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A STUDY OF STICKERS FOR LEAD ARSENATE SPRAYS ON FRUIT TREES

PHILIP GARMAN

Connecticut
Agricultural Experiment Station
New Haven

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Philip Garman

Adhesives for preventing removal of insecticides by rain from apple or other fruit foliage are important in Connecticut. "Stickers", as they are frequently called, increase the effectiveness of horticultural sprays and at the same time reduce the labor involved in growing fruit.

The main objective of this study has been to provide adequate spray control for Connecticut apples with fewer applications than are commonly recommended. Even one less spray in an orchard of any size means a substantial saving in travel by sprayer and tractor. A saving of two or three sprays would reduce the cost of production considerably. Economies in labor and gasoline, as well as reduced depreciation of machinery and tires, become more and more apparent as the number of sprays is reduced.

Opposed to the idea that spray schedules may be shortened by proper planning and use of improved materials, there is always the possibility of increased pest abundance necessitating *more* rather than fewer applications. There is also the problem of treating thoroughly trees that are growing rapidly. Surprisingly enough, these problems have not proved to be insurmountable. There is also the important consideration, always present, that *too much spray* may remain at harvest. Timing of sprays and the quantity of insecticide used per 100 gallons are the main factors in the solution of the latter problem.

A survey of New England spray calendars indicates a general need for more or heavier sprays within the first two weeks after petal fall, mainly for curculio and other insect control. Why not, then, increase the dose of insecticide and fungicide (if necessary) at this point, adding stickers and safeners as needed? Our experiments since 1939 have been along this line. Thus, instead of pink, calyx, several cover sprays, and several treatments for maggot, the plan calls for *the same amount of insecticide* or *fungicide* applied in three or not more than four sprays. Pink, calyx and one or two cover sprays are apparently all that are needed to control most Connecticut insects, provided adequate stickers and safeners are available. Ceasing all spray operations after June 15 provides a low residue on the fruit at harvest, and inclusion of adhesives and safeners insures continuous

[1]The Department of Analytical Chemistry of this Station has been responsible for all the chemical analyses reported herein. Without the help of Mr. C. E. Shepard and Dr. H. J. Fisher much of the work with stickers would have been impossible. It is a pleasure to acknowledge here their important contribution to this investigation. All photographs are the work of Mr. B. W. McFarland.

protection for fruit and foliage throughout the season. As intimated above, a sudden increase in the abundance of insects, such as curculio, apple maggot or others, may upset calculations. However, such phenomena often cause revision or extension of any spray schedule, so that it may be assumed with reasonable safety that a seven-spray schedule would do better in those times if increased to nine, or a four-spray schedule would do better if increased to five. There would still be a saving in the number of sprays if we reason in this manner.

Stickers for increasing the tenacity of lead arsenate should cause no increased spray burn. They should spread reasonably well and should provide a thick layer of poison on the fruit and foliage. Furthermore, they should not reduce the effectiveness of the spray ingredients, either insecticide or fungicide. The problem, therefore, involves more than a study of stickers or adhesives alone. It includes a study of spreaders and deposit builders to improve the nature and completeness of the spray. It should include consideration of safeners or materials to prevent arsenical or other spray injury to plant tissues, for increased spray injury often accompanies increased adhesion. However, because of the extent of such an investigation only minor consideration will be given here to spreaders and safeners.

A large number of materials have been advocated at one time or another for increasing the adhesiveness of lead arsenate or other spray materials. Some of them are effective, some have little effect, while some are actually detrimental from the standpoint of tenacity. Combinations of various stickers have also been frequently advocated and commercial preparations may contain more than one ingredient. Occasionally, very effective stickers have resulted from such combinations. The use of flocculants, like zinc sulfate, may also accompany a sticker, such as an oil, in order to increase the initial deposit as well as its tenacity. This has been a fairly recent development and the combinations are well known in the Northwest, where they originated, as "dynamite" sprays.

The list below shows what a wide variety of materials have been employed by entomologists and others.

1. Aluminum hydroxide, aluminum silicate, aluminum sulfate.
2. Bordeaux mixture.
3. Blood albumin.
4. Casein preparations (casein-lime, casein glue).
5. Clays (bentonite and others).
6. Ferric hydroxide, ferrous sulfate (with lime).
7. Flour (wheat, soybean, etc.) Soybean phosphatides.
8. Furfural with amines and acetones. U. S. Patents 2,146,257, 2,146,258.
9. Gels (alumina, silica).
10. Gelatin.
11. Glues and gums (casein glue, fish glue, dextrine, gum arabic, etc.)
12. Lime and combinations, such as lime and copper sulfate, lime and ferrous sulfate, lime and aluminum sulfate or zinc sulfate. Lime and sulfur, lime and oils.
13. Oils (fish, cottonseed, soybean, white mineral oil, etc.)
14. Resins (rosin residue emulsion, resin and oil).
15. Rubber compounds (rubber plus 20-30 per cent by weight of methyl ester of dehydro abietic acid). U. S. Patent 2,285,458.

16. Skim milk.
17. Soaps and combinations (soaps and clays; soaps and flour; soaps and zinc sulfate; soaps, zinc sulfate and oil).
18. Sodium silicate.
19. Starches (benzyl-ethyl starch).
20. Sugar and molasses.
21. Zinc sulfate.

Stickers are frequently discussed in the literature on insecticides. Typical of the comments are the following:

"Petroleum oils act as stickers as well as spreaders, and certain animal and vegetable oils such as fish oil, cottonseed and soybean oils are excellent adhesives. Casein, in the form of calcium caseinate or skim milk powder, is chiefly a sticker but also to a certain extent a spreader . . . . . Wheat flour and soybean flour are good stickers. Some bentonite clays become glue-like when wet and make good stickers." Entoma, 1941, p. 13.

"Adhesive agents or stickers as the name implies are those substances which function to increase the retention or tenacity of spray deposits. Certain of the materials used as spreaders and wetting agents may also function as adhesives, such as milk products, flour, gelatin, and blood albumin mentioned previously. These are hydrophyllic colloids, and apparently form a very tenacious coating upon the plant surfaces when dried. Similar in action although different chemically are the bentonites and other clays. It is the oils, however, that constitute the most important group of adhesive agents." Frear, Chemistry of Insecticides and Fungicides, 1942, pp. 193-194.

"Many wetting agents and emulsifiers are also good adhesives. Those materials are adhesives which become sticky, gummy, or varnish-like at high concentrations or upon drying in contact with the air. Soaps, gelatin, glue, gums, resins, casein, flour, Bordeaux mixture and certain oils are commonly used for their adhesive qualities. The so-called drying oils such as linseed oil, have been used to make arsenicals adhere to forest and shade trees for long periods to avoid the heavy expense of repeated applications . . . . . Adhesiveness varies with the nature of the surface. Some adhesives require a considerable drying period to set them properly before they are resistant to rainfall." Shepard in Chemistry and Toxicology of Insecticides, 1939, p. 171.

"Substances recommended as adhesives include soap, molasses, glue, size, glucose, resin, gelatin, saponin and sodium silicate." Wardle and Buckle in The Principles of Insect Control, 1923, pp. 80-81.

Stickers "are used primarily when the spray is to leave a deposit on the leaf which otherwise would be easily removed by rain, dew or wind and would therefore fail to protect the plant for the required length of time . . . . . To secure a good 'sticking' it is essential that the spray should be prepared so that the ultimate particle which adheres to the foliage should be as small as possible . . . . . Flour paste, starches of various kinds, gums such as gum arabic, dextrines (British gum) and crude treacle or molasses have all been prepared and used." Martin in Scientific Principles of Plant Protection, 1928, p. 51.

In the quotations from different authors above there is a notable lack of commitment regarding comparative efficiency of the stickers mentioned. With the exception of Frear, none give the relative merits of the different stickers. Frear specifically states that oils are better than others, but even he does not differentiate between the various kinds of oil. Since the work of Hood (1926), it has been generally accepted that oils *are* better than other stickers, but the problem studied by him included only adhesives for lead arsenate and was not complicated by fungicides in the spray mixture. For use on fruit, both insecticides and fungicides are required, so it would seem important to study the adhesive materials from the standpoint of the spray mixture as a whole in order to be able to select the best.

It has proved impossible in the scope of this work to test every product that has been mentioned as a spray adhesive. Glass slide tests supplemented by foliage washing experiments have cleared up some points regarding relative efficiency. The data obtained, we believe, tell some of the reasons why certain frequently mentioned stickers have not proved more effective in insect control.

It was found necessary to study the spray materials themselves without stickers in order to measure the increased adhesion supplied by the sticker materials.

LABORATORY EXPERIMENTS

The laboratory experiments consisted of glass slide tests and small scale foliage washing experiments with an improvised rain chamber. Evaluation by any one method proved difficult, especially where the tenacity of the different stickers was close or nearly equal. Several different techniques were therefore employed in the slide tests. These consisted mainly of dosage series such as (1) variable percentages of the sticker under consideration, (2) variable amounts of spray deposit with a constant amount of sticker, and (3) a variable amount of wash with other factors constant. Foliage tests consisted of a somewhat similar type of experiment based in part on visual examination where the deposits were readily seen, or on chemical analysis where there was any doubt concerning results. Concentrations several times those usually employed in the field were used deliberately in some experiments to exaggerate the effects of the sticker in the hope of evaluating it more readily.

Glass Slide Tests.

Methods.

The slides used in the laboratory work were 3 1/4 by 4 inch glass lantern slides, uncoated, or coated with cellulose nitrate. Uncoated slides were first carefully cleaned with soap, "Bon Ami" and water, then immersed for several minutes in a solution of approximately 1 per cent hydrochloric acid and 10 per cent alcohol. They were washed again, thoroughly rinsed and dried. After wiping off any residue from "Bon Ami" with paper towels, the slides were then dried over $CaCl_2$ before weighing. Weights were taken before and after spraying and again after washing. Spraying was accomplished by atomizing the spray into a settling tower for a definite interval, usually five seconds, and allowing the spray to settle for two minutes. This process was repeated three times in order to obtain a deposit of sufficient size for weighing. After removal from the spray tower, the slides were dried, weighed and washed. The washing was done by moving the slide back and forth 10 times each way in a four-gallon container of distilled water. After each stroke the slide was removed and the water shaken off. On completing the wash the slides were placed with the residue side up and air circulated over them with an electric fan. When dry, they were placed in racks over calcium chloride until final weights could be taken.

In order to check up on the actual removal of lead arsenate, the deposits were determined by chemical analysis in a few experiments. In the latter, two to four slides were sprayed at the same time (uniformity of the deposits was good enough to permit this procedure). Half were washed by the method described and half were left unwashed. All were then stripped of arsenate and analyzed for As_2O_3. Calculations of arsenic deposit and the amount removed were then possible.

In the case of coated slides, the slides were dipped in a 0.6 per cent solution of collodion cotton dissolved in butyl acetate and allowed to dry. After this, the spraying and washing procedure was the same as for plain slides.

The uniformity of results obtained is indicated in Table 1 which represents a sample series of tests. Residue weights were fairly uniform here and the amounts removed by the washing process were also consistent. Results appeared to be more uniform in mid-winter than in summer, possibly because of the more variable temperatures and humidities during the summer months.

Slides were sprayed in lots of four and the total weight on the four slides as well as the total weight lost from the four slides were used in computing percentages. The main difficulty encountered was in eliminating small amounts of weight variations which inevitably occurred from day to day. This was in the order of one to two tenths of a milligram per slide.

