HILGARDIA

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DEPOSITIONAL AND WEATHER-RESISTING QUALITIES OF SOME COPPER FUNGICIDES AFFECTING THE CONTROL OF PEACH BLIGHT[1]

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INTRODUCTION

IN THE TESTS reported in this paper, comparisons were made between the depositional and weather-resisting qualities of bordeaux and three so-called fixed copper fungicides used to control peach blight caused by the fungus *Coryneum beijerinckii* Oud. Each fixed copper preparation was combined with a supplement to increase the tenacity, or weather resistance, of the deposit.

STUDIES ON DEPOSITION

On Peach Twigs.—In field tests conducted for three seasons, water suspensions of basic copper sulfate A,[3] basic copper sulfate Z (containing zinc), cuprous oxide, and bordeaux mixture were applied in mid-November to peach trees after most of the leaves had fallen. One-half per cent of a cream-type oil emulsion, designated as supplement A,[4] was added to basic copper sulfate A. One and one-half per cent of an emulsive oil, supplement B, was added to basic copper sulfate Z and to cuprous oxide. The emulsifying agents and other ingredients of these supplements are unknown to the writer. Except in the first year of the tests, each preparation was applied to three randomized plots with an ordinary orchard sprayer operated at a pressure of 450 to 500 pounds per square inch.

In addition to these treatments, basic copper sulfate Z, suspended in an emulsive oil which was then emulsified in water (1 gallon of oil to 1 gallon of water), was applied by means of vapor-spraying equipment. This machine produces a finely divided mist by injecting the preparation into an air stream, which issues from ducts at the side of the machine.

After the sprays had dried, samples of twigs produced in the previous growing season were collected; the copper deposits were determined by the iodo-

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[3] The basic copper sulfate designated as A (Basi-Cop) contained 52 per cent metallic copper; that designated as Z (Zinc-Coposil) contained 19 per cent copper; the cuprous oxide (yellow coprocide) contained 84–85 per cent copper.

[4] The trade name of supplement A is Basi-Spred; of supplement B, Ortho-Adhesive.

metric method as described in another paper (Wilson, 1942). In late February, other samples were taken and the residues remaining after weathering were determined. Table 1 gives these data, the results of four trials conducted in three different years.

Average initial deposits shown in the second column of table 1 differed considerably among the various preparations. This finding might be expected, since the copper content of the prepared sprays also differed. For example,

TABLE 1

COMPARISON OF COPPER FUNGICIDES WITH INITIAL DEPOSITS, RESISTANCE TO WEATHERING, AND CONTROL OF PEACH-TWIG INFECTION BY *Coryneum beijerinckii*, 1941–1944

Fungicide material, pounds per 100 gallons, and supplement used, expressed in per cent by volume	Milligrams of copper on 100 grams of twigs		Average coefficient of tenacity†	Average number of lesions on 100 twigs
	Average initial deposit	Average residue*		
Unsprayed	....	....	.....	1,770
Bordeaux, 10–10–100	32.8	8.0	0.239	62
Bordeaux, 10–10–100; plus supplement B, 1 per cent	29.6	9.6	0.348	16
Bordeaux, 8–8–100; plus supplement B, 1 per cent	26.3	10.4	.....	.....
Basic copper sulfate A, 5–100; plus supplement A, 0.5 per cent	47.2	9.8	0.207	99
Basic copper sulfate Z, 6–100; plus supplement B, 1.5 per cent	19.6	4.5	0.222	78
Basic copper sulfate Z, 8–100, plus supplement B, 1.5 per cent	26.9	4.3	.....	.....
Cuprous oxide, 1.5–100; plus supplement B, 1.5 per cent	24.7	5.6	0.239	186
Vapor application, basic copper sulfate Z, 75–100, in 50 gallons of an emulsive oil and 50 gallons of water, applied at the rate of 20 gallons per acre	19.4‡	6.7‡	0.345‡	28
Difference required for significance 19:1 odds	9.6	3.6	0.135	.....
Difference required for significance 99:1 odds	13.5	5.1	0.189	.....
Calculated *F* value	10.2	5.1	1.61	.....

* After weathering for approximately 3.5 months; average rainfall, 8.59 inches.

