mixture, whereas an entirely different order of combination may give a different appearance. What goes on under these conditions as regards the ingredients themselves has only been conjectured by the entomologist, and it is in an attempt to throw some further light on what happens when various insecticides and fungicides are put together that the present work was undertaken.

Historical Summary

Probably the earliest studies of spray mixtures from a chemical standpoint were made by Bradley[2] and Bradley and Tartar[3], who found that there was a distinct chemical reaction between lime-sulphur and lead arsenate resulting in the formation of soluble arsenic. The latter undesirable condition was found to be greatly helped by the addition of lime to the mixture. Robinson[15], following this clue, described the beneficial action of lime upon the standard spray mixture and came to the conclusion that lime prevents the reaction between lime-sulphur and lead arsenate and does not lower the polysulphide sulphur in the lime-sulphur to a harmful extent. Ruth[17] made an extensive investigation of spray mixtures from a chemical standpoint, reaching the general conclusion that when these two components are mixed, a thioarsenate of some kind is formed which holds it insoluble in lime-sulphur solution, and that thiosulphates and sulphites are increased, possibly accounting for the improved fungicidal properties of the mixture. More recently Thatcher and Streeter[22] have investigated the addition of casein, gelatin,

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nicotine and other preparations to the combined lead arsenate, lime-sulphur sprays, finding that casein-lime and nicotine exert a beneficial action upon the spray mixture. Still more recently, with the use of somewhat different methods, Goodwin and Martin[10] reached somewhat different conclusions, stating that casein and gelatin do not always protect lead arsenate from harmful reactions with lime-sulphur and in fact give an increased amount of soluble arsenic, contrary to the conclusions of Thatcher and Streeter. They found furthermore that lime decreased the amount of sulphur in solution in the spray mixture, thereby reducing its fungicidal value, but that lime, if carbonated, exerted little or no effect upon the mixture.

Plan of Study and Methods Employed

All of the work thus far described was done with double or triple combinations of spray materials but the possible effect upon the composition of the mixture due to the sequence in which the separate ingredients were added was not considered. The work herein reported began with a study of the effect of different orders of mixing upon the composition of a mixture containing four ingredients, but as the work progressed it seemed advisable to extend its scope to include all possible double and triple combinations as well.

In preparing the experimental mixtures the conditions obtaining in practical spraying operations were followed as closely as possible. Thus, the materials used were market products of standard grades, and the proportions in which they were mixed, and the method of mixing, are fairly representative of field practice. It will be seen that the period of agitation was one hour, which is about the maximum time required to apply a two hundred gallon tank of spray mixture, using one gun or two rods. With many outfits much less time than this would be required so that this agitation period is probably nearer the maximum than the minimum for the average spray rig.

FORMULA

The complete formula used and its equivalent in actual spraying practice are as follows:

	Experimental Mixture	Corresponding Field Practice
(1) Arsenate of lead (acid)	2.4 grams	4.0 pounds
(2) Nicotine sulphate	0.6 cc	0.96 pint
(3) Casein-lime	0.55 grams	0.917 pounds
(4) Lime-sulphur	14.5 cc	2.6 gallons
(5) Water (distilled), to make	500.0 cc	100.0 gallons

PREPARATION OF EXPERIMENTAL MIXTURES

In mixing the ingredients, whatever the number chosen, the final volume was brought to 500 cc and the manipulation was uniformly as follows:

Place about 485 cc of water in a 500 cc graduated shaking flask. Add the ingredients separately, in the amounts indicated by the formula, shaking by hand for two minutes after each addition. Stopper the flask securely, place in a shaking machine of the revolving type and agitate the mixture for one hour. Remove the flask from the shaking device and allow the mixture to stand for one hour. Filter on a 9 cm filter paper using a Buchner funnel with gentle suction, transferring as much of the insoluble material as possible to the filter. Do not rinse the flask or wash the residue upon the filter. Transfer the yellow filtrate (A), to a suitable flask, stopper, and hold for analysis.

Return the filter with the insoluble residue to the original graduated shaking flask and wash into the flask also any of the insoluble residue which may have adhered to the funnel. Fill the flask to the 500 cc mark, stopper securely, place in the shaking machine and agitate the contents for one hour. Remove the flask from the shaking device and allow to stand for one hour, after which filter through a large filter. Do not wash the residue. Reserve the filtrate, solution (B), for analysis.