In the experiments, the following questions were considered.

1. Are coated slides preferable to uncoated ones?
2. What is the effect of variable amounts of stickers in the spray mixtures?
3. What effect will variable deposits have on the adhesion?
4. What can be learned from a variable wash on a constant spray deposit?
5. Which of the three methods (2, 3, or 4) will give the most reliable estimate of the adhesive under consideration?

Coated versus uncoated slides.

Slides coated with cellulose nitrate[1] and slides without any film were compared. Washing was uniform and the amounts per slide were approximately the same in each series. From these tests, results of which are shown in Figure 1 and Table 2, it appears that lead arsenate adheres slightly better to plain glass than it does to cellulose film. However, the differences are so small and the rate of residue removal following a standard wash parallels that of the cellulose film so closely that there seems to be no practical advantage in the coated slides. There was occasional loss from the coated slides, due to break-

[1] Pyralin.

TABLE 1. RESULTS OBTAINED FROM SPRAYING AND WASHING GLASS LANTERN SLIDES

Spray Time, 15 Seconds; Settling Time in Tower, 6 Minutes. Washed 20 Strokes in Distilled Water.

	Materials and dilution		Weight of spray on slides before washing mg.	Weight lost mg.	Per cent lost
(1)	Lead arsenate	3 gms.	1.6	.4	
	Dry flotation sulfur	5 gms.	1.7	.2	
	Bentonite	3 gms.	1.9	.3	
	Skim milk powder	.5 gms.	1.9	.5	
	Water	837 ml.			
	Totals		7.1	1.4	19.7
(2)	Same as (1) only		3.3	.5	
	Water	418 ml.	3.7	.6	
			2.9	.3	
			3.2	.3	
	Totals		13.1	1.7	12.9
(3)	Lead arsenate	6 gms.	6.3	1.4	
	Dry flotation sulfur	10 gms.	6.2	1.0	
	Bentonite	6 gms.	6.2	1.1	
	Skim milk powder	1 gm.	6.4	.9	
	Water	418 ml.			
	Totals		25.1	4.4	16.9
(4)	Same as (3) only		7.0	.9	
	Water	209 ml.	7.8	1.1	
			7.4	1.1	
			8.4	1.2	
	Totals		30.6	4.3	13.9

age of the film when washing, but the number of slide tests ruined thereby was small. On the other hand, it is possible to put a more even deposit on the coated slides because of the nature of the surface. Probably either coated or uncoated slides can be used successfully, but from experience with both, compared with removal of lead arsenate from apple leaves in our laboratory washer, it seems that neither is completely analogous to leaf surfaces. Except for the comparison of lead arsenate alone, all tests were made on uncoated slides.

TABLE 2. COMPARISON OF LEAD ARSENATE LOST FROM COATED AND UNCOATED GLASS PLATES

Coated, cellulose nitrate		Uncoated	
mg. per slide	mg. lost in wash[1]	mg. per slide	mg. lost in wash[1]
2.44	1.59	2.03	1.26
2.93	1.80	2.55	1.44
2.83	2.23	2.82	1.55
4.20	2.03	3.31	1.70
4.46	2.37	4.88	2.29
5.80	2.80	6.55	2.55
8.52	3.55	8.85	3.12

[1] 20 strokes in distilled water.

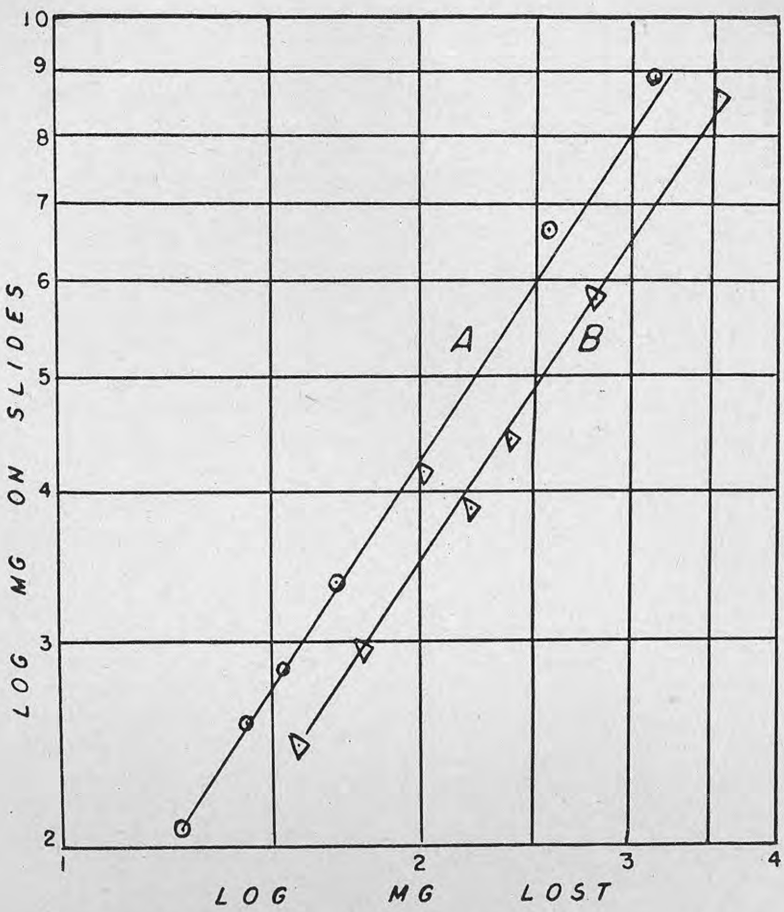

FIGURE 1. Data from Table 2 showing comparative results from spraying and washing coated and uncoated glass slides. A. Uncoated. B. Coated. Amount of wash uniform—20 strokes in each test.

Variable stickers: Lead arsenate constant, amount of solution constant, wash constant, but sticker materials varied.

In these tests, it soon became apparent that there were differences between adhesives. For example, on increasing the percentage of sticker, some materials showed a definite tendency to increase the tenacity of lead arsenate, while others at first increased the tenacity but then decreased it. Chemical analysis covering several lots confirmed these results. A few so-called "stickers" *removed the lead arsenate* faster than it was removed by the same wash from slides with no sticker (Figure 2).

The following materials were used and their behavior is described individually. Lead arsenate at the same concentration was used with

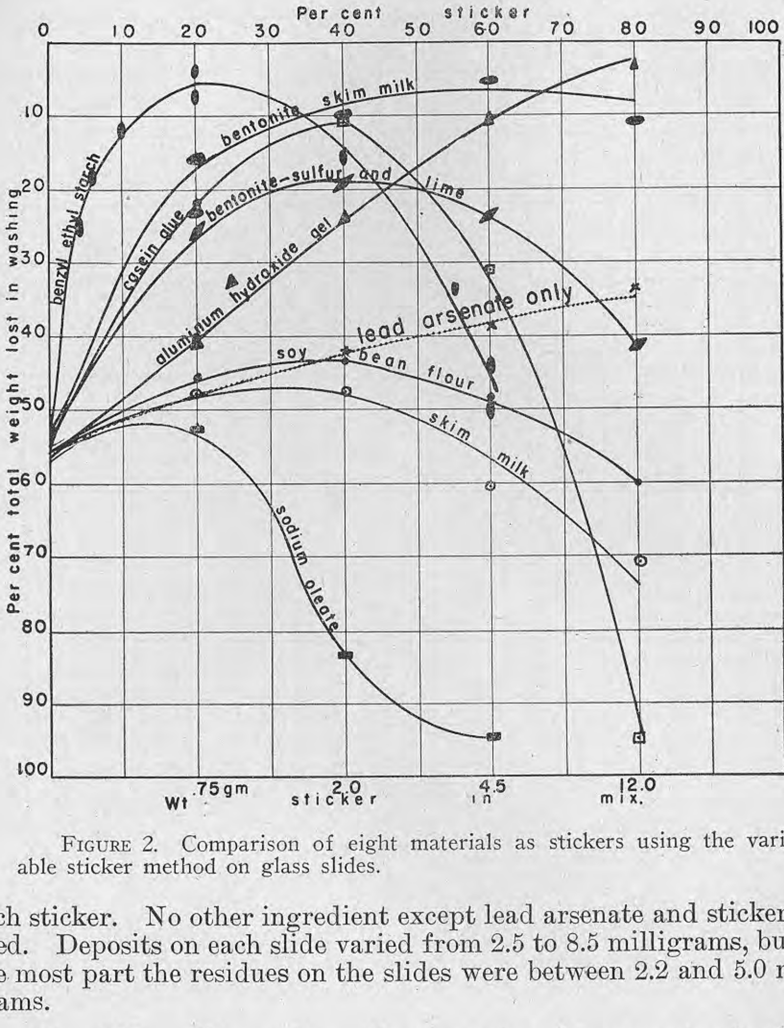

FIGURE 2. Comparison of eight materials as stickers using the variable sticker method on glass slides.

each sticker. No other ingredient except lead arsenate and sticker was used. Deposits on each slide varied from 2.5 to 8.5 milligrams, but for the most part the residues on the slides were between 2.2 and 5.0 milligrams.

(1) *Skim milk powder.* On increasing the amounts of milk in the mixture from 20 to 80 per cent of the total solids, there was first a slight rise in tenacity up to about 40 per cent, then a steady decline so that at 80 per cent more total weight was lost than was the case where no sticker was employed. The most favorable amount was about 40 per cent skim milk, 60 per cent lead arsenate.

(2) *Sodium oleate.* This showed only a very slight increase at first, then a sharp decline so that the 40 and 60 per cent levels were greatly reduced in adhesiveness over that of lead arsenate alone without any adhesive.

(3) *Casco waterproof glue*, fresh sample. This showed a very marked rise in tenacity up to 40 per cent of the total solids, but then

a sharp decline passing below the no-sticker level somewhere between 60 and 80 per cent.

(4) *Soybean flour.* This material appears to be slightly better than skim milk at the 40 per cent level but declines considerably at 80 per cent where it is slightly below the no-sticker level.

(5) *Benzyl ethyl starch.* This sticker seems to fit the pattern of the glues but the rise in adhesiveness is much more rapid at low concentrations. Thus, the greatest tenacity appears to be at about 20 per cent, if total weights are considered, and at 40 per cent, based on chemical analyses. There is, however, the same tendency for the total weight adhering to decline with added amounts, apparently indicating that some of the sticker comes off and may drag the arsenical with it.

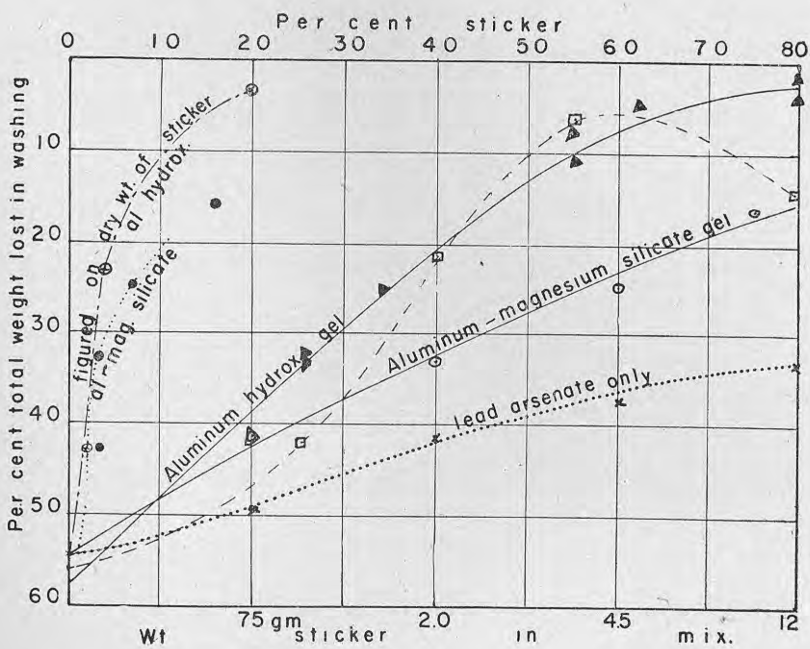

FIGURE 3. Comparison of two aluminum gels by the variable sticker method. The dash line gives results of chemical analyses in the lead arsenate, aluminum hydroxide test. Glass slide tests.