† Tenacity coefficient = ratio $\frac{\text{residual spray deposit}}{\text{initial spray deposit}}$. These values, being the averages of the individual coefficients of tenacity, are not necessarily the same as those obtained by dividing the average residue by the average initial deposit.

‡ Excluded from analysis of variance.

preparations of basic copper sulfate Z, 6 pounds per 100 gallons of water, and cuprous oxide, 1½ pounds per 100 gallons, contain 0.137 and 0.152 per cent copper, respectively, as against 0.299 per cent for bordeaux of 10–10–100 strength. These preparations deposited, respectively, 19.6 and 24.7 milligrams of copper on each 100 grams of twigs, as against 32.8 milligrams to each 100 grams for bordeaux. When the initial deposits were compared with respect to the copper content of the spray preparation, however, all fixed copper materials proved to be deposited in greater relative amounts than bordeaux. The coefficients of deposit reported in figure 1 were computed as follows: The amount of copper deposit, y, of the material in question proportional to the deposit, b, of bordeaux (10–10–100) was obtained by $y = \frac{bx}{0.299}$, where x is the copper content (in per cent) of the preparation of the material in question and 0.299 is the per cent of copper in the bordeaux preparation. The observed deposit divided by the expected deposit gave the coefficient. The coefficient for bordeaux, 10–10–100, of course, would always be 1.0.

Bordeaux preparations with and without supplement B were deposited at the same relative level; but all fixed copper materials were deposited in amounts 29 to 49 per cent higher than bordeaux, 10–10–100, without supplement. A difference of 32 per cent is required for significance at 19:1 odds.

Since the amount of preparation applied per tree with the vapor equipment varied somewhat between tests and since each test of this treatment consisted of one plot only, the results given in table 1 were excluded from the statistical

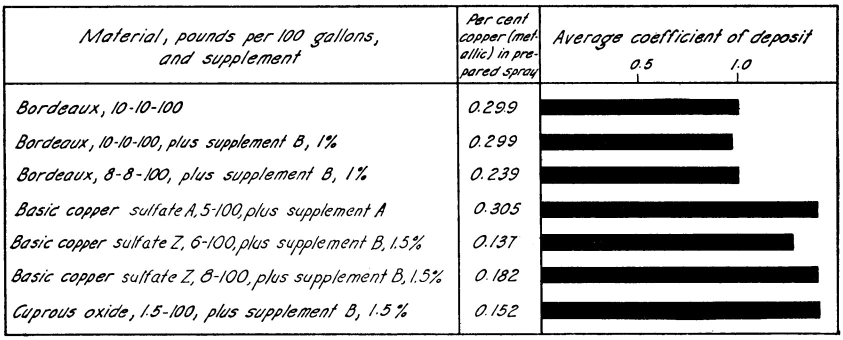

Fig. 1.—Deposition of copper fungicides on peach twigs relative to equivalent copper contents of the prepared sprays.

analyses. In these trials the vapor preparation gave deposits about equal to that of basic copper sulfate Z, 6–100, applied with the regular sprayer, and only 41 per cent lower than that of bordeaux, 10–10–100. On the other hand, deposits of basic copper sulfate Z applied by vapor equipment in a commercial almond orchard were 58 per cent lower than deposits of bordeaux, 10–10–100. Large variations in deposits by this method of application might arise from difference in the speed with which the sprayer is drawn past the trees. As will be shown later, the amount of spray retained by a solid surface up to the time the liquid begins to drain away is directly proportional to the length of the application period. Since the rate of liquid delivery from the vapor equipment is low, under ordinary circumstances the amount deposited on twig surfaces is seldom great enough to cause runoff. Thus, marked variations in the application period should result in differences in the amount of spray deposited on the surfaces; and since the vapor spray issues from more or less fixed outlets, the speed of the sprayer will determine the amount of deposit.

With the ordinary spray rig, on the other hand, the amount of liquid required to cover a given number of trees was approximately equal for all materials. Why, therefore, did the fixed copper materials consistently deposit relatively greater amounts of copper than did bordeaux? For a study of this point, the sprays had to be applied under conditions less variable than those in the orchard. A laboratory atomizing applicator, described earlier (Wilson, 1942), was employed. The surface to be sprayed was a thin film of cellulose nitrate deposited on glass slides.