EXAMINATION OF MIXTURES

The various experimental mixtures were examined with reference to certain physical characteristics and to chemical composition, the latter being confined to determinations of total sulphur in the lime-sulphur solution (filtrate A), and of total arsenic, as arsenic pentoxide (As_2O_5), both in filtrate A and filtrate B. The results obtained for total sulphur are of interest as an index to the extent of chemical change which has taken place in the mixture so far, at least, as the sulphur originally present has been converted into insoluble forms. Foliage injury, in part, results from excessive amounts of soluble arsenic in the lime-sulphur solution; and it seems not improbable that the insoluble arsenic-containing residue which is deposited upon foliage in the process of spraying might become, upon exposure to weather conditions, a potential source of further injury. For this reason the water-soluble arsenic in the insoluble residue was determined.

METHODS OF ANALYSIS

The determination of the small amounts of soluble arsenic involved in preparations made on the scale of these laboratory mixtures presented some difficulty. After some preliminary trials, the method used by Bradley[2] and by others whereby sulphur is oxidized by means of hydrogen peroxide and arsenic finally titrated with dilute iodine solution appeared to be promising. The results, however, were not satisfactory and the method is objectionable chiefly for the following reasons: it requires large quantities of a relatively expensive reagent (hydrogen peroxide); the evaporation of a large volume of liquid is time consuming; the filtration of the large amount of sediment which forms during the evaporation, and the necessary washing, introduce potential errors; and finally, the iodine titration does not give a sharply defined end point.

About this time Cox[5] published a critical review of certain methods for the determination of small quantities of arsenic, citing particularly the methods of Bang and Ramberg, his experience favoring the last named. As pointed out by Cox, neither method involves any new principle, but, on trial, the Ramberg method was found to be adaptable to our problem. Briefly, the procedure consists in oxidizing the sulphur and destroying organic matter by digestion with nitric and sulphuric acids, removing the excess of nitric acid by means of ammonium oxalate, distilling with hydrochloric acid and titrating the arsenic with potassium bromate solution, using methyl orange (1 : 5000) as as indicator.

The digestion was conducted in a long-neck Kjeldahl flask made to fit a condensing tube with a ground glass joint; thus the digestion and distillation were both made without a transfer of material. Arsenic-free reagents, tested by means of suitable blanks, were used throughout. The standard potassium bromate solution was prepared of such strength that 1 cc was equivalent to 0.0005 gm. of arsenic pentoxide (As_2O_5).

The procedure in detail as used by us is as follows:

Arsenic in lime-sulphur solution (Solution A). Transfer 100 cc of the solution to the digestion-distillation flask, add a few glass beads, 50 cc of concentrated nitric acid and evaporate over a low flame until the volume is reduced to about 25 cc. Cool, add 25 cc of concentrated sulphuric acid and heat until fumes of sulphuric acid appear. From a suitable dropping device add 50 cc of concentrated nitric acid dropwise, meanwhile boiling the solution very gently. Continue the boiling until sulphuric acid fumes appear. Cool, add 25 cc of saturated ammonium oxalate solution and again boil until fumes of sulphuric acid are noticed. Cool, rinse the neck of the flask with 20 cc of water and then add 2 grams of ferrous sulphate, 50 cc of concentrated hydrochloric acid and 0.1 gram of potassium bromide. (If any yellow or brown color appears at this point nitrogen acids are present and the experiment must be rejected.) Connect the flask with the condensing tube, adjust a receiving flask containing 150 cc of water, and allow the condenser to dip about 1 cm. below the surface of the liquid therein. Distill at such a rate that 20 to 25 cc of distillate are obtained in about 10 minutes. Heat the distillate to 50° C., add three drops of methyl orange and titrate at once with standard potassium bromate solution, adding this reagent very slowly as the end point is approached. The end point is reached when the red color of the indicator is discharged. Each cc of potassium bromate used corresponds to 0.0005 gram of As_2O_5.

Arsenic in Solution B. Transfer 50 cc of the solution to the digestion-distillation flask, add 50 cc of concentrated nitric acid and evaporate over a low flame until the volume is reduced to about 25 cc. Cool, add 25 cc of concentrated sulphuric acid and boil until sulphuric acid fumes appear.

Cool, add 10 cc of concentrated nitric acid and again heat until fumes of sulphuric acid are noted. Cool, add 25 cc of saturated ammonium oxalate solution and from this point proceed as directed in the previous paragraph.

Total sulphur in Solution A. Total sulphur was determined substantially according to the official procedure[1] except that oxidation of sulphur was effected by means of hydrogen peroxide in alkaline solution as allowed by a former optional method.[13]

Transfer 10 cc of solution A to a 250 cc beaker containing 10 cc of a 10 per cent solution of sodium hydroxide, 50 cc of water and 50 cc of hydrogen peroxide. Cover the beaker with a watch glass and heat for one hour on a steam bath. Cool, acidify with dilute hydrochloric acid (1 to 1), and precipitate the sulphur as barium sulphate. Calculate the percentage of sulphur from the weight of barium sulphate, using the factor 0.1374.