(6) *Aluminum hydroxide gel.* Careful and repeated tests and analyses indicate that aluminum gel increases the adhesiveness rather slowly as the amount is increased, but there is little or no sign of decrease when the gel is increased to 80 per cent of the total solids in suspension. The decline of tenacity noted in the chemical analyses in this case (Figure 3) is probably due to great difficulty in removing the materials from the slides in the acid baths.

(7) *Talc-lime.* Two series of talc-lime combinations were tried. There was some indication that there was a steady rise with the 20 per cent talc-80 per cent lime employed at different percentages of the total weight and that the 20 per cent talc is better than 80 per cent talc as a sticker.

(8) *Bentonite-lime.* Four series (20 slides each) of bentonite-lime were run which showed similar tendencies to the talc-lime sticker. It also showed considerably better adhesiveness for the 20 per cent bentonite over the 80 per cent mixture. These differences did not hold up in foliage tests.

(9) *Bentonite-casein, bentonite-flour, bentonite-skim milk.* These three combinations were compared and the bentonite-casein and bentonite-skim milk gave best results. A series of dilutions sprayed on slides indicated, furthermore, that the amounts of casein or skim milk are important, for an 80 per cent bentonite-20 per cent skim milk proved to be a much better sticker than 80 per cent skim milk and 20

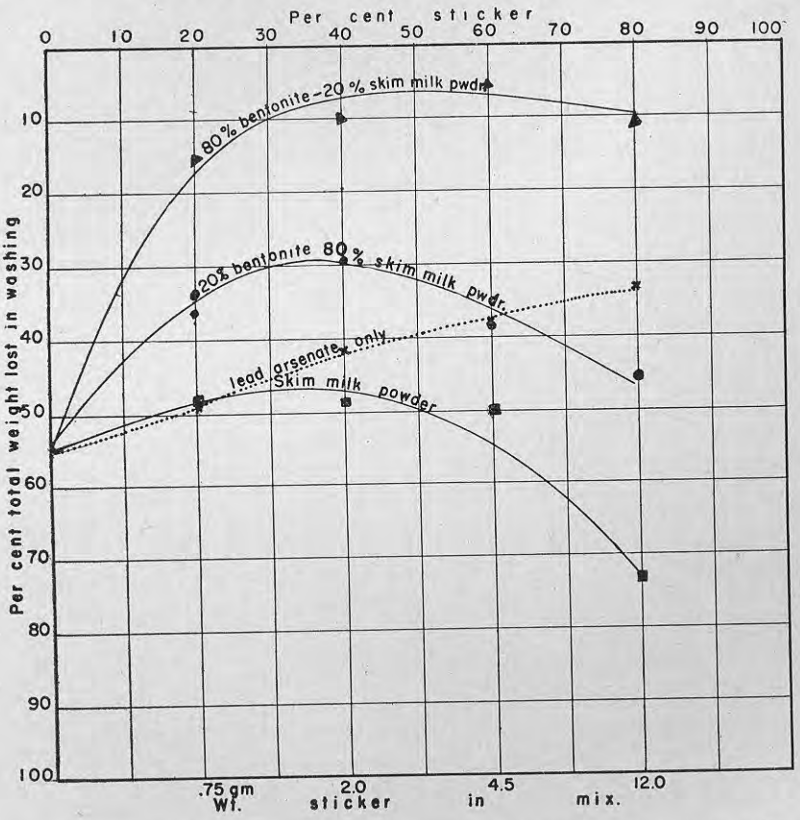

FIGURE 4. Comparison of lead arsenate with and without skim milk, and lead arsenate plus bentonite and skim milk in different proportions. Variable sticker tests on glass slides.

per cent bentonite (Figure 4). When skim milk or casein is mixed with bentonite, flocculation occurs, which may or may not be the result of a chemical combination between the protein and clay.

(10) *Casein-lime.* This combination used as a sticker proved to be better with more casein than lime in the mixture. The commercial preparations sold consist of about 80 per cent lime and 20 per cent casein. Slide tests indicate that four parts casein and one part lime provide much better adhesiveness than the reverse. A washing test with potted peach trees gave similar results.

(11) *Aluminum sulfate-lime.* Combinations of aluminum sulfate and lime appeared to follow the adhesion pattern of bentonite-lime. Four parts lime-one part aluminum sulfate adhered better in these tests than a mixture of four parts aluminum sulfate and one part lime.

(12) *Lead arsenate only.* Starting with the standard dose of lead arsenate, amounts of the same insecticide were added, equal to the amount of sticker used in preceding experiments. The rise in adhesion appears to be a function of the amount on the slides, as will be shown later in experiments with variable deposits. The curve tends to cut across many of the curves obtained when higher concentrations of stickers were used.

Commercial preparations.

Acco. A commercial casein-lime, which showed better adhesiveness than many commercial and other preparations, was consistently better than lead arsenate.

Alkote. This sticker, still in the experimental stage, showed a steady rise in adhesion as the amounts increased. The general picture for glass slides is similar to that of aluminum gel.

Filmfast. This sticker showed a similar tendency to Alkote, but the rise was not so rapid. Chemical analysis, however, indicated a greater tenacity for lead arsenate towards the end of the series (80 per cent sticker) than was apparent from the total weights given in Figure 5. According to analysis, page 159, "Filmfast" contains 45 per cent skim milk, 36 per cent bentonite. From Figure 4 it would appear that the proportion of skim milk is too high in this product for best adhesion.

Grasselli Spreader-Sticker. The sample used may not be entirely typical of the product, but showed rather poor results compared with other stickers. There was only a slight rise in adhesion at about 10 per cent and then a very rapid and steady decline. Beyond 10 per cent, the tenacity was far below the no-sticker level.

Orthex. There are two and possibly more stickers that have been marketed under this name. The one used here is a paste or thick paint. A steady rise in tenacity up to about 40 per cent was noted,

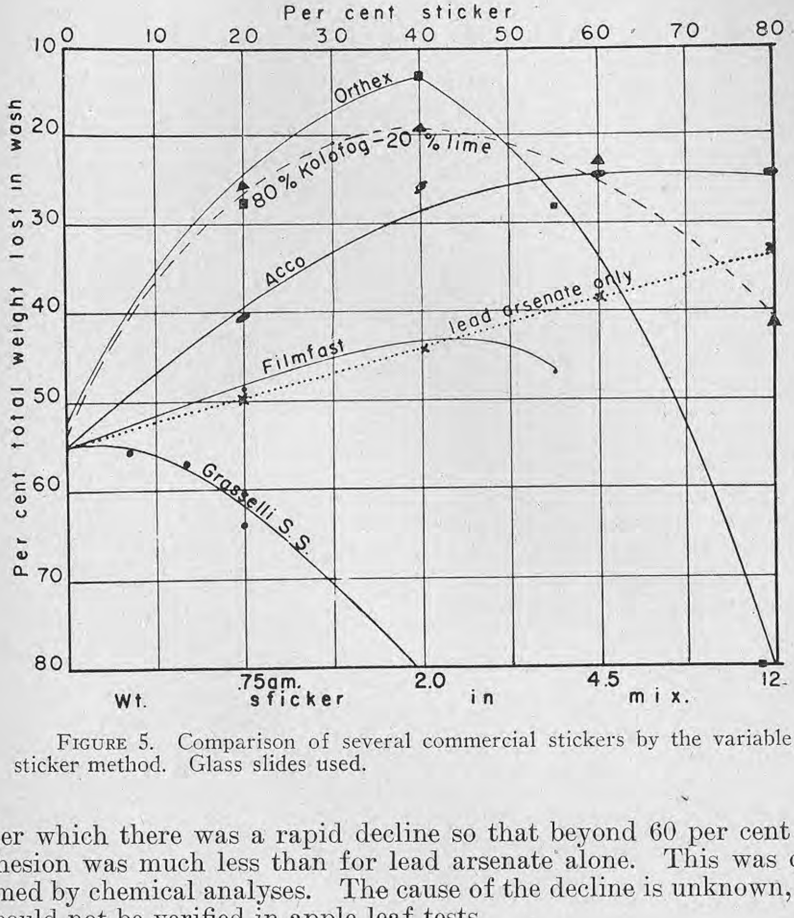

FIGURE 5. Comparison of several commercial stickers by the variable sticker method. Glass slides used.

after which there was a rapid decline so that beyond 60 per cent the adhesion was much less than for lead arsenate alone. This was confirmed by chemical analyses. The cause of the decline is unknown, but it could not be verified in apple leaf tests.

Kolofog-lime. Kolofog is a trade name for fused bentonite-sulfur. It is not generally sold as a sticker, but its value for this purpose is apparent. Two series of slide tests gave a slow rise in adhesion as the percentage of sticker was increased. The tests also indicated that bentonite-sulfur is beneficial between 40 and 60 per cent of the total solids but was not so good beyond 60 per cent. As a practical application, this would indicate that, as a sticker, 2 to 4 pounds of Kolofog-lime per 100 gallons is all that is needed. Foliage tests indicate that too much lime removes the mixture from the foliage faster than where less is used and that an excess of lime over Kolofog is not beneficial. In this respect the Kolofog-lime resembles casein-lime.

Tables 3 to 7 give the total weights of materials placed on uncoated slides and the amount removed with the 20-stroke method employed throughout these tests. The data are shown graphically in Figures 3 to 5.