On Artificial Surfaces.—To understand the method by which supplements might affect the spray deposits, one must consider how the liquid behaves during application. Hensill and Hoskins (1935) emphasized the dynamic nature of deposition. In the first place, the sprayed surfaces are seldom horizontal, so that gravity greatly affects the retention of liquid by the surface. Second, the forces that influence wetting and spreading properties are not permitted to attain equilibrium during application, because the deposited droplets are constantly being disturbed by the oncoming spray. Methods for determining the wetting and spreading under static conditions give results that are of little value for assessing the effects of these properties on retention of spray deposits. In general, however, if the surface is partially wetted by the preparation, an increase in the wetting properties will result in a decrease in deposit (Evans and Martin, 1935; Fajan and Martin, 1937; Hoskins and Ben-Amotz, 1938). Surfaces not wetted by a liquid will retain none of the deposit, because the droplets roll off. Under such conditions, an increase in the wetting properties increases the deposit (Hensill and Hoskins, 1935). Maximum retention of solutions and ordinary suspensions by a surface, therefore, occurs at some intermediate stage of wetting.

For solutions and ordinary suspensions, the maximum deposit is present when the liquid begins to run from the surface (Evans and Martin, 1935; Fajan and Martin, 1937). Continuing to spray beyond this stage ordinarily results in a decrease in the amount retained. Under certain conditions, however, an increase in deposit of a suspended solid occurs when application is continued beyond the stage at which the liquid runs off. Fajan and Martin (1938), for example, reported preferential retention of cuprous oxide by artificial surfaces when the preparation contained petroleum oil emulsified by Agral II. Such was not the case, however, with oil containing sulfite lye as an emulsifier. Under the microscope the oil droplets were seen to aggregate about the cuprous oxide particles when Agral II, but not when sulfite lye, was the emulsifier. Such observations indicate that a partial wetting of the cuprous oxide by the oil occurred with the Agral but not with the sulfite lye. A still more striking case of increased deposits resulting from application beyond the runoff stage is reported for the "dynamite" spray by Marshall (1937) and Marshall and Groves (1937). This spray is prepared by adding a petroleum oil containing one of the univalent soaps, such as ammonium or triethanolamine oleate, to a water suspension of lead arsenate. According to Marshall (1937), the lead arsenate becomes wetted by the oil before, or at the time the liquid comes in contact with the sprayed surface. Very high deposits of lead arsenate are obtained with this preparation.

Although the supplements used in the field trials herein reported contain oil, information on the nature of the emulsifying agents or other added materials was not available to the writer. When these supplements were added to water suspensions of the fixed copper fungicides, a distinct flocculation occurred. Under the microscope the flocculated phase was seen to consist of fungicide particles and water droplets surrounded by oil. Thus the system is apparently much like that of the "dynamite" spray described by Marshall (1937).

Aside from a slight curding, bordeaux was not affected by either supplements A or B, nor by a supplement prepared with oil and ammonium oleate. According to field tests, moreover, bordeaux deposition was not affected by supplement B. To show how supplements affect the deposition of the fixed copper fungicides and of bordeaux, the laboratory applicator was employed. Although the earlier work of this nature has been largely concerned with the amount of deposit at certain stages of spray application, such as "runoff"[5] (Evans and Martin, 1935; Fajan and Martin, 1937 and 1938), or after a definite amount of liquid had drained from the surface (Hensill and Hoskins, 1935; Hoskins and Ben-Amotz, 1938), more detailed data were desired in the