PRELIMINARY EXPERIMENTS

The adaptability of the method for the determination of arsenic as described may be illustrated by the following experiments. Blanks on the reagents, in the amounts used in the method, showed titerable substances equivalent to 0.3 cc of standard potassium bromate and this correction was uniformly made in all determinations.

	Arsenic, as As_2O_5			
Material	Present gm.	Added gm.	Total gm.	Recovered gm.
100 cc water+1 gm. sugar		0.01160	0.01160	0.01160
100 cc water+1 gm. sugar		0.01160	0.01160	0.01160
Lime-sulphur-Lead arsenate	0.00613	0.01160	0.01773	0.01775
		0.01160	0.01773	0.01773

INTERPRETATION OF RESULTS

In the analytical data herein reported total sulphur is expressed in terms of grams per 100 cc of the lime-sulphur solution. Arsenic is expressed in percentages of As_2O_5 based on the amount of lead arsenate, 2.4 grams, present in the mixture.

In the tables also abbreviations are necessary and the following are used: L.A. = Lead arsenate; L.S. = Lime-sulphur; N. S. = Nicotine sulphate; C.L. = Casein-Lime; L. = Lime; Blk. = Black; G. = Grey; G.B. = Greyish-black.

TABLE 1. EFFECT OF COMBINING LIME-SULPHUR WITH LEAD ARSENATE

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
A-1	L. A.	....	....	....	....	....	....	....	0.05	0.05	....
A-2	L. S.	....	....	....	....	....	....	....	....	....	.923
B-1	L. A.	L. S.	....	....	....	....	....	0.98	5.48	6.46	.907
B-2	L. S.	L. A.	....	....	....	....	....	1.49	5.72	7.21	.890

TABLE 2. EFFECT OF ADDING LIME-SULPHUR TO LEAD ARSENATE AND NICOTINE SULPHATE ALREADY IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	Order of Mixing 1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
B-3	L. A.	N. S.	....	....	....	....	....	....	0.06	0.06	....
B-4	N. S.	L. A.	....	....	....	....	....	....	0.03	0.03	....
C-2	L. A.	N. S.	L. S.	....	Light	G. B.	Clear	1.03	4.20	5.23	.890
C-1	L. A.	L. S.	N. S.	....	Light	Blk.	Clear	1.74	0.52	2.26	.604
C-3	L. S.	L. A.	N. S.	....	Light	Blk.	Clear	1.28	0.30	1.58	.611
C-4	L. S.	N. S.	L. A.	....	Light	G. B.	Clear	1.77	4.63	6.40	.820
C-5	N. S.	L. S.	L. A.	....	Light	G. B.	Clear	1.06	4.40	5.46	.884
C-6	N. S.	L. A.	L. S.	....	Light	G. B.	Clear	1.06	3.78	4.84	.873

TABLE 3. EFFECT OF ADDING LIME-SULPHUR TO LEAD ARSENATE, NICOTINE SULPHATE AND CASEIN-LIME ALREADY IN COMBINATION, AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	Order of Mixing				Physical Characteristics			Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used			Total Sulphur In Lime-Sulphur solution gm/100 cc
	1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	
C-14	L. A.	N. S.	C. L.	....	....	....	Turbid	0.20	0.48	0.68	....
1	L. A.	N. S.	C. L.	L. S.	Light	G. B.	Clear	0.40	2.55	2.95	.930
12	L. S.	L. A.	N. S.	C. L.	Light	Blk.	Clear	0.90	0.41	1.31	.678
C-13	L. A.	C. L.	N. S.	....	....	....	Turbid	0.30	0.60	0.90	....
2	L. A.	C. L.	N. S.	L. S.	Dark	G. B.	Clear	0.47	2.83	3.30	.925
9	L. S.	L. A.	C. L.	N. S.	Light	G. B.	Turbid	0.47	0.98	1.45	.907
C-15	C. L.	L. A.	N. S.	....	....	....	Turbid	0.31	0.56	0.87	....
8	C. L.	L. A.	N. S.	L. S.	Dark	G. B.	Clear	0.60	2.65	3.25	.916
15	L. S.	C. L.	L. A.	N. S.	Dark	G. B.	Turbid	0.55	1.35	1.90	.912
C-16	N. S.	L. A.	C. L.	....	....	....	Turbid	0.23	0.40	0.63	....
7	N. S.	L. A.	C. L.	L. S.	Light	G. B.	Clear	0.39	2.55	2.94	.919
16	L. S.	N. S.	L. A.	C. L.	Light	Dark	Clear	0.65	2.40	3.05	.838
C-17	N. S.	C. L.	L. A.	....	....	....	Turbid	0.25	0.94	1.19	....
17	N. S.	C. L.	L. A.	L. S.	Light	G. B.	Clear	0.41	2.56	2.97	.906
23	L. S.	N. S.	C. L.	L. A.	Light	G. B.	Turbid	0.39	1.40	1.79	.907
C-18	C. L.	N. S.	L. A.	....	....	....	Clear	0.30	1.20	1.50	....
14	C. L.	N. S.	L. A.	L. S.	Dark	G. B.	Turbid	0.33	2.77	3.10	.920
21	L. S.	C. L.	N. S.	L. A.	Dark	G. B.	Clear	0.48	1.71	2.19	.916