TABLE 3. GLASS SLIDE TEST
Aluminum Gel
1943

Material	Total weight on 4 slides	Loss in grams	Per cent loss
Lead arsenate + Alugel 25%	6.4 mg.	2.1 mg.	32
Lead arsenate + Alugel 40%	5.5 mg.	1.3 mg.	23
Lead arsenate + Alugel 55%	5.5 mg.	.6 mg.	10
Lead arsenate + Alugel 80%	4.4 mg.	.5 mg.	11

TABLE 4. GLASS SLIDE STICKER TESTS
Orthex
1943

Material	Total weight on 4 slides	Loss in grams	Per cent loss
Lead arsenate	4.8 mg.	2.6 mg.	54.1
Lead arsenate + 20% Orthex	6.8 mg.	1.9 mg.	27.9
Lead arsenate + 40% Orthex	7.6 mg.	1.1 mg.	14.4
Lead arsenate + 60% Orthex	9.4 mg.	3.1 mg.	36.9
Lead arsenate + 80% Orthex	15.0 mg.	13.5 mg.	89.9

TABLE 5. GLASS SLIDE STICKER TESTS
Filmfast
1943

Material	Total weight on 4 slides	Loss in grams	Per cent loss
Lead arsenate	5.6 mg.	2.9 mg.	51.7
Lead arsenate + 20% Filmfast	6.6 mg.	2.6 mg.	39.2
Lead arsenate + 40% Filmfast	7.4 mg.	2.9 mg.	37.8
Lead arsenate + 60% Filmfast	10.3 mg.	3.5 mg.	33.9
Lead arsenate + 80% Filmfast	15.3 mg.	4.9 mg.	32.0

TABLE 6. GLASS SLIDE STICKER TESTS
Alkote
1943

Material	Total weight on 4 slides	Loss in grams	Per cent loss
Lead arsenate	4.5 mg.	2.2 mg.	48.8
Lead arsenate + 20% Alkote	5.8 mg.	2.5 mg.	43.1
Lead arsenate + 40% Alkote	4.8 mg.	.8 mg.	17.0
Lead arsenate + 60% Alkote	6.1 mg.	0.0	0.0
Lead arsenate + 80% Alkote	7.4 mg.	0.0	0.0

TABLE 7. GLASS SLIDE STICKER TESTS
Benzyl Ethyl Starch
1943

Material	Total weight on 4 slides	Loss in grams	Per cent loss
Lead arsenate	4.5 mg.	2.5 mg.	55
Lead arsenate + benzyl ethyl starch 10%	4.9 mg.	.6 mg.	12
Lead arsenate + benzyl ethyl starch 20%	5.3 mg.	.3 mg.	5
Lead arsenate + benzyl ethyl starch 40%	6.8 mg.	1.4 mg.	20
Lead arsenate + benzyl ethyl starch 60%	9.3 mg.	4.2 mg.	50

Variable deposits on slides: Concentration of spray mixture constant, wash constant.

From preceding tests the optimum concentration for the sticker was generally utilized and the amounts per slide were then varied. Data were plotted and compared on double-log cross-section paper (Figure 7). Sprays such as lead arsenate alone showed a rather steep slope, indicating a smaller per cent removal as the deposit increased. When flotation sulfur (5 pounds per 100 gallons) was added, the rate of removal was much faster and the slope not so steep. The *percentages* removed by washing the flotation sulfur and lead arsenate combination were approximately the same, regardless of the amounts per slide. This is shown by the slope which approximates a 45° angle. The tests indicated that lead arsenate adhered slightly better than either lead arsenate-flotation sulfur or lead arsenate-flotation sulfur and lime. When lime alone was added there appeared to be a significant advantage over lead arsenate alone. Unsuccessful attempts to verify the latter finding for apple foliage will be described later. Lime-lead arsenate combinations were also subjected to variable wash experiments (Figure 6) which indicated that the amount of wash may have been too little with those materials to show much difference in the variable deposit tests.

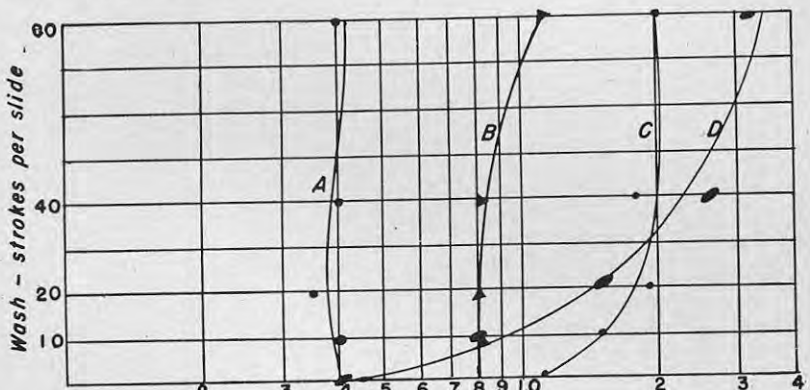

FIGURE 6. Rate of loss from glass slides with variable amounts of wash. The rate of loss appears to be much greater here in combinations C and D than for either A or B.

A. Lead arsenate, Fermate, bentonite, skim milk, and oil. Average deposit 26.8 mg.
B. Lead arsenate, flotation sulfur, bentonite, skim milk. Average deposit 42.9 mg.
C. Lead arsenate, flotation sulfur. Average deposit 33.1 mg.
D. Lead arsenate, flotation sulfur and lime. Average deposit 55.5 mg.

Adhesives such as bentonite-skim milk displaced the curve strongly to the left (Figure 7), indicating much better adhesion than was obtained with lead arsenate plus flotation sulfur or lead arsenate alone.

Adhesion of bentonite-skim milk with either lead arsenate or lead arsenate and flotation sulfur corresponds with apple foliage tests.

Owing to the difficulty of obtaining skim milk powder, attempts were made to find other spreader materials which combine with bentonite without reducing the adhesive qualities of the mixture. Flour, lime, and Ultrawet, a commercial spreader, were unsuccessful. Gelatin and casein, however, were equal to the skim milk powder. A commerical deposit builder was combined successfully.

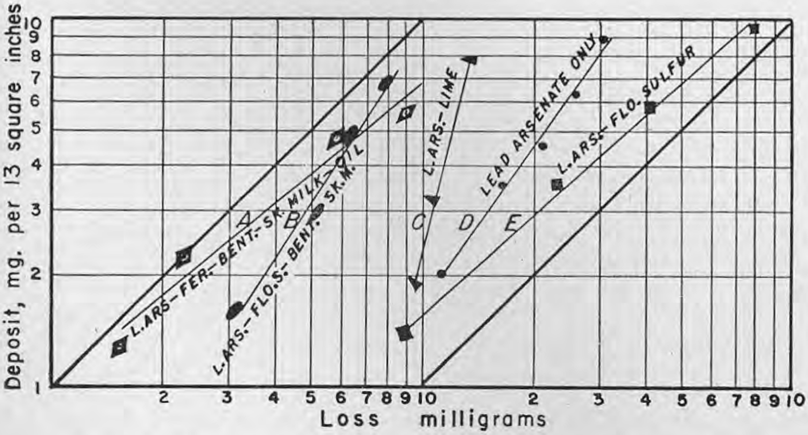

FIGURE 7. Loss of weight in tests with various spray combinations, showing relation to the amounts deposited on the slides. A slope steeper than the 45-degree angle indicates a lower loss as the deposit increases. Note position of lead arsenate and lime, and compare this with Figure 6 showing greater loss of mixtures containing lime with increased amount of wash. Combinations A and B are field formulae and show definite improvement in adhesion. Amount of wash, 20 strokes.

Tests with lead arsenate, Fermate, bentonite, skim milk and oil, all in one mixture, showed only slightly better adhesion than the combination of lead arsenate and flotation sulfur with bentonite-skim milk sticker. Comparison of lead arsenate, Fermate, bentonite, skim milk and the same combination with aluminum hydroxide gel in place of bentonite showed very little difference between the two.

Variable wash: Deposits uniform, sticker constant.

Several experiments were conducted with variable washing in an attempt to differentiate between stickers which could not be evaluated easily by the preceding method. Results plotted on semi-log paper are shown in Figure 6. It was difficult to place entirely uniform deposits on the slides, so that comparisons between the materials can be made only with some reservations. About the only differences between the variable wash and the preceding variable deposit tests seemed to be in the more definite crossover that occurs with lead arsenate, flotation sulfur and lime combined and the lead arsenate and flotation sulfur.

With a variable wash method it seems better to place more dependence on the slope of the curves (Figure 6) than on their actual displacement to the left or right. The line representing lead arsenate, bentonite, skim milk and oil is nearly vertical, indicating little or no additional removal with increased amounts of wash. Foliage tests with this formula, however, showed considerable removal from apple leaves when washed in the rain chamber. This is probably due to the very noticeable flaking from the leaf surfaces which could not be obtained on the glass slides. Final evaluation here obviously should not be made without foliage tests. The flaking was easily prevented by substituting soybean oil for mineral oil in the formula.

Discussion of slide results.

Study of the three methods for evaluating adhesiveness of spray materials seems to show that the variable sticker type of test is suitable for determination of the optimum quantity needed for maximum adhesion. There seems to be no particular advantage in using variable deposits except to check doubtful stickers or to compare those that are too nearly identical for evaluation by the variable sticker method. The variable deposit and the variable wash methods are useful where there are a number of sticker components such as spray mixtures often contain. Here the slope of the curve may tell something of value.

Of the different materials tested for holding on lead arsenate, the best appeared to be aluminum hydroxide gel, Kolofog-lime, bentonite-skim milk, and Orthex. Benzyl ethyl starch is very promising and Alkote is good. The first three are all alumina gels or contain alumina gels. Oils may be added to any of the gels to increase their adhesion. It is apparent, from the tests, that spray mixtures containing bentonite-skim milk adhere much better than the same mixtures containing lime or soybean flour or skim milk alone. It is also apparent that oil added to the bentonite-skim milk and Fermate increases the adhesiveness, for the curves are moved consistently to the left with both variable wash and variable deposit methods. As already stated, none of the results correspond fully with foliage tests and some of them may be actually misleading if not compared carefully with foliage washing experiments. For the most part, however, results of slide and foliage tests are in reasonable agreement. It appears to be entirely practical to eliminate poor stickers from the results of glass slide tests alone. The main points of difference so far, between foliage and slide tests, have resulted from (1) the difficulty of obtaining results comparable to long weathering in the field, (2) the tendency of some materials such as hydrated lime or Fermate-bentonite, skim milk and mineral oil to flake off from the leaves but not from slides. Wherever flaking from the foliage occurs, results obtained from slide washing experiments will be *much better* than results from the same sprays used on foliage. The generally better adhesion to glass than to leaves with the materials and methods employed is illustrated in Figures 17 and 18. In each case the deposit is given for the same area on both leaves and slides. The leaves were washed uniformly in a rain chamber, the slides by stroking back and forth in distilled water as described on page 112. In three of the four tests there was much faster removal of the same spray from leaves washed in a rain chamber.

Foliage Experiments.

Methods.

Small Baldwin apple trees grown in eight-inch pots were first used, but proved too bulky to handle conveniently, and small shoots, approximately six inches high, placed in water bottles were substituted. Several of the shoots were sprayed at a time in a tower (Figure 21) at constant pressure. Samples for analysis were taken before and after washing, using a punch to remove a disc 1 square centimeter in area (Figure 20). Washing was accomplished with an overhead sprinkler installed in an ordinary oil drum (with bottom removed) raised about 1 foot from the floor on legs (Figure 21). The rate of flow was adjusted to 2 gallons per minute and the pressure from the city main reduced to 20 pounds. Shoots to be sprayed were placed upright in water bottles on a turntable constructed from a 1/8 horsepower motor and speed reducing gear (Figure 21). A large number of visual tests were handled in this outfit. The method is very simple

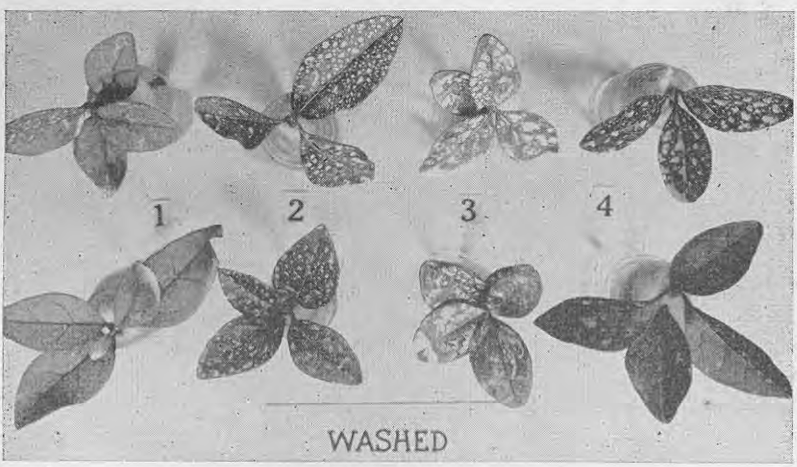

FIGURE 8. Laboratory sticker test.