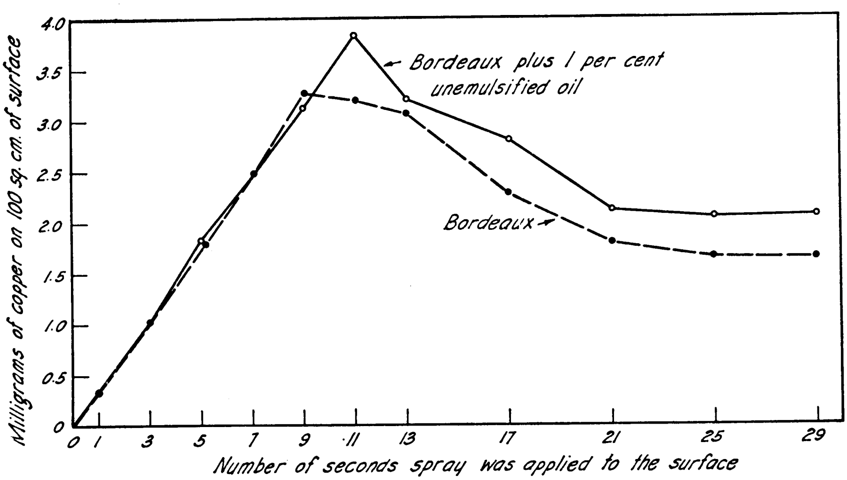

Fig. 2.—Deposition of 1 per cent bordeaux (by weight), and the same bordeaux plus 1 per cent of unemulsified petroleum oil, on cellulose nitrate surfaces.

present tests. In an attempt to determine the building up of the copper deposit before runoff and the status of that deposit after liquid had drained from the surface, glass slides coated with cellulose nitrate in series of five were sprayed for increasing lengths of time, and the amount of copper was ascertained for each spraying interval. In this way the amount of copper deposited by each fungicidal preparation could be compared at the same stage of application relative to runoff.

The atomizer type of applicator has one main limitation: it will not deliver coarsely flocculated preparations at a constant rate, because the floccules tend to accumulate in the atomizer. Since this difficulty was encountered particularly with basic copper sulfate A combined with supplement A and with cuprous oxide combined with supplement B, bordeaux and basic copper sulfate Z with and without supplement B were used in the more detailed tests.

The first point to be examined is the deposition of bordeaux, which will illustrate what happened when an ordinary suspension or, for that matter, a solution was applied for increasing lengths of time. Figure 2 shows the results of tests in which series of slides were sprayed with 1 per cent bordeaux

[5] "Runoff" is used for convenience in designating the stage when the liquid deposit begins to run from the surface, but before any is lost.

with and without unemulsified oil for 1, 3, 5, 7, 9, 11, 13, 17, 21, 25, and 29 seconds. Preliminary trials determined the length of time spraying must continue before runoff begins, and the time intervals were spaced so that one series of slides was sprayed just to the runoff stage. These slides, therefore, bore the maximum deposit.

Before runoff started, deposition of bordeaux or bordeaux with an unemulsified oil was proportional to the length of time the spray was applied. The addition of 1 per cent unemulsified petroleum oil increased the length of time

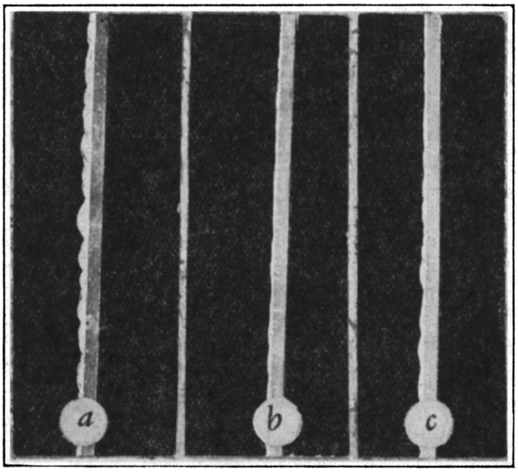

Fig. 3.—Edge view of glass slides showing the liquid deposits of various sprays at the stage just before the liquid began to run off: *a*, 1 per cent copper sulfate solution; *b*, 1 per cent bordeaux mixture; *c*, 1 per cent bordeaux mixture plus 1 per cent of an unemulsified petroleum oil. The spraying time necessary to start these sprays running down the surface was 13.4, 5.5, and 6.8 seconds, respectively.

spraying was necessary to cause running of the liquid from the surface. Thus, when spraying was ended at the runoff stage, the deposit of copper was increased by the addition of unemulsified oil. This increased deposit had one or both of two causes: the oil decreased the wetting properties of the preparation, or the oil increased the viscosity of the preparation. The thickness of the liquid deposits of copper sulfate, bordeaux, and bordeaux plus an unemulsified oil sprayed to the runoff stage is illustrated by the photographs in figure 3. Here the liquid deposit of bordeaux is seen to be much thinner than that of bordeaux containing oil or that of copper sulfate. Apparently, therefore, bordeaux spray droplets spread over larger areas than those of the other preparations, probably because they wetted the surface to a greater degree.