Discussion

Effect of Adding Lime-Sulphur to Different Ingredients Separately and Combined (Tables 1 to 3)

It will be seen that addition of lime-sulphur to lead arsenate brings about a tremendous increase in soluble arsenic,—nearly 136 times the original content of the lead arsenate alone. When lime-sulphur is added to nicotine sulphate and lead arsenate in combination there is likewise a great increase,—34 to 140 times, while in the complete quadruple combination the increase is not so great, due probably to addition of casein-lime in the mixture. It is thus evident that there is an important reaction between lime-sulphur and lead arsenate, but that this is not increased by nicotine sulphate, and is lessened when casein-lime is added.

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
Table 4. Effect of Combining Nicotine Sulphate with Lead Arsenate and Lime-Sulphur											
A-1	L. A.	....	....	....	....	....	....	....	0.05	0.05	....
B-3	L. A.	N. S.	....	....	....	....	....	....	0.06	0.06	....
B-4	N. S.	L. A.	....	....	....	....	....	....	0.03	0.03	....
A-2	L. S.	....	....	....	....	....	....	....	....	....	.923
B-7	L. S.	N. S.	....	....	....	....	....	....	....	....	.933
B-8	N. S.	L. S.	....	....	....	....	....	....	....	....	.928
Table 5. Effect of Adding Nicotine Sulphate to Lime-Sulphur and Casein-Lime Already in Combination and of Combining It with These Ingredients in Other Ways											
B-9	L. S.	C. L.	....	....	....	....	....	....	....	....	.916
B-10	C. L.	L. S.	....	....	Light	....	....	....	....	....	.905
C-20	L. S.	C. L.	N. S.	....	....	....	....	....	....	....	.930
C-22	C. L.	L. S.	N. S.	....	....	....	....	....	....	....	.936
Table 6. Effect of Adding Nicotine Sulphate to Lead Arsenate and Casein-Lime Already in Combination and of Combining It with These Ingredients in Other Ways											
B-5	L. A.	C. L.	....	....	....	....	....	....	0.28	0.28	....
B-6	C. L.	L. A.	....	....	....	....	....	....	0.28	0.28	....
C-13	L. A.	C. L.	N. S.	....	....	....	....	0.30*	0.60	0.90	....
C-15	C. L.	L. A.	N. S.	....	....	....	....	0.31*	0.56	0.87	....

* Soluble in water.

TABLE 7. EFFECT OF ADDING NICOTINE SULPHATE TO LEAD ARSENATE AND LIME-SULPHUR ALREADY IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
B-1	L. A.	L. S.	....	....	Light	G. B.	Clear	0.98	5.48	6.46	.907
B-2	L. S.	L. A.	....	....	Light	G. B.	Clear	1.49	5.72	7.21	.890
C-1	L. A.	L. S.	N. S.	....	Light	Blk.	Clear	1.74	0.52	2.26	.604
C-3	L. S.	L. A.	N. S.	....	Light	Blk.	Clear	1.28	0.30	1.58	.611
C-5	N. S.	L. S.	L. A.	....	Light	G. B.	Clear	1.06	4.40	5.46	.884
C-6	N. S.	L. A.	L. S.	....	Light	G. B.	Clear	1.06	3.78	4.84	.873
C-4	L. S.	N. S.	L. A.	....	Light	G. B.	Clear	1.77	4.63	6.40	.820
C-2	L. A.	N. S.	L. S.	....	Light	G. B.	Clear	1.03	4.20	5.23	.890

TABLE 8. EFFECT OF ADDING NICOTINE SULPHATE TO LEAD ARSENATE, CASEIN-LIME AND LIME-SULPHUR ALREADY IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