Privet leaves sprayed uniformly and washed in a laboratory rain chamber delivering 2 gallons per minute. Period of wash 1 hour. Upper row unwashed. Paired whorls with same visible deposit before wash.

Basic formula: lead arsenate 3 gms., flotation sulfur 3 gms., water 250 ml. to which was added:

1. Alkote 3 gms.
2. Aluminum gel 3 gms.
3. Kolofog and lime 3 gms. each.
4. No sticker.

and, for sprays in which the deposit is not masked by oils or other materials so that the deposit is readily seen, is satisfactory. For small differences, however, or differences not easily seen chemical analysis appears to be necessary. All tests for amount of deposit by given sprays were by chemical analysis.

Visual foliage and fruit tests.

Visual foliage tests with the washing apparatus described were run in series of four or five shoots, since it was possible to wash the entire lot at one time, thereby avoiding possible discrepancies due to unequal washing. Shoots were paired before washing and one was held without washing for comparison after the operation was complete. Both privet and apple leaves were used and several lots of small green apples were also sprayed and washed.

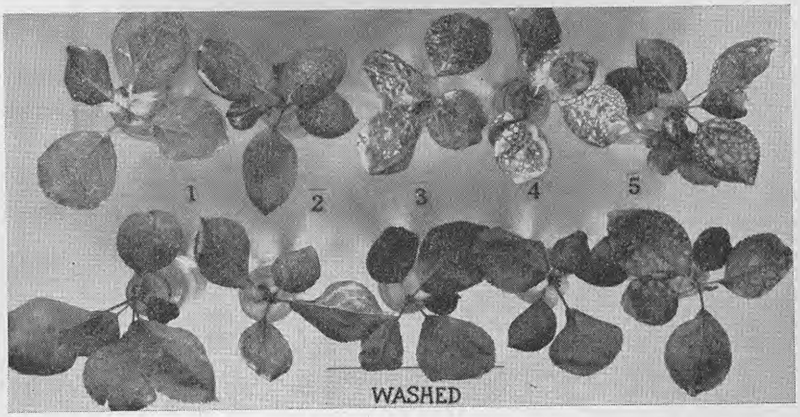

FIGURE 9. Laboratory sticker test.

Apple spurs sprayed uniformly and washed in a laboratory rain chamber delivering 2 gallons per minute. Period of wash 1 hour. Upper row unwashed. Paired spurs with same visible deposit before wash.

Basic formula: lead arsenate 3 gms., water 205 ml. to which was added:

1. Wheat flour 2 gms. (40%)
2. Filmfast 4.5 gms. (60%)
3. 80% talc-20% lime, 4.5 gms. of mixture
4. 20% talc-80% lime, 4.5 gms. of mixture.
5. No sticker.

Note removal of talc-lime combination.

Test No. 1. Soybean flour, Orthex, aluminum gel and Alkote were compared. Aluminum gel and Alkote appeared to be better than the others. (See Figure 10.)

Test No. 2. Orthex (40 per cent), soybean flour, sodium oleate, skim milk powder and bentonite-lime were compared. Orthex seemed to be the best.

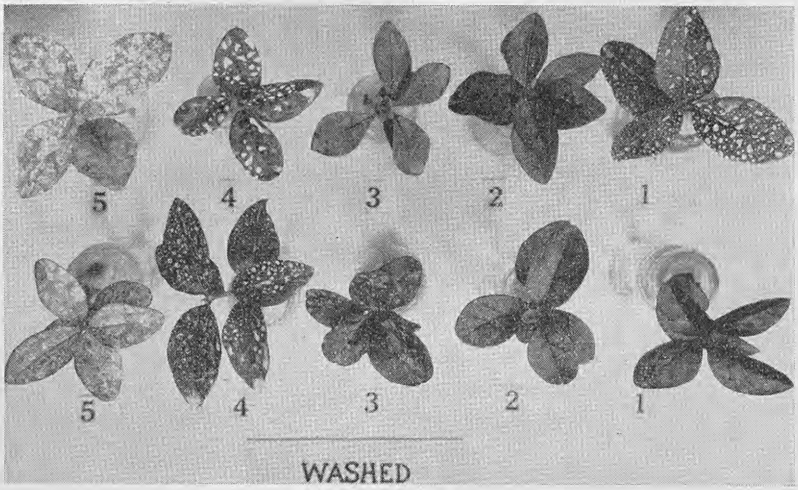

FIGURE 10. Laboratory sticker test.

Privet leaves sprayed uniformly and then washed in a rain chamber delivering 2 gallons per minute. Period of wash 1 hour. Upper row unwashed, lower row washed. Paired whorls with same visible deposit before washing.

Basic formula: lead arsenate 2 gms. to 205 ml. to which was added:

1. No sticker—lead arsenate only.
2. Soybean flour 4.5 gms.
3. Orthex 3 gms.
4. Aluminum hydroxide gel 4.5 gms.
5. Alkote 4.5 gms.

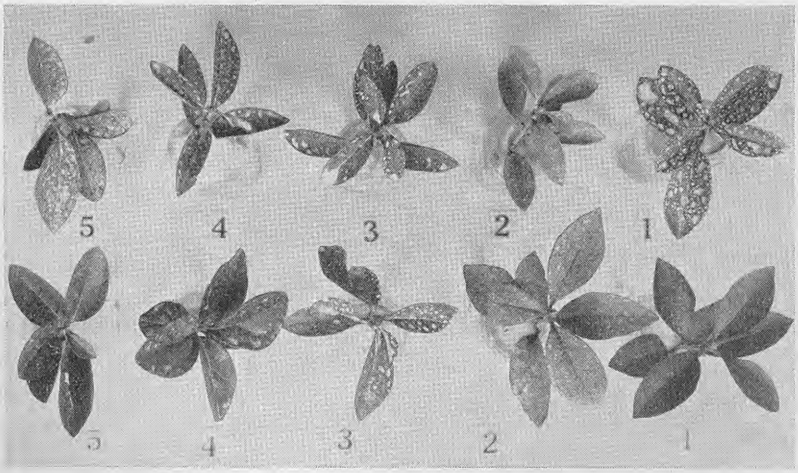

FIGURE 11. Laboratory sticker test.

Privet leaves sprayed uniformly and then washed in a rain chamber delivering 2 gallons per minute. Period of wash 1 hour. Upper row unwashed. Paired whorls with same visible deposit before wash.

Basic formula: lead arsenate 2 gms. to 205 ml. to which was added:

1. No sticker—lead arsenate only.
2. Alkote 60 per cent of total solids in mixture.
3. Aluminum hydroxide gel 60 per cent of total.
4. Benzyl ethyl starch 60 per cent of total.
5. Filmfast 80 per cent of total.

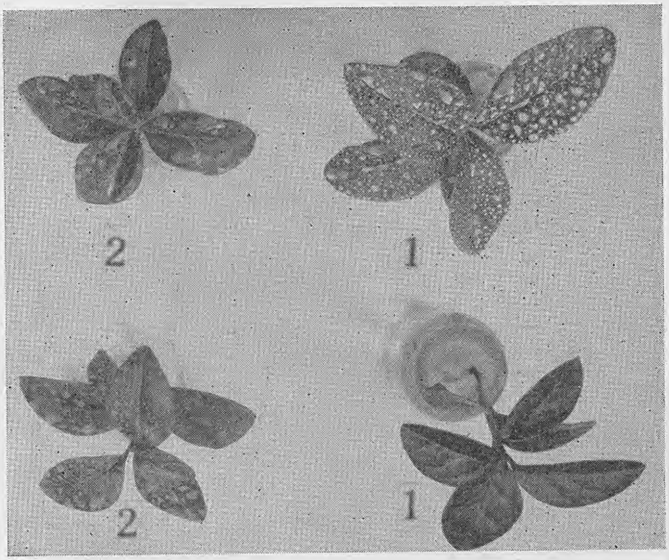

FIGURE 12. Laboratory sticker test.

Privet leaves sprayed uniformly and then washed in a rain chamber delivering 2 gallons per minute. Period of wash 1 hour. Upper row unwashed. Paired whorls with same visible deposit before wash.

1. Lead arsenate 3 gms. to 205 ml.
2. Same plus lime sulfur 8 ml., soy flour ½ gm. and manganese borate ¼ gm.

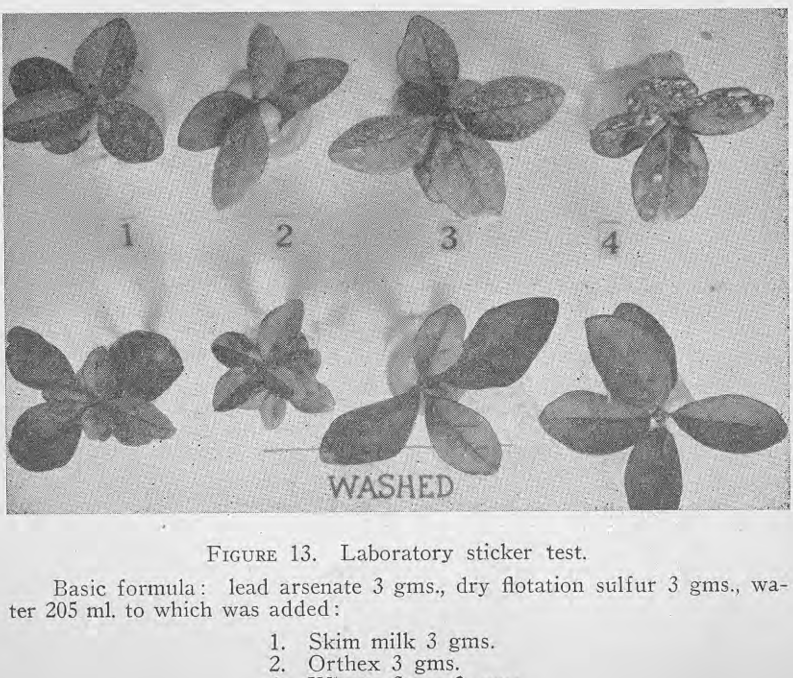

FIGURE 13. Laboratory sticker test.

Basic formula: lead arsenate 3 gms., dry flotation sulfur 3 gms., water 205 ml. to which was added:

1. Skim milk 3 gms.
2. Orthex 3 gms.
3. Wheat flour 3 gms.
4. Filmfast 3 gms.

Test No. 3. Alkote, aluminum gel and Kolofog[1] were compared. All three seemed to be about equal, with the advantage in favor of Alkote and Kolofog. (See Figure 8.)

Test No. 4. Wheat flour, Filmfast, and talc-lime (two formulae, see Figure 9) were compared on apple leaves. None adhered perceptibly better than lead arsenate alone.