Preparations of fixed copper fungicides without supplements wetted cellulose nitrate surfaces less than bordeaux. In consequence, when application ended at the runoff stage, these materials were deposited in greater amounts than bordeaux. On the whole, the supplements increased the amounts of these fungicides present when the runoff began. Although, for reasons given earlier, the results with cuprous oxide plus supplement B and basic sulfate A plus supplement A were not always reliable, the data given in figure 4 are believed to represent the situation fairly well.

In practice, spraying is seldom discontinued at the runoff stage. Dripping of spray from the surface occurs particularly on twigs at the periphery of the trees. From the artificial surface (fig. 2), bordeaux lost as much as 40 per cent of the deposit present at runoff when spraying was continued beyond that stage. It seemed desirable, therefore, to determine the behavior of the copper deposit during the time the spray was running from the surface. For this purpose, bordeaux and basic copper sulfate Z with and without supplements were applied to cellulose nitrate surfaces for 0, 4, 8, 12, 16, and 20 seconds after

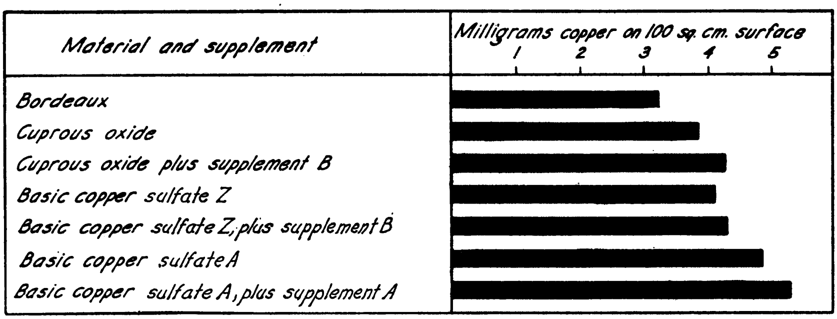

Fig. 4.—Deposition of bordeaux and of various other copper fungicides (with and without supplements) on cellulose nitrate surfaces sprayed to the runoff stage.

the liquid began to run off. The three supplements used were: first, the proprietary material designated B in the field tests; second, a petroleum oil (70 per cent U.R., 108 seconds Saybolt viscosity) containing 0.5 per cent ammonium oleate; third, the same petroleum oil emulsified with 6 milligrams of blood albumin per 100 cubic centimeters of oil. Both supplement B and the supplement containing ammonium oleate flocculated the fixed copper fungicide but did not affect bordeaux in this respect, whereas petroleum oil containing blood albumin did not flocculate either material.

According to the results in figure 5, all supplements tended to lower somewhat the amount of bordeaux deposit retained by the surface at the time runoff began (0 seconds). As will be remembered, supplement B in the field tests (table 1) did not affect the deposit of bordeaux on peach twigs to a significant extent, though there appeared to be a very slight decrease. Either with or without supplements, the bordeaux deposit on cellulose nitrate decreased when spraying was continued beyond the runoff stage. In contrast, when no supplement or when oil containing blood albumin was added to the fixed copper, the deposit decreased when spraying was continued after runoff began; but when either supplement B or oil containing ammonium oleate was added, the curve was strikingly different. Deposits (curves *b* and *c* for basic copper sulfate Z) are seen to decrease as the liquid begins to run from the surface (4 to 8 seconds after runoff begins); but as application continues, they increase. Such behavior presumably results from the preferential retention of the copper phase. The liquid that runs off, consequently, contained less solid than when it struck the surface. Apparently, therefore, only certain types of emulsifying agents promote this phenomenon. Judging from the results with supplement A in the basic sulfate A and supplement B in cuprous oxide, preferential retention occurred here also; but detailed trials similar to those reported in figure 5 were not attempted, since the floccules of these materials clogged the atomizer, and thus reduced the accuracy of the results.