C-7	L. A.	C. L.	L. S.	....	Light	G. B.	Turbid	0.41	2.58	2.99	.915
6	L. A.	C. L.	L. S.	N. S.	Dark	G. B.	Turbid	0.50	2.33	2.83	.916
7	N. S.	L. A.	C. L.	L. S.	Light	G. B.	Clear	0.39	2.55	2.94	.919
C-8	L. A.	L. S.	C. L.	....	Light	G. B.	Turbid	0.35	1.56	1.91	.916
3	L. A.	L. S.	C. L.	N. S.	Light	G. B.	Turbid	0.43	1.19	1.62	.915
10	N. S.	L. A.	L. S.	C. L.	Light	G. B.	Turbid	0.29	1.33	1.62	.912
C-9	C. L.	L. A.	L. S.	....	Dark	L. G.	Clear	0.40	2.56	2.96	.928
11	C. L.	L. A.	L. S.	N. S.	Dark	G. B.	Clear	0.69	2.60	3.29	.918
17	N. S.	C. L.	L. A.	L. S.	Light	G. B.	Clear	0.41	2.56	2.97	.906
C-10	L. S.	L. A.	C. L.	....	Light	G. B.	Turbid	0.40	1.93	2.33	.920
9	L. S.	L. A.	C. L.	N. S.	Light	G. B.	Turbid	0.47	0.98	1.45	.907
13	N. S.	L. S.	L. A.	C. L.	Light	Blk.	Clear	0.55	2.31	2.86	.800
C-11	L. S.	C. L.	L. A.	....	Light	G. B.	Turbid	0.46	1.91	2.37	.920
15	L. S.	C. L.	L. A.	N. S.	Dark	G. B.	Turbid	0.55	1.35	1.90	.912
19	N. S.	L. S.	C. L.	L. A.	Light	G. B.	Turbid	0.40	1.06	1.46	.907
C-12	C. L.	L. S.	L. A.	....	Light	G. B.	Turbid	0.45	2.52	2.97	.922
18	C. L.	L. S.	L. A.	N. S.	Dark	G. B.	Turbid	0.50	2.80	3.30	.922
24	N. S.	C. L.	L. S.	L. A.	Dark	G. B.	Clear	0.48	2.73	3.21	.916

Effect of Adding Nicotine Sulphate to Different Ingredients Separately and Combined

(Tables 4 to 8)

A study of Tables 4 to 8 shows that there is a negligible action when nicotine sulphate and lime-sulphur are mixed together as regards total sulphur in solution. There is likewise little or no action when nicotine sulphate and lead arsenate are mixed together. When nicotine sulphate is added to lime-sulphur and casein-lime in combination, not so much sulphur is precipitated from the solution although the difference is small and of doubtful importance. When added to lead arsenate and casein-lime there is a distinct increase in soluble arsenic and when nicotine sulphate is added to lead arsenate and lime-sulphur in combination there is a decrease in soluble arsenic, and also a decrease in the amount of sulphur in solution. Added to triple combinations as in Table 8, there are variable results. The sulphur content of the filtrate is only slightly altered and the soluble arsenic is decreased in 8 cases but increased in 4.

TABLE 9. EFFECT OF COMBINING CASEIN-LIME WITH LEAD ARSENATE AND LIME-SULPHUR

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
A-1	L. A.	....	....	....	....	....	....	....	0.05	0.05	....
B-5	L. A.	C. L.	....	....	....	....	....	....	0.28	0.28	....
B-6	C. L.	L. A.	....	....	....	....	....	....	0.28	0.28	....
A-2	L. S.	....	....	....	....	....	....	....	....	....	.923
B-9	L. S.	C. L.	....	....	....	....	....	....	....	....	.916
B-10	C. L.	L. S.	....	....	Light	....	....	....	....	....	.905

TABLE 10. EFFECT OF ADDING CASEIN-LIME TO LEAD ARSENATE AND LIME-SULPHUR ALREADY IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur gm/100 cc
B-1	L. A.	L. S.	....	....	Light	G. B.	Clear	0.98	5.48	6.46	.907
B-2	L. S.	L. A.	....	....	Light	G. B.	Clear	1.49	5.72	7.21	.890
C-8	L. A.	L. S.	C. L.	....	Light	G. B.	Turbid	0.35	1.56	1.91	.916
C-10	L. S.	L. A.	C. L.	....	Light	G. B.	Turbid	0.40	1.93	2.33	.920
C-7	L. A.	C. L.	L. S.	....	Light	G. B.	Turbid	0.41	2.58	2.99	.915
C-9	C. L.	L. A.	L. S.	....	Dark	L. G.	Clear	0.40	2.56	2.96	.928
C-11	L. S.	C. L.	L. A.	....	Light	G. B.	Turbid	0.46	1.91	2.37	.920
C-12	C. L.	L. S.	L. A.	....	Light	G. B.	Turbid	0.45	2.52	2.97	.922

TABLE 11. EFFECT OF ADDING CASEIN-LIME TO LEAD ARSENATE AND NICOTINE SULPHATE ALREADY IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur gm/100 cc
B-3	L. A.	N. S.	....	....	....	....	....	....	0.06	0.06	....
B-4	N. S.	L. A.	....	....	....	....	....	....	0.03	0.03	....
C-14	L. A.	N. S.	C. L.	....	....	....	Turbid	0.20	0.48	0.68	....
C-16	N. S.	L. A.	C. L.	....	Clear	....	Turbid	0.23	0.40	0.63	....
C-13	L. A.	C. L.	N. S.	....	Clear	....	Turbid	0.30	0.60	0.90	....
C-15	C. L.	L. A.	N. S.	....	Clear	....	Turbid	0.31	0.56	0.87	....
C-17	N. S.	C. L.	L. A.	....	Clear	....	Turbid	0.25	0.94	1.19	....
C-18	C. L.	N. S.	L. A.	....	Clear	....	Clear	0.30	1.20	1.50	....

TABLE 12. EFFECT OF ADDING CASEIN-LIME TO LIME-SULPHUR AND NICOTINE SULPHATE IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
B-7	L. S.	N. S.	....	....	....	....	....	....	....	....	.933
B-8	N. S.	L. S.	....	....	....	....	....	....	....	....	.928
C-19	L. S.	N. S.	C. L.	....	Dark	....	....	....	....	....	.925
C-21	N. S.	L. S.	C. L.	....	Dark	....	....	....	....	....	.930
C-20	L. S.	C. L.	N. S.	....	....	....	....	....	....	....	.930
C-22	C. L.	L. S.	N. S.	....	....	....	....	....	....	....	.936
C-23	N. S.	C. L.	L. S.	....	....	....	....	....	....	....	.934
C-24	C. L.	N. S.	L. S.	....	....	....	....	....	....	....	.935

TABLE 13. EFFECT OF ADDING CASEIN-LIME TO LEAD ARSENATE, NICOTINE SULPHATE AND LIME-SULPHUR IN COMBINATION AND OF COMBINING IT WITH THESE INGREDIENTS IN OTHER WAYS

Exp. No.	Order of Mixing 1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
C-1	L. A.	L. S.	N. S.	....	Light	Blk.	Clear	1.74	0.52	2.26	.604
4	L. A.	L. S.	N. S.	C. L.	Light	Blk.	Turbid	0.71	1.62	2.33	.827
11	C. L.	L. A.	L. S.	N. S.	Dark	G. B.	Clear	0.69	2.60	3.29	.918
C-2	L. A.	N. S.	L. S.	....	Light	G. B.	Clear	1.03	4.20	5.23	.890
5	L. A.	N. S.	L. S.	C. L.	Light	Blk.	Clear	0.81	0.29	1.10	.716
8	C. L.	L. A.	N. S.	L. S.	Dark	G. B.	Clear	0.60	2.65	3.25	.916
C-3	L. S.	L. A.	N. S.	....	Light	Blk.	Clear	1.28	0.30	1.58	.611
12	L. S.	L. A.	N. S.	C. L.	Light	Blk.	Clear	0.90	0.41	1.31	.678
18	C. L.	L. S.	L. A.	N. S.	Dark	G. B.	Turbid	0.50	2.80	3.30	.922
C-4	L. S.	N. S.	L. A.	....	Light	G. B.	Clear	1.77	4.63	6.40	.820
16	L. S.	N. S.	L. A.	C. L.	Light	Dark	Clear	0.65	2.40	3.05	.838
20	C. L.	L. S.	N. S.	L. A.	Dark	G. B.	Clear	0.50	2.69	3.19	.906
C-5	N. S.	L. S.	L. A.	....	Light	G. B.	Clear	1.06	4.40	5.46	.884
13	N. S.	L. S.	L. A.	C. L.	Light	Blk.	Clear	0.55	2.31	2.86	.800
22	C. L.	N. S.	L. S.	L. A.	Dark	G. B.	Clear	0.41	2.54	2.95	.913
C-6	N. S.	L. A.	L. S.	....	Light	G. B.	Clear	1.06	3.78	4.84	.873
10	N. S.	L. A.	L. S.	C. L.	Light	G. B.	Turbid	0.29	1.33	1.62	.912
14	C. L.	N. S.	L. A.	L. S.	Dark	G. B.	Turbid	0.33	2.77	3.10	.920

Effect of Adding Casein-Lime to Different Ingredients Separately and Combined

(Tables 9 to 13)

It will be seen from Table 9 that the addition of casein-lime increased the soluble arsenic and reduced the sulphur when mixed with lead arsenate and lime-sulphur alone. When added to lead arsenate and lime-sulphur in combination, the amount of soluble arsenic is greatly reduced and the sulphur in solution is increased.

When added to nicotine sulphate and lead arsenate in combination the soluble arsenic is distinctly increased, but when added to lime-sulphur and nicotine sulphate the sulphur content of the solution is not greatly altered. In quadruple mixtures, Table 13, there seems to be, in general, an increase of sulphur in solution where casein-lime is used over mixtures where this material is omitted; and, in general, the soluble arsenic is reduced, but it may sometimes be increased.

Effect of Replacing Casein-Lime with Pure Lime (Table 14)

In order to find out whether the casein or lime of the casein-lime mixture was responsible for the results noted in Tables 9 to 13, a quantity of pure lime (CaO), equivalent to the amount used in the casein-lime, was substituted (D1). This amount was then doubled (D2). It will be seen that the amount of soluble arsenic is decreased as much or more by lime alone as by casein-lime (Exp. No. 2); also that the amount of sulphur in solution is not greatly reduced by the additional lime.

Effect of Different Orders of Mixing on Quadruple Mixtures (Table 15)

It is easily demonstrated that different orders of mixing produce differently colored mixtures, but to determine if possible the value of this criterion for judging spray mixtures Table 15 was prepared. It will be seen that some of the mixtures are dark in color while others are light. It was noted in the course of the work that some of the blackness of the resulting spray was due to the mixture of lime-sulphur and nicotine sulphate as well as the formation of lead sulphide as noted by others. The actual color of the sediment does not vary greatly, but there is a considerable variation in the turbidity of the filtrate, certain ones remaining clear, while others produce a decided murkiness. The turbid filtrates were tested by chemical means and found to be due to a very finely divided sulphur and not to lead, calcium or

TABLE 14. EFFECT OF REPLACING CASEIN-LIME WITH PURE LIME, EQUAL IN AMOUNT AND DOUBLE THE ORIGINAL CONTENT OF THE CASEIN-LIME

Exp. No.	Order of Mixing 1	2	3	4	Physical Characteristics: Color of finished mixture	Color of sediment	Filtered solution	Arsenic, As_2O_5, per cent. Based on amount of lead arsenate used: In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur In Lime-Sulphur solution gm/100 cc
C-2	L. A.	N. S.	L. S.	....	Light	G. B.	Clear	1.03	4.20	5.24	.890
D-1	L. A.	L.*	N. S.	L. S.	Light	G.	Clear	0.31	1.21	1.52	.921
D-2	L. A.	L.**	N. S.	L. S.	Light	G.	Clear	0.25	0.27	0.52	.915
2	L. A.	C. L.	N. S.	L. S.	Dark	G. B.	Clear	0.47	2.83	3.30	.925

* 0.3 gm.
** 0.6 gm.

TABLE 15. EFFECT OF DIFFERENT ORDERS OF MIXING ON QUADRUPLE MIXTURES

Exp. No.	1	2	3	4	Color of finished mixture	Color of sediment	Filtered solution	In L.-S. solution %	Water-soluble in sediment %	Total soluble %	Total Sulphur gm/100 cc
1	L. A.	N. S.	C. L.	L. S.	Light	G. B.	Clear	0.40	2.55	2.95	.930
2	L. A.	C. L.	N. S.	L. S.	Dark	G. B.	Clear	0.47	2.83	3.30	.925
3	L. A.	L. S.	C. L.	N. S.	Light	G. B.	Turbid	0.43	1.19	1.62	.915
4	L. A.	L. S.	N. S.	C. L.	Light	Blk.	Turbid	0.71	1.62	2.33	.827
5	L. A.	N. S.	L. S.	C. L.	Light	Blk.	Clear	0.81	0.29	1.10	.716
6	L. A.	C. L.	L. S.	N. S.	Dark	G. B.	Turbid	0.50	2.33	2.83	.916
7	N. S.	L. A.	C. L.	L. S.	Light	G. B.	Clear	0.39	2.55	2.94	.919
8	C. L.	L. A.	N. S.	L. S.	Dark	G. B.	Clear	0.60	2.65	3.25	.916
9	L. S.	L. A.	C. L.	N. S.	Light	G. B.	Turbid	0.47	0.98	1.45	.907
10	N. S.	L. A.	L. S.	C. L.	Light	G. B.	Turbid	0.29	1.33	1.62	.912
11	C. L.	L. A.	L. S.	N. S.	Dark	G. B.	Clear	0.69	2.60	3.29	.918
12	L. S.	L. A.	N. S.	C. L.	Light	Blk.	Clear	0.90	0.41	1.31	.678
13	N. S.	L. S.	L. A.	C. L.	Light	Blk.	Clear	0.55	2.31	2.86	.800
14	C. L.	N. S.	L. A.	L. S.	Dark	G. B.	Turbid	0.33	2.77	3.10	.920
15	L. S.	C. L.	L. A.	N. S.	Dark	G. B.	Turbid	0.55	1.35	1.90	.912
16	L. S.	N. S.	L. A.	C. L.	Light	Blk.	Clear	0.65	2.40	3.05	.838
17	N. S.	C. L.	L. A.	L. S.	Light	G. B.	Clear	0.41	2.56	2.97	.906
18	C. L.	L. S.	L. A.	N. S.	Dark	G. B.	Turbid	0.50	2.80	3.30	.922
19	N. S.	L. S.	C. L.	L. A.	Light	G. B.	Turbid	0.40	1.06	1.46	.907
20	C. L.	L. S.	N. S.	L. A.	Dark	G. B.	Clear	0.50	2.69	3.19	.906
21	L. S.	C. L.	N. S.	L. A.	Dark	G. B.	Clear	0.48	1.71	2.19	.916
22	C. L.	N. S.	L. S.	L. A.	Dark	G. B.	Clear	0.41	2.54	2.95	.913
23	L. S.	N. S.	C. L.	L. A.	Light	G. B.	Turbid	0.39	1.40	1.79	.907
24	N. S.	C. L.	L. S.	L. A.	Dark	G. B.	Clear	0.48	2.73	3.21	.916

nicotine. This fact is of some significance in spraying practices since it has been demonstrated that colloidal sulphurs are important fungicides.[28] Whether such combinations as these, however, contain enough colloidal sulphur to affect the efficiency of the spray has not been determined.

It will be noted that combinations showing the lowest arsenic in solution (Nos. 5 and 12) are both extremely low in soluble sulphur and that both filtrates are clear. It would probably not be wise to select merely on the basis of soluble arsenic and sulphur content alone, although we know from the work of Saffro[19] that spray injury may be caused by calcium polysulphides and to a less extent by calcium thiosulphate (p. 32). An attempt to avoid spray injury would, therefore, include selection of mixtures low in sulphur and arsenic in solution, but these would probably be reduced in fungicidal action since the filtrates are clear and the total sulphur, supposedly the active forms, is reduced 25% or more (Nos. 5 and 12). It is important to note that in all cases the greater part of the soluble arsenic is found in the residue which emphasizes the necessity of cleaning the spray tank frequently, in order to avoid accumulation of sludge from previous tanks, and the importance of ample agitation to avoid this difficulty.

General Conclusions

(1) The Bramberg method of determining small amounts of arsenic has been found adaptable to the determination of soluble arsenic in spray mixtures.

(2) *Lime-sulphur* reacts strongly with lead arsenate* giving increased soluble arsenic and decreased sulphur in solution. It reacts similarly with lead arsenate and nicotine sulphate in combination and with lead arsenate and casein-lime but the reaction is not as great in the latter case.

(3) *Nicotine sulphate* does not react with lead arsenate or with lime-sulphur so far as indicated by the chemical data; a color change is noted, the significance of which is not explained. When added to lead arsenate and casein-lime together the soluble arsenic is increased; added to lead arsenate and lime-sulphur together there is a marked decrease in soluble arsenic and also a decrease in the amount of sulphur in solution. When added to triple combinations of lead arsenate, casein-lime and lime-sulphur, variable results are noted.

(4) *Casein-lime* increases the soluble arsenic content of lead arsenate when mixed with it alone. When mixed with

* Acid lead arsenate is implied wherever lead arsenate is mentioned.

lime-sulphur alone the amount of sulphur in solution is somewhat reduced. When added to nicotine sulphate and lead arsenate the soluble arsenic is distinctly increased, but when added to lime-sulphur and nicotine sulphate the sulphur content of the solution is not greatly altered. In quadruple mixtures there is, in general, an increase of sulphur in solution due to the casein-lime and there is in general a decrease in soluble arsenic. The latter, however, may sometimes be increased.

(5) The lime in casein-lime is largely responsible for the decrease in soluble arsenic where this material is used.

(6) Different orders of mixing quadruple mixtures give different results, but so many factors are involved and the variations are so small that the selection of improved mixtures seems an impossibility.

(7) Colloidal sulphur is sometimes formed in the spray mixtures.

(8) The color of the resulting mixture is not a satisfactory means of judging a spray solution.

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