Test No. 5. Several series with the special curculio spray (10 pounds hydrated lime, 3 pounds lead arsenate to 100 gallons) were run with a view to finding the best adhesive material for this spray. Fish oil, Alkote, Orthex, Kolofog, and aluminum sulfate were used. Aluminum sulfate did not equal the four other materials, and the more effective concentrations of the latter appeared to be as follows:

Fish oil	1 quart to 100 gallons.
Alkote	8 pounds to 100 gallons.
Orthex	8 pounds to 100 gallons.
Kolofog	4 pounds to 100 gallons.

It was apparent from comparisons in which the lime was reduced to less than 10 pounds per 100 gallons that the sticking properties of the

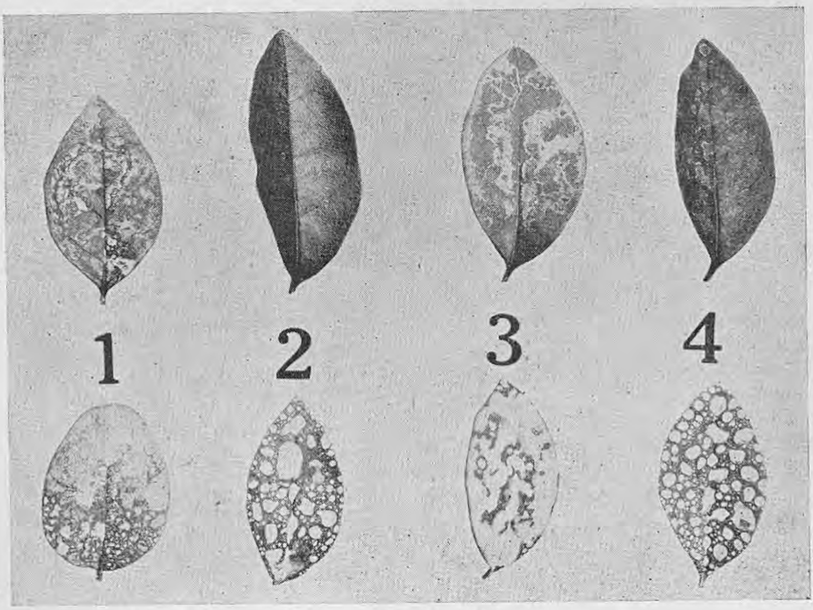

FIGURE 14. Laboratory sticker test.

Privet leaves sprayed with different combinations of sprays and washed in a laboratory rain chamber delivering 2 gallons per minute. Wash period one-half hour. Top row washed, lower row unwashed. Paired leaves with the same visible deposit before washing.

1. Lead arsenate 3 gms., bentonite 3 gms., flotation sulfur 3 gms., casein 1 gm., water 205 ml.
2. Same except wheat flour 1 gm., substituted for casein.
3. Same with skim milk 1 gm., substituted for casein.
4. Same with lime 1 gm., substituted for casein.

[1] Bentonite-sulfur.

mixture were much improved. This was especially noticeable in the case of Kolofog and was probably due to the flaking action of excess lime.

Test No. 6. This was a test mainly for determining the best spreaders to use with bentonite. Casein, wheat flour, skim milk, and lime were compared. Casein and skim milk are outstanding in this test, as will be seen from the photograph (Figure 14).

Test No. 7. Oils for combining with Fermate were considered here. Preliminary mixing gave considerable separation of oil-Fermate unless an emulsifier was employed for the oil. Bentonite-skim milk and aluminum gel-skim milk were used. Soybean oil and white mineral oil were compared. According to visual results (Figure 15),

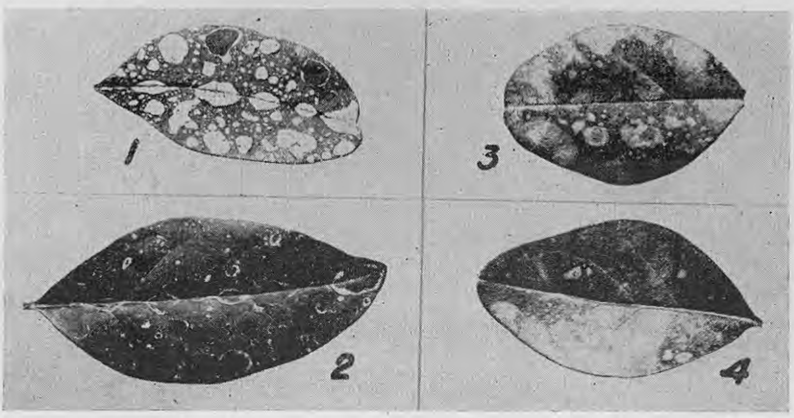

FIGURE 15. Washing experiment with spray mixtures on privet leaves. Leaves 2 and 4 washed one-half hour in rain chamber at 20 to 21 lbs. pressure. Rate 2 gallons per minute.

Nos. 1 and 2. Lead arsenate—bentonite—skim milk—Fermate—mineral oil.

Nos. 3 and 4. Lead arsenate—aluminum gel—skim milk—Fermate—mineral oil.

Note better adhesion of No. 4 and evidence of flaking in Nos. 1 and 2.

soybean oil was much better than mineral oil. Much flaking of the mixture from the leaf surfaces was noted in all tests with bentonite-skim milk-mineral oil. Considerably less was seen where soybean oil was substituted. Aluminum gel at the same rate as bentonite gave much less flaking and appeared to be satisfactory when combined with mineral oil as well as soybean oil.

Test No. 8. This was a visual test on green apples (Figure 16) using the same procedure as with leaves. Both rows A and B had equal deposits before washing. The illustration shows a notably lower deposit remaining in numbers 2 and 3 than in 4 and 5. It is apparent that skim milk at the dosage used cut down the amount deposited in the beginning and failed to hold it on during the washing period.

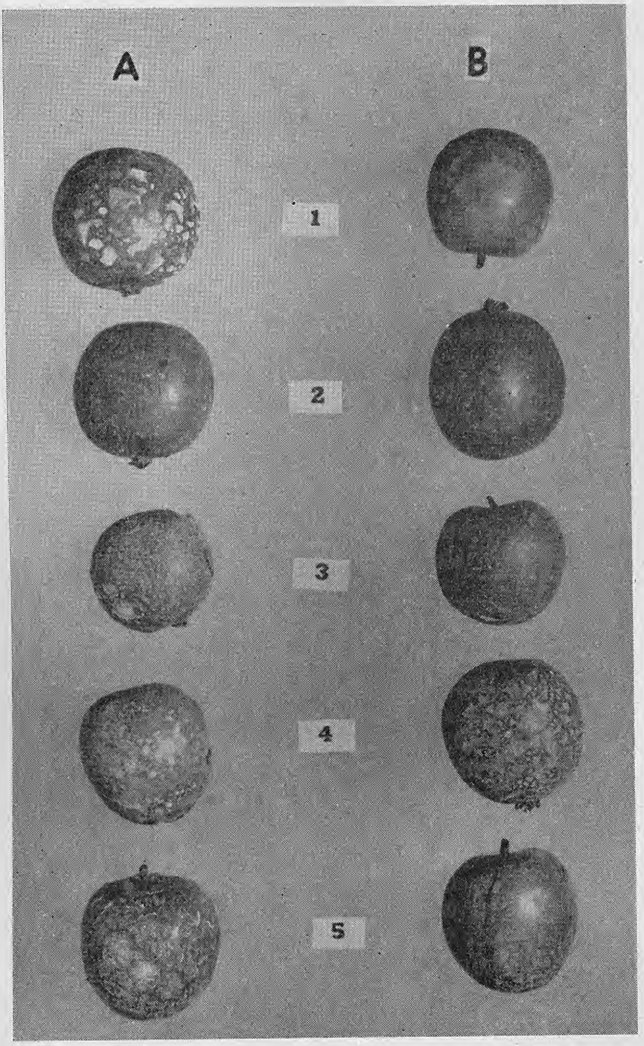

FIGURE 16. Row A, unwashed. Row B, washed one hour in washer delivering two gallons per minute.

Each pair of apples sprayed for 10 seconds in a spray tower; both with the same visible deposit before washing.

1. Lead arsenate 3 gms., water 205 ml.
2. Lead arsenate 3 gms., skim milk powder 2 gms., water 205 ml.
3. Lead arsenate 3 gms., commercial spreader-sticker 4.5 gms., water 205 ml.
4. Lead arsenate 3 gms., aluminum hydroxide gel 4.5 gms., skim milk powder .5 gm., water 205 ml.
5. Lead arsenate 3 gms., commercial calcium caseinate 4.5 gms., water 205 ml.

To summarize: Visual foliage tests indicated that aluminum gel, Alkote, Orthex, Kolofog, bentonite-skim milk, and oils were outstanding. Soybean oil was much better than mineral oil for combining with skim milk and bentonite. Field observations in 1943 support these results.

Variable stickers: Wash constant.

Several tests along this line were run in order to learn if the decline in adhesion with greater sticker concentrations, noted in slide tests, could be duplicated on apple foliage. The results indicate that there may not be the same relation between increased percentages of sticker and the amounts removed, as occurred in the slide experiments. In these tests, Orthex at 40 and 80 per cent of the total solids in suspension gave much better adhesion than Alkote, aluminum gel or Filmfast, which could possibly have been predicted from the fact that Orthex contains some oil. While there are not any tests comparing Orthex with other oil stickers, a field experiment in 1943 on small Wealthy trees gave much better adhesion for aluminum hydroxide gel plus white oil (tank emulsified) with lead arsenate and flotation sulfur than Orthex did with the same materials.

Variable deposits: Wash constant.

With any spray material, it is useful from the standpoint of insect control to know how much remains after a rain, for it is what is left that is important. A material that gives an initial deposit of 5 mg. lead arsenate per 50 sq. cm. and is weathered to .7 mg. by rain is obviously not worth as much as one which deposits 2.5 mg. and weathers to 2 mg. Some of our results along this line are given in Table 8. They are rain chamber results only. It will be seen that an unusually heavy deposit of lead arsenate alone, 14,000 to 15,000 micrograms per 50 sq. cm., was reduced to 2,487 micrograms after washing one-half hour, whereas one of 8 - 9,000 micrograms resulting from the use of a sticker was reduced to only 4,890 micrograms lead arsenate. The latter would thus provide nearly twice the protection against insects, based on the amount of lead arsenate present. Similarly, a deposit of 5 - 6,000 micrograms of lead arsenate with flotation sulfur was washed to 756 micrograms which is less than one-fifth the deposit remaining in column 6 after washing a deposit of 4 - 5,000 micrograms of lead arsenate-bentonite, oil, etc. It is evident from the table that dry flotation sulfur or dry flotation sulfur and hydrated lime *do not increase the tenacity* of lead arsenate but rather *decrease it.* The deposit after wash was greater, however, where bentonite plus skim milk was used as an adhesive, or where other effective stickers were employed (columns 5, 6 and 7).

Apple leaf tests outlined in the above paragraph should be compared with variable deposit-constant wash slide tests (Figure 7). The contrast between lead arsenate alone, lead arsenate plus dry flotation sulfur, and the same sprays with stickers added make it further ap-

TABLE 8. RESULTS OF A STANDARD WASH ON VARIABLE DEPOSITS (ON APPLE FOLIAGE) OF DIFFERENT MATERIALS AND COMBINATIONS. Washed One-Half Hour in Laboratory Rain Chamber. Figures are Micrograms Lead Arsenate Remaining per 50 Square Centimeters. Column 1 gives Approximate Deposit in Micrograms $PbHAsO_4$ Before Washing.