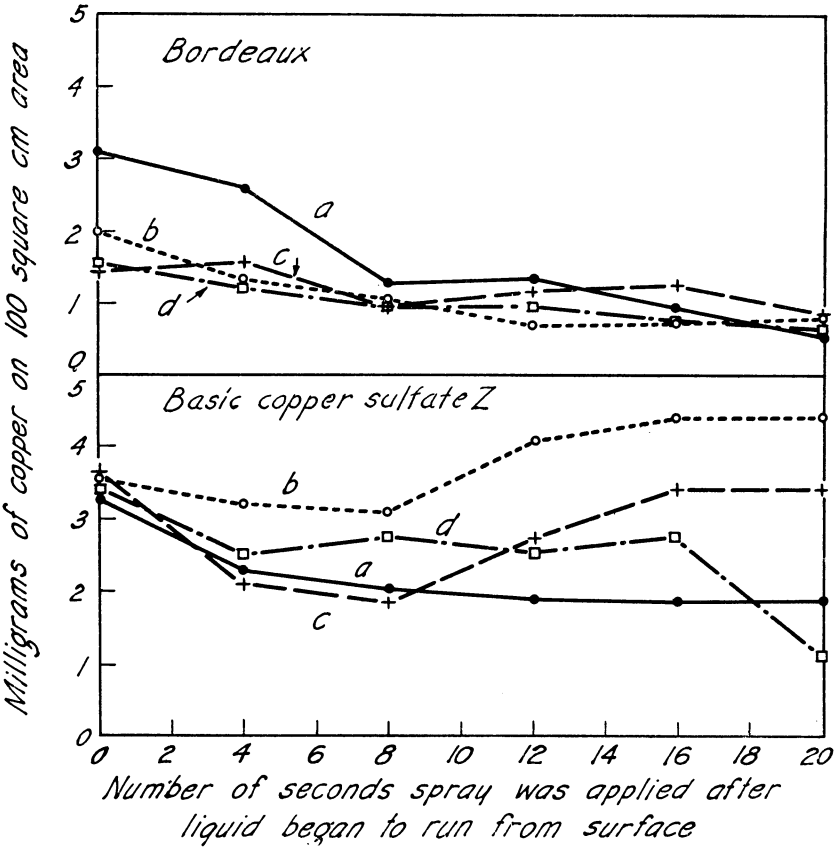

Fig. 5.—Effect of oil-containing supplements on the deposition of bordeaux and basic copper sulfate Z on cellulose nitrate surfaces: *a*, no supplement; *b*, 1.5 per cent supplement B; *c*, 1.5 per cent petroleum oil emulsified by ammonium oleate; *d*, 1.5 per cent petroleum oil emulsified by blood albumin.

WEATHER RESISTANCE

The standard program for preventing the peach-twig infection caused by *Coryneum beijerinckii* consists of a single spray applied in the fall after the leaves are off the trees. To remain effective against the disease, therefore, the fungicide must resist washing away by rains over a long period (as much as 100 days in some seasons).

Table 1, fourth column, shows the weather resistance (tenacity) of bordeaux with and without a supplement, and of the fixed copper fungicides with their respective supplements. The data for the vapor application were excluded from the analysis of variance because this material was applied to one plot only. On the whole, deposits by the vapor preparation resisted weatherings better than any of the other deposits. There was one exception: bordeaux with supplement B proved significantly more tenacious than basic copper sulfate A plus supplement A, or basic sulfate Z plus supplement B, and exhibited a strong tendency to resist weathering better than bordeaux without a supplement, or cuprous oxide plus supplement B.

CONTROL OF TWIG INFECTION

Twig infection, severe in 1942 and 1943, became too sparse for test purposes in 1944. According to the results in the fifth column of table 1, all materials

TABLE 2

EFFECTIVENESS OF COPPER FUNGICIDES IN CONTROLLING PEACH-TWIG INFECTION CAUSED BY *Coryneum beijerinckii*, 1945

Fungicide material, pounds per 100 gallons, and supplement used, expressed in per cent by volume	Average number of lesions on 100 twigs
Unsprayed	388
Bordeaux, 10–10–100	45
Bordeaux, 8–8–100; plus supplement B, 1 per cent	26
Basic copper sulfate A, 5–100; plus supplement A, 0.5 per cent	47
Basic copper sulfate Z, 6–100; plus supplement B, 1.5 per cent	43
Cuprous oxide, 1.5–100; plus supplement B, 1.5 per cent	67

reduced the disease greatly. Some differences in effectiveness, however, were apparent. For example, cuprous oxide appeared somewhat less effective than the other materials. On the whole, bordeaux (without supplement) gave better control than the fixed copper materials that were applied with the regular spray equipment. On the other hand, the vapor application of basic copper sulfate Z was, if anything, superior to bordeaux without supplement. Bordeaux containing supplement B (one year's tests), however, apparently surpassed all other materials.

Table 2 gives additional data secured in 1945, when the disease was moderately severe. Again, bordeaux with supplement B proved most effective and cuprous oxide least effective, whereas the control by bordeaux without supplement, by basic copper sulfate A, and by basic copper sulfate Z were of the same order of effectiveness.

Table 1 shows a lack of correlation between the amount of copper residue remaining on the twigs throughout the winter and the prevention of twig infection. For example, the average residues of bordeaux, 10–10–100, plus supplement B and basic copper sulfate A differed but little; yet the bordeaux treatment was the more effective. Although the amount of copper was less on trees sprayed with basic copper sulfate Z than on trees sprayed with bordeaux 10–10–100, control of twig infection differed little between the two. Basic copper sulfate Z, as will be recalled, contains 19 per cent zinc, which possibly helped to prevent the disease.

SUMMARY AND CONCLUSIONS

Studies herein reported concerned orchard and laboratory comparisons of bordeaux and three fixed copper fungicides (plus proprietary adhesive) with respect to their depositional, weather-resisting, and disease-preventive qualities.

In proportion to the amount of copper in the spray preparations, the fixed copper materials deposited 29 to 49 per cent more copper than bordeaux did. On the other hand, various preparations of bordeaux, some with and some without an oil-type supplement, differed but little in this respect.

Laboratory tests were designed to study the deposition of the various preparations on an artificial surface. The materials were applied to glass slides (coated with cellulose nitrate) by means of a precision applicator for the same length of time, and the amount of copper retained by the surface was determined. The liquid deposit of bordeaux was retained by the surface in direct proportion to the length of the application period up to the time the liquid began to run from the vertically held surface. If application was continued beyond runoff, however, the deposit decreased for a time, but then reached a stage where it remained approximately constant. Sometimes the loss of copper through runoff was 40 per cent of the deposit present just before runoff began.

Addition of an unemulsified petroleum oil to bordeaux increased the amount of liquid deposit and, consequently, the amount of copper deposit retained by the surface at the runoff stage. The increased deposit was evidenced by the longer period of application necessary to cause the liquid to run from the surface, and was probably due to one or both of two factors: a decrease in the wetting properties of the spray preparation, or an increase in the viscosity of that preparation.

Water suspensions of the fixed copper fungicides wetted cellulose nitrate less readily than did bordeaux. For this reason the amount of liquid retained by vertical surfaces at the runoff stage was higher than when bordeaux was used. When application was continued beyond runoff, the liquid deposit of the suspensions decreased much as did that of bordeaux. When, however, certain proprietary supplements or a supplement containing a petroleum oil emulsified with ammonium oleate was added to these suspensions, copper was retained by the surface in increasing amounts as application continued beyond the runoff stage. This situation was attributed to the preferential retention of the oil, and the copper suspended therein, by the sprayed surface. According to microscopic evidence, the flocculated phase of these preparations consisted of oil globules enclosing fungicide particles and droplets of water. When petroleum oil emulsified with blood albumin was added to suspensions of fixed copper fungicides, no flocculation occurred; that is, the copper particles were not wetted by the oil. Preferential retention of these particles by the sprayed surface, moreover, did not occur with such preparations.

Under the experimental conditions, the solid phase of bordeaux was not wetted by the supplements; neither was there evidence of preferential retention.

Loss of deposit by weathering was determined in the orchard. In three seasons when rainfall averaged 8.59 inches, the coefficients of tenacity were as follows: bordeaux, 0.239; bordeaux with supplement B, 0.348; basic copper sulfate A (vapor application), 0.345; cuprous oxide, 0.239; basic copper sulfate Z (applied with regular spray rig), 0.222; basic copper sulfate A, 0.207. All fixed copper preparations were combined with an oil-type supplement.

Though all preparations greatly reduced twig infection by *Coryneum beijerinckii,* bordeaux with supplement B and the vapor application of basic copper sulfate Z appeared somewhat more effective than basic copper sulfate A, basic copper sulfate Z, and cuprous oxide.

The amount of copper residue remaining on the tree throughout the infection period (the winter months) was not always correlated with the degree of twig-infection control. This finding suggests that some residues may have been more toxic to fungus spores than others; but the data are insufficient for conclusions.

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