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*Died, May 12th, 1895.

SOME EXPERIMENTS WITH FUNGICIDES ON PEACH FOLIAGE.

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Early in the present season some experiments were begun on peach rot in the orchard of Mr. J. W. Patton, at Cleveland, Tennessee. Tests were made with the standard Bordeaux mixture, with and without London purple, and ammoniacal copper carbonate. Some hope of success was entertained with respect to the Bordeaux and London purple mixture, for no less than three investigators have reported that this mixture has no injurious effects on peach foliage, while others found serious damage resulting from the use of the Bordeaux alone. It was soon found, however, that there was no prospect of success with the mixtures employed. As a result of one application of them most of the leaves fell. It was plain that the more fundamental problem of finding a fungicide that is not destructive to peach foliage must be solved before any hope of success in this method of combating the rot can be entertained. A new series of experiments was, therefore, undertaken with the hope of contributing something toward the solution of this question. While the work is not complete, it was thought best to put on record the results of the experiments, together with a detailed description of the method of performing them.

The results reported by different investigators as to the effect of fungicides on peach foliage are conflicting; and since they were made with care, the only conclusion is that the behavior of the foliage treated with fungicides varies in different sections of country or under different conditions. Much of the reported diversity of behavior is probably due to the varying degrees of purity of the chemicals composing the mixtures, as well as to the different methods of compounding them. Gillette[1] and Kilgore[2] found no injury resulting from the application of London purple in a standard Bordeaux mixture, no counter tests being made with the Bordeaux alone. In his experiments on peach rot, Chester[3] found serious damage to the foliage as a result of spraying with several fungicides, including ammoniacal copper carbonate and Bordeaux mixture. He records less injury from

1 Experiments with Arsenites, Iowa Exp. Station, Bull. No. 10, pp. 416, 417.
2 Combination of Arsenites with Fungicides, N. C. Exp. Station, Bull. No. 77b, pp. 8-11.
3 Can Peach Rot be Controlled by Spraying? Del. Exp. Station, Bull. No. XIX.

the latter. Lodeman[1] reports injury from ammoniacal copper carbonate, but none from Bordeaux, with or without London purple. It is interesting to note, in the light of the experiments recorded in this bulletin, that Chester used a neutral Bordeaux, while others who found no injury to the foliage used the standard Bordeaux, containing four parts of lime to six parts of copper sulphate. Theoretically, 6 parts of copper sulphate would be neutralized by 1.3 parts of quicklime. In an experiment made by the writer with commercial copper sulphate and fresh quicklime, 1.62 parts of lime neutralized 6 parts of the sulphate.

The standard Bordeaux properly made is strongly alkaline, and it is possible that the neutral Bordeaux used by Chester in Delaware and found to injure foliage would have had the same effect in New York, Iowa, or North Carolina.

Besides testing the effect on the foliage of the fungicides in common use, made according to the usual methods, an attempt was made to determine the effect of their by-products and of the isolated copper compounds on the foliage. These were applied at the same time with the regular fungicides, in order to test their relative injurious effects. The list of these mixtures, with the method of making them, is here given. The same numbers are assigned them as were used in labeling the leaves in the field.

1. NEUTRAL BORDEAUX.—In 100 cc. of water was dissolved 1.79 g. of copper sulphate; then just enough milk of lime added to give an alkaline reaction with phenol phthalein. This is at the rate of six pounds copper sulphate to forty gallons water.

2. BORDEAUX WITH LONDON PURPLE.—To 100 cc. of 1 was added .075 g. of London purple.

3. BORDEAUX TREATED WITH CARBON DIOXIDE.—Through 100 cc. of 1 a current of carbon dioxide was passed until the blue color changed to a distinct green.

4. BORDEAUX TREATED WITH CARBON DIOXIDE THEN MIXED WITH LONDON PURPLE.—To 100 cc. of 3 was added .075 g. London purple.

5. BORDEAUX AND LONDON PURPLE TREATED WITH CARBON DIOXIDE. —Through 100 cc. of 2 a current of carbon dioxide was passed for some time.

6. COPPER HYDROXIDE.—To a solution of 1.79 g. copper sulphate in water was added a small quantity of ammonium chloride.[2] To this was added a slight excess of potassium hydroxide. The precipitate was washed by decantation with distilled water until the washings ceased to form a precipitate with silver nitrate or to react with phenol phthalein. The cleaned precipitate was applied in 100 cc. of water.

1 Test of some Fungicides and Insecticides upon Peach Foliage, Cornell Exp. Station, Bull. No. 60, pp. 280, 281, 295.

2 Roscoe and Schorlemmer, Treatise on Chemistry, Vol. II, pt. I, p. 381.

7. COPPER-DICUPRIC HYDROXIDE.—To a solution of 1.79 g. copper sulphate in water, an excess of potassium hydroxide was added. This was then boiled for ten or fifteen minutes, and washed until free from alkali. The black precipitate was added to 100 cc. of water.

8. COPPER CARBONATE.—To a solution of 1.79 g. copper sulphate was added sodium carbonate as long as a precipitate formed. This was washed until washings failed to react with barium chloride, and added to 100 cc. of water.

9. AMMONIACAL COPPER CARBONATE.[1]—To 8 was added nearly enough ammonia to dissolve the precipitate; the whole then diluted to 500 cc.

10. AMMONIACAL COPPER CARBONATE WITH LONDON PURPLE.—To 100 cc. of 9 was added .075 g. of London purple.

11. BORDEAUX MADE WITH EXCESS OF COPPER SULPHATE.—To solution of 1.79 g. copper sulphate in water was added just enough milk of lime to produce alkaline reaction with phenol phthalein; then a large excess of copper sulphate was added. The precipitate was then washed free of sulphates and diluted with 100 cc. of water.

12. BORDEAUX FOLLOWED BY MILK OF LIME.—The neutral Bordeaux was applied to leaves, and in about 24 hours was followed with an application of milk of lime.

13. BORDEAUX TREATED WITH CARBON DIOXIDE AND WASHED.—The precipitate obtained in 3 after passing carbon dioxide was washed free of sulphates.

14. WASHED BORDEAUX.—The precipitate obtained in 1 was washed until no precipitate formed with barium chloride, and then applied in 100 cc. of water.

15. ALKALINE BORDEAUX.—To 1 was added a large excess of milk of lime.

16. BASIC COPPER SULPHATE.—To solution of 1.79 g. copper sulphate in water enough potassium hydroxide was added to neutralize the sulphate, then copper sulphate added in excess and the precipitate washed free of sulphates.

18. CALCIUM SULPHATE.—The same quantity of milk of lime as required to neutralize 1.79 g. of copper sulphate was treated with dilute sulphuric acid until it gave a neutral reaction. This was diluted to 100 cc.

19. CALCIUM SULPHATE AND CALCIUM CARBONATE.—To 18 was added

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1 By an error in calculation here this fungicide was made too strong. Assuming that normal copper carbonate is formed when sodium carbonate is added in excess to copper sulphate, the proportion of copper carbonate was about 1 lb. to 50 gallons of water. The general conclusions reached in this bulletin are not affected, however, since trees sprayed in the spring of '95 with ammon. cop. carb., containing 1 oz. carbonate to 9 gallons water, revealed great injury to their foliage as the result of one application.

a small quantity of calcium carbonate freshly precipitated from calcium chloride with sodium carbonate and washed.

20. CALCIUM SULPHATE AND CALCIUM HYDROXIDE.—To 18 was added a little milk of lime.

22. MILK OF LIME.—Thin enough to apply as a spray.

23. COPPER HYDROXIDE AND LIME.—Copper hydroxide was prepared as in 6. To this a small quantity of milk of lime was added.

24. COPPER HYDROXIDE AND CALCIUM SULPHATE.—To 6 was added a small quantity of calcium sulphate prepared as in 18.

25. COPPER HYDROXIDE WITH SULPHATE AND HYDROXIDE OF LIME.—To 6 was added calcium sulphate and milk of lime. This is a synthetic Bordeaux.

26. COPPER HYDROXIDE WITH SULPHATE, HYDROXIDE, AND CARBONATE OF LIME.—To 6 were added these three compounds of lime prepared as above.

29. BORDEAUX WITH SODIUM CARBONATE.—To 100 cc. of 1 were added 2 g. of sal soda.

30. QUADRUPLE STRENGTH BORDEAUX.—To a solution of 7.16 g. of copper sulphate in water milk of lime was added until a distinct blue color was observed. There was doubtless a considerable excess of lime in the mixture thus made, which would account for its producing less injury to the foliage than the normal Bordeaux.

31. BORDEAUX (1) TREATED WITH A CURRENT OF AIR FOR A LONG TIME.

36. CALCIUM CARBONATE.—A thin milk of chalk made as in 19.

METHOD OF CONDUCTING THE EXPERIMENTS.

The various mixtures were applied as a spray with an ordinary toilet atomizer, care being taken to spray both sides of the leaves thoroughly. Ten trees were employed for experimental purposes. Healthy twigs were labeled with ordinary nursery labels, marking off ten leaves from the distal end. Thus, with each of the above mixtures, 100 leaves were sprayed, ten on ten different trees. At the same time a set of untreated leaves was labeled for control. Applications of the sprays were made June 20 and 21; and July 5 and 6.

The object of treating several of the mixtures with carbon dioxide was to get evidence as to whether any reaction occurs between the chemicals composing the fungicides and the carbon dioxide of the air, resulting in the formation of compounds injurious to the foliage. It is quite clear, however, as shown by the results tabulated below, that the injury to the foliage cannot be estimated as a mathematical quantity. Although in a general way some of the mixtures did not cause the leaves to fall as soon as others, the difference in many cases, such as in those mixtures applied with and without previous treatment with

carbon dioxide, is so slight that no accurate estimation of their relative injurious effects can be made.

In the following table are given the results of the application of the various mixtures as shown by the number of leaves remaining in each case from the 100 originally treated. Observations were made June 29; July 8 and 9; July 18; and September 25.

	Leaves remaining June 29.	Leaves remaining July 8 and 9.	Leaves remaining July 18.	Leaves remaining September 25.
1. Neutral Bordeaux	98	20	10	0
2. Bordeaux with London purple	97	18	0	0
3. Bordeaux treated with carbon dioxide	100	19	0	0
4. Bordeaux treated with carbon dioxide, then mixed with London purple	99	10	0	0
5. Bordeaux and London purple treated with carbon dioxide	94	17	1	0
6. Copper hydroxide	99	26	0	0
7. Copper-dicupric hydroxide	95	20	0	0
8. Copper carbonate	88	2	0	0
9. Ammoniacal copper carbonate	97	45	12	3
10. Ammon. copper carbonate with London purple.	83	14	0	0
11. Bordeaux made with excess of copper sulphate	94	13	0	0
12. Bordeaux followed by milk of lime	100	84	52	8
13. Bordeaux treated with carbon dioxide and washed	98	10	0	0
14. Washed Bordeaux	94	16	0	0
15. Alkaline Bordeaux	100	98	95	51
16. Basic copper sulphate	95	6	0	0
18. Calcium sulphate	100	100	98	41
19. Calcium sulphate and calcium carbonate	100	100	100	38
20. Calcium sulphate and calcium hydroxide	100	100	100	32
22. Milk of lime	97	96	96	30
23. Copper hydroxide and lime	100	98	81	3
24. Copper hydroxide and calcium sulphate	89	9	0	0
25. Copper hydroxide with sulphate and hydroxide of lime	99	96	78	0
26. Copper hydroxide with sulphate, hydroxide, and carbonate of lime	97	82	61	0
29. Bordeaux with sodium carbonate	100	28	0	0
30. Quadruple strength Bordeaux	100	92	37	0
31. Bordeaux treated with a current of air	90	15	0	0
36. Calcium carbonate	100	99	96	38
Control	99	98	91	50

CONCLUSIONS.

So far as these results go, I think the following conclusions are justified:

1. That the injury to peach foliage by the neutral Bordeaux mixture and ammoniacal copper carbonate is increased by applying with London purple.

2. That of all the copper compounds and mixtures tried, a Bordeaux mixture containing a large excess of lime does least injury to the foliage, apparently producing none at all; that lime following the neutral Bordeaux after one day reduces the injury, but not so effectively.

3. That none of the lime compounds of the Bordeaux mixture (including the hydroxide), formed either before or after its application to the leaves, are injurious.

4. That copper-dicupric hydroxide and the hydroxide, carbonate, and basic sulphate of copper are more injurious to peach foliage than the ordinary Bordeaux mixture.

5. That the injury to the foliage by the neutral Bordeaux cannot be prevented by rendering it alkaline with sodium carbonate.

6. That the injury caused by copper hydroxide, like that caused by the Bordeaux mixture, may be greatly reduced by adding milk of lime, or by adding milk of lime with the carbonate or the sulphate of lime, or with both; but the sulphate of lime will not diminish the injury.

The actual amount of lime added to the neutralized Bordeaux mixture was not determined; but it cannot have been less than one pound to ten gallons. In the light of the results given in this bulletin, the following formula is suggested for a Bordeaux mixture to be used on the peach:

Copper sulphate	6 pounds.
Quicklime	8 pounds.
Water	50 gallons.

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