Lead arsenate deposit before wash	Lead arsenate only (1)	Lead arsenate plus lime (2)	Lead arsenate plus flotation sulfur (3)	Lead arsenate flotation sulfur and soy flour (4)	Lead arsenate flotation sulfur and lime (5)	Lead arsenate flotation sulfur bentonite skim milk (6)	Lead arsenate Fermate bentonite skim milk oil (7)
1 — 2000	557	514	407	558	406	723	
2 — 3000	1140		875	507	304	837	1928
3 — 4000	964	406		659		1167	1674
4 — 5000							3906
5 — 6000			756				
6 — 7000			558	862			
7 — 8000	1270				304		
8 — 9000							5395
9 — 10000						5022	
11 — 12000		279					
14 — 15000	2487						

Formulae:
(1) Lead arsenate without additions.
(2) Lead arsenate and lime, equal parts.
(3) Lead arsenate 3 parts, flotation sulfur 5 parts.
(4) Lead arsenate 3 parts, flotation sulfur 5 parts, soybean flour 1/2 part.
(5) Lead arsenate 3 parts, flotation sulfur 5 parts, lime 3 parts.
(6) Lead arsenate 3 parts, flotation sulfur 5 parts, bentonite 3 parts, skim milk 1/2 part.
(7) Lead arsenate 3 parts, Fermate 2 parts, bentonite 1 1/2 parts, skim milk 1/2 part, industrial white oil (Shell 8859) 1 per cent of final dilution.

parent that lead arsenate alone adheres slightly better than lead arsenate and flotation sulfur. The curve for lead arsenate, flotation sulfur, bentonite and skim milk is considerably steeper than either of the others mentioned, indicating better adhesion. The combination of lead arsenate, Fermate, oil and bentonite-skim milk throws the curve further to the left, all of which corresponds in general to variable deposit tests on glass slides and the foliage washing experiment. The main difference here between slide and foliage tests is the much better showing on foliage for stickers containing oils. The leaf test with lead arsenate and lime appears to have given poorer adhesion than was obtained in tests with the same combination on slides.

Laboratory study of spray deposits resulting from different concentrations sprayed for the same length of time; and several formulae sprayed for consecutively increasing lengths of time.

Selected shoots with leaves were placed on a turntable in a spray tower and sprayed with an atomizer from above for 10 seconds, using increasing concentrations. Analyses indicated a steady rise for lead arsenate alone in deposit up to 12 pounds per 100 gallons. When that concentration was doubled, however, the deposit was not doubled. When lead arsenate was combined with dry flotation sulfur and the concentrations increased there was a consistent doubling of the deposit. There was also a definite tendency in that direction with flotation sulfur and lime. The results in general indicate that within limits there is a doubling of the deposit on apple leaves when the concentration is doubled, but there are some discrepancies and a general trend towards lower than expected deposits with higher concentrations. The results of Isely and Horsfall (1943) are similar in the decreased deposits observed with increasing concentrations.

In order to compare the rate of deposit by several mixtures and especially to determine the value of oil as a deposit builder, several mixtures were sprayed at constant pressures for consecutively greater lengths of time beginning with 5 seconds and ending with 50. The results, given in Table 10 and Figure 17, show no consistent advantage for Fermate-aluminum gel-skim milk sticker over lead arsenate alone, but when white mineral oil was added, there was a conspicuous and significant rise in the amounts left on the apple leaves. Aside from its value as a killing agent, then, oil evidently has both sticking and deposit building characteristics.

TABLE 9. DEPOSITS OF LEAD ARSENATE ON APPLE FOLIAGE AFTER SPRAYING WITH CONSTANT PRESSURE IN A SPRAY TOWER FOR 10 SECONDS.

Figures Are Milligrams Lead Arsenate per 50 Square Centimeters.

Lead arsenate in mixture lbs. per 100 gals.	Materials added to the lead arsenate before spraying		
	None	Dry flotation sulfur[1]	Dry flotation sulfur and lime[2]
3	2.25	1.11	1.21
6	4.73	2.77	2.33
12	10.82	4.01	2.94
24	13.22	8.29	7.55

[1] Dry flotation sulfur—5, 10, 20 and 40 lbs. per 100 gals.
[2] Lime—3, 6, 12 and 24 lbs. per 100 gals.

TABLE 10. LABORATORY TEST FOR AMOUNTS OF LEAD ARSENATE DEPOSITED BY DIFFERENT SPRAY MIXTURES.

The Deposits Are Given in Micrograms ($PbHAsO_4$) per 70 Square Centimeters.

Time of spray seconds	(1) Lead arsenate 6 lbs. per 100 gals.	(2) Lead arsenate 6, Fermate 3, aluminum gel 3, skim milk ½ lb. per 100 gals.	(3) Same as 2 plus ½ per cent white oil
5	3,216	3,752	3,752
10	3,856	4,542	5,379
20	5,253	5,655	5,984
30	5,789	5,414	8,115
40	6,057	5,333	8,120
50	5,789	5,708	9,163

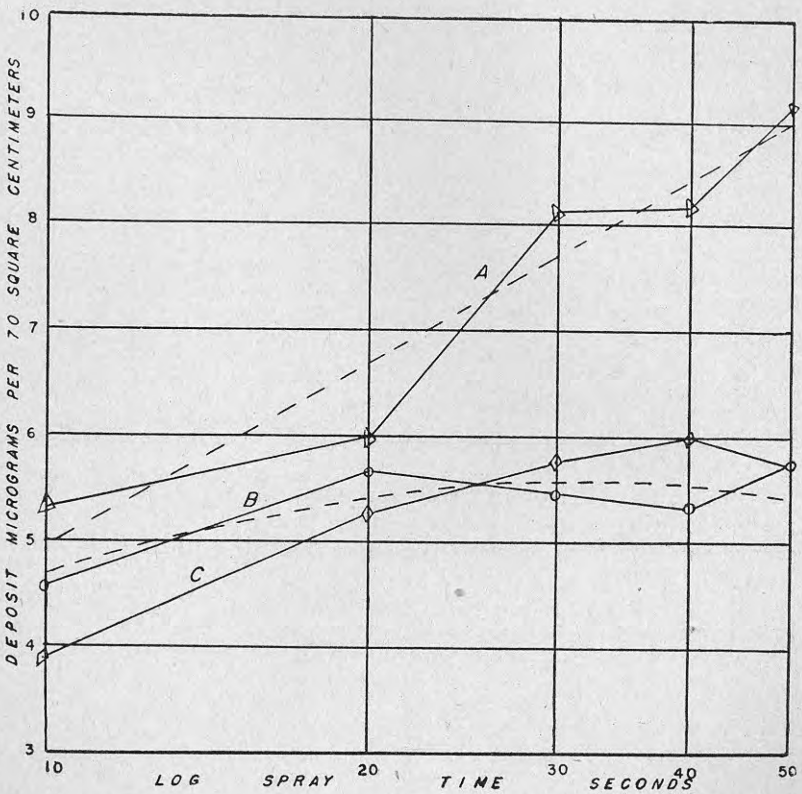

FIGURE 17. Graphic representation of data from Table 10. Laboratory spray experiment showing comparative deposit building properties of three sprays. (A) Lead arsenate 6 pounds, Fermate 3 pounds, skim milk one-half pound, white mineral oil one-half per cent, in 100 gallons. (B) Same formula as A but without the oil. (C) Lead arsenate 6 pounds to 100 gallons.

Because of the increased dosage being used in the field in some of our schedules, a series of analyses were made from foliage sprayed with 6 pounds lead arsenate per 100 gallons, together with several other ingredients. The increase in deposit after a 10-seconds spray is conspicuous where either Fermate, bentonite, skim milk and oil, or Fermate, aluminum gel, skim milk and oil were used. These data are given in Table 11.

TABLE 11. SPRAY DEPOSITS. ANALYSES OF LEAD ARSENATE DEPOSITED ON APPLE LEAVES BY A 10-SECOND SPRAY IN A SPRAY TOWER.

Materials	Lbs. per 100 gals.	Amounts deposited in 10 seconds Micrograms $PbHAsO_4$ per 50 sq. cm.
Lead arsenate	6	
Flotation sulfur (dry)	5	2,676
Lead arsenate	6	
Flotation sulfur (dry)	5	
Hydrated lime	3	2,334
Lead arsenate	6	
Flotation sulfur (dry)	5	
Soybean flour	.5	2,689
Lead arsenate	6	
Fermate	2	
Bentonite	3	
Skim milk powder	.5	
White mineral oil	1%	4,743
Lead arsenate	6	
Fermate	2	
Aluminum hydroxide gel	3	
Skim milk powder	.5	
White mineral oil	1%	4,702

A further comparison of three materials for increasing the deposit from Fermate and lead arsenate is given in Table 12. No significant difference could be seen between the three deposit building materials.

TABLE 12. COMPARISON OF DEPOSIT BUILDING PROPERTIES OF A COMMERCIAL DEPOSIT BUILDER, ALUMINUM HYDROXIDE GEL PLUS SKIM MILK AND OIL, AND BENTONITE PLUS SKIM MILK AND OIL, WHEN COMBINED WITH FERMATE AND LEAD ARSENATE AND SPRAYED ON APPLE FOLIAGE IN A SPRAY TOWER.

Figures are Micrograms Lead Arsenate per 50 Square Centimeters.

Spray time	Bentonite, etc. (1)	Aluminum hydroxide gel, etc. (2)	Commercial deposit builder (3)
5 seconds	2,917	2,701	2,486
10 seconds	4,058	3,450	2,638
20 seconds	4,933	5,086	4,921

Formulae: No. 1. Lead arsenate 6 lbs., Fermate 4 lbs., bentonite 6 lbs., skim milk 2 lbs., soybean oil 1 qt. to 100 gals.
No. 2. Lead arsenate 6 lbs., Fermate 4 lbs., Alugel 6 lbs., skim milk 2 lbs., white oil 1/2 gal. to 100 gals.
No. 3. Lead arsenate 6 lbs., Fermate 4 lbs., bentonite 6 lbs., deposit builder 1/2 gal. to 100 gals.

From Tables 10 to 12 it would appear that lead arsenate alone is a fair deposit builder, and materials such as bentonite, skim milk and oil, or aluminum hydroxide gel, skim milk and oil deposit more lead arsenate per second of spray than such combinations as lead arsenate and flotation sulfur, or lead arsenate, flotation sulfur and lime. The commercial deposit builder offered no improvement over the bentonite and aluminum hydroxide gel combinations.

Comparison of slide and foliage results.

Evaluation of the various stickers by the different methods has not always given the same results. Some stickers appear to be the same with all. Poor stickers may be eliminated very easily by glass slide tests and moderately good ones may be evaluated without too much difficulty. One of the most confusing materials, from the standpoint of these tests, is hydrated lime. The explanation for this is obscure.

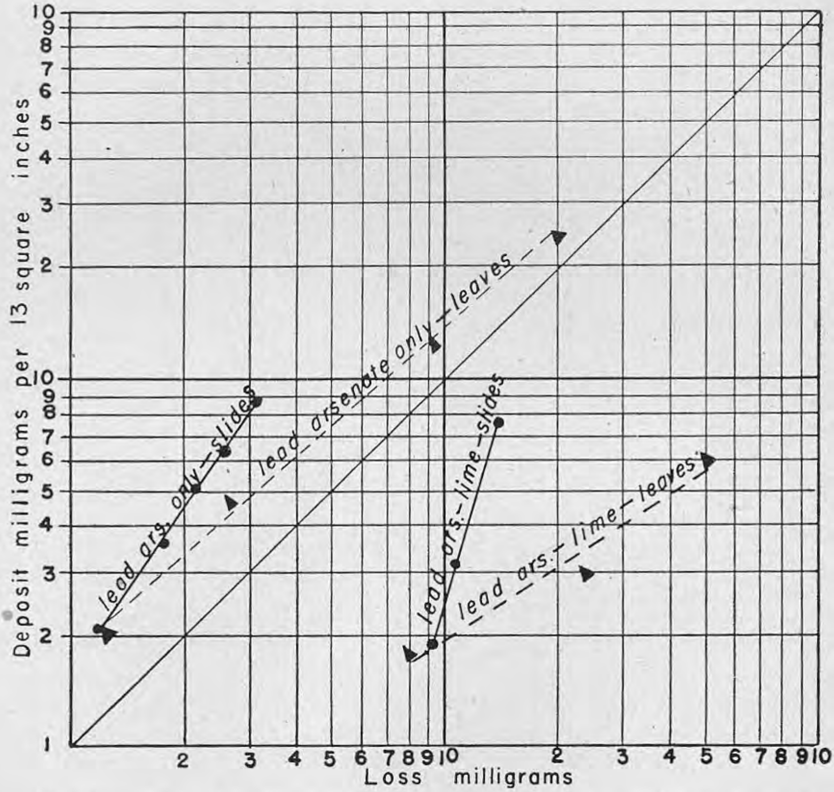

FIGURE 18. Comparison of the rate of loss from glass slides with the rate from leaves—following the procedures outlined in this paper. Note the wide divergence in the amounts lost in the case of lead arsenate when mixed with lime.

Appraised by the slide percentage method, pages 112-113, hydrated lime appears to be less efficient than lead arsenate alone. When evaluated by the variable deposit method, pages 122-123, there appears to be a distinct advantage in the addition of lime to lead arsenate, and the same is true if the variable wash method is used. When combined with lead arsenate and flotation sulfur and compared with lead arsenate and flotation sulfur without lime, there appears to be a distinct advantage on slides with a low deposit and a light wash but a distinct disadvantage with a heavy deposit and heavy wash, both by the variable deposit and variable wash evaluations. Sprayed onto foliage and washed heavily[1] in our rain chamber, lime appeared to be distinctly detrimental as a retainer for the spray deposit. Here rapid removal was accompanied by flaking from the leaf surfaces. This is also reflected in the residues remaining (Table 8) where it will be seen that the heavier the deposit, the less remained after a constant wash. All this seems to mean that lime in the spray mixture may be beneficial from the standpoint of adhesion, only if the deposits are light and the rainfall moderate. If, then, no other stickers are to be used, and the lime added merely for its safening value, it would seem to be much better from the standpoint of adhesion to use the minimum amount necessary for correction rather than a large excess which would remove the poison more rapidly. If larger amounts are used, as in the special curculio spray (Conn. Spray Calendar, 1944, p. 5), then it is very important to add other materials to improve the adhesion.

Mixtures containing oil have also been difficult to evaluate. Oils, if used in sufficient quantity, will mask a deposit so that visual foliage tests are worthless. Chemical analysis must then be used. Oil stickers used in glass slide tests often result in such a low rate of removal that it is unusually difficult to distinguish between different combinations. Compared with non-oil bearing mixtures, however, those with oil appeared to be better than most stickers when evaluated by either variable deposit, variable wash or foliage wash-chemical analysis methods. From what has been seen so far, oils in general are superior to other stickers, but it may be necessary to qualify this statement because of combinations which flake off from the leaf even with oil present, and because small quantities of oil may be no more efficient than certain non-oil combinations. Adhesion here depends on the amount of solids in the spray mixture and the proportion of oil used.

General conclusions from laboratory tests.

(1) In general, soaps and related materials have given poor to harmful results, i.e., removal of residue. (See Figure 2, sodium oleate.)

(2) Flour and skim milk used alone have not improved the adhesion of spray mixtures to any extent in these experiments.

(3) Bentonite-skim milk, bentonite-casein or bentonite-gelatin all showed a decided improvement over lead arsenate alone.

[1] Estimated to equal 60 inches of rainfall.

(4) Aluminum hydroxide gel gave a definite improvement in adhesion. It must be used at the rate of 50 to 60 per cent of the total solids.

(5) Bentonite-sulfur plus lime was decidedly beneficial.

(6) Oils have generally improved adherence to foliage.

(7) Combinations of alumina gel and oil are particularly lasting. Skim milk added as a spreader apparently does not detract from their effectiveness.

(8) Spray mixtures containing sulfur adhered best when stickers such as bentonite-sulfur plus lime, or bentonite-casein, etc. were added. (Oils in general are incompatible.)

(9) Spray mixtures containing Fermate apparently adhered better with white petroleum oil plus alumina gel plus skim milk than with the same oil plus bentonite plus skim milk. (No difference could be seen in 1944 insect control.)

(10) Vegetable oils such as soybean oil behave differently with bentonite and appear to give better results than the mineral oils tested.

(11) Hydrated lime may be detrimental from the standpoint of adhesion, but there are some indications that it is slightly beneficial at low concentrations with a light wash.

(12) In general, materials that adhere well to apple foliage also remain on apple fruits. The above conclusions would therefore generally apply to fruit as well as foliage.

ORCHARD EXPERIMENTS

General Discussion.

Laboratory experiment without verification by field work is not necessarily final. Along with the investigations already reported, various types of field spray experiments were conducted on the hypothesis that equal control can be secured with fewer sprays. The idea is not new and it is believed that the principles involved in this study have a firm scientific basis in the work of others as well as our own. For example, the adhesive properties of aluminum compounds have been known for a long time. Moore (1921) understood their value as adhesives. He investigated several and reported excellent adhesion to plants by aluminum hydroxide which he made from ammonium hydroxide and aluminum chloride. He discovered that plants carried a negative electrical charge and that aluminum hydroxide and other aluminum compounds being strongly positive adhere much better than chemicals carrying negative charges. The electrical charge theory of Moore has since been confirmed by Hoskins and Wampler (1936). Moore also tried ferric hydrate, which carries similar electrical charges, but noted that arsenic is adsorbed by ferric hydrate which probably accounts for its lowered toxicity when combined with it. Moore states furthermore that such materials as gelatin, casein and protein act as protective colloids and this addition to the spray "might result in complete loss of electric charge". He adds, however, that a "mutual precipitation may occur or if the positive charges are in excess, the material may retain its positive character. *Only field tests will solve these problems*" (italics mine). In this minor point it would appear that our field tests have begun where Moore left off. We have seen the precipitation which he describes, but both field and laboratory tests have shown very little decrease in adhesive properties from addition of certain proteins, such as casein, skim milk or gelatin.

In regard to the protective action of aluminum compounds, it has been shown by Knight and Cleveland (1934) that soluble aluminum compounds such as aluminum naphthenate dissolved in oil change the character of the oil and prevent injury to plant foliage, without decreasing the control of the insects for which they were applied. It has been our observation that aluminum hydroxide, aluminum magnesium silicate gel and Wyoming bentonite have the property of reducing the number of yellow leaves which usually form shortly after an oil spray. Whether these aluminum compounds act the same as those described by Knight and Cleveland is uncertain but there is evidently a similarity of protective action. Eddy (1938) observed that addition of "zinc hydroxide, freshly precipitated bordeaux, basic calcium sulfate and freshly precipitated aluminum hydroxide and similar products to calcium arsenate increased their safety on plants in most instances without reducing their toxicity". Any tendency to adsorb excess soluble arsenic would, of course, carry with it a safening action, but it might easily result in reduced toxicity as reported for ferric hydroxide. Eddy's observations seem a little uncertain on this latter point for he introduces the qualifying phrase "in most instances" in connection with his statement.

With the exception of bentonite which conceivably belongs here, none of the aluminum gels have been obtainable in commercial quantities until recently. As previously mentioned, Moore made his own aluminum hydroxide by combining ammonium hydroxide and aluminum chloride. This would leave ammonium chloride in solution, an undesirable ingredient from the standpoint of complex spray mixtures assuming a tank mix preparation. Without elimination of aluminum chloride the increased adhesion in this case would be offset by a decrease in safety. It was discovered by us that aluminum aceto-borate plus benzoic acid created a small amount of aluminum hydroxide without giving any harmful ingredients, at least when combined with lead arsenate alone. In fact, the safety was outstanding both in greenhouse and orchard tests. Because of the war, aluminum aceto-borate soon became unobtainable. Work was therefore begun with commercial aluminum gels containing 5 to 8 per cent aluminum oxide which, as demonstrated in laboratory experiments, gave increased adhesion.

As might be suspected, they, too, appeared to increase the safety of spray mixtures to the tree. These materials are of such a nature that they are relatively inert in the usual spray mixtures.

Up to this point it was abundantly evident that increased adhesion, improved safety and satisfactory control of insects were the main factors for consideration in solving the spray schedule reduction problem. In connection with these there appeared to be another important factor, the deposit or amount of toxic materials left on the leaves and fruit by any given spray. Laboratory tests have indicated a marked increase in deposit from the use of oils in conjunction with aluminum gels and other ingredients. The inverted emulsion (Washington "dynamite") stickers discovered by Marshall (1937) were the first of a class of stickers designed to increase the amount of spray deposited. Marshall and others have also demonstrated their value for insect control. Such combinations, however, become hazardous in the East on the introduction of necessary fungicides and, in our moist climate, considerable defoliation may occur even without the fungicide. This may possibly be due to a breakdown of monoethanol amine oleate soap and a liberation of free arsenic. At any rate it appears desirable to provide a safer mixture for our conditions, but with essentially the same deposit building properties. It is mainly for that reason that we have substituted aluminum compounds, and so forth, as emulsifiers for the oil in the general type of mixture provided by the Washington State College "dynamite". The addition of skim milk and casein in the presence of bentonite provides a flocculant somewhat similar to the ethanol amine oleate of the "dynamite", and the oil gives the necessary adhesive and deposit building properties.

The effect of reducing the number of sprays was considered carefully by Frear and Worthley in 1940, and we find in their conclusions 8 and 9 essentially the same conclusions that we have reached. They state that in 1938 "a treatment involving two cover sprays the second of which was applied on June 6, and composed of a double concentration of lead arsenate in a 'modified Washington State College dynamite' spray mixture, applied at a double dosage per tree showed deposits of lead and arsenic nearly as great as those in treatments receiving the last of four lead arsenate sprays in non-inverted mixtures on June 30, when fruit samples were analyzed on July 1". Codling moth control was equal in these reduced schedules to the "more extended spraying schedules". However, all the Pennsylvania reduced schedule work was apparently done with "dynamite" mixtures which, as already explained, are not entirely suitable for Connecticut conditions. The length of time which lead arsenate remains on foliage and fruit has also been considered by Frear and Worthley (1937, 1940) who found that heavy "dynamite" applications provided a somewhat lower deposit (in midseason) than standard schedules except when early dosages were increased. These findings are also in accordance with ours. Field tests such as those of 1944 have given significantly better insect control from increased concentrations. However, instead of a single increased dose in a three-spray program it has been necessary for us to increase all three sprays from 3 to 6 pounds of lead arsenate in 100 gallons in order to get the desired pest control. Referring also to the work of Taylor (1937) in this connection, it is apparent that increases of spray materials on fruit and foliage from increasing the volume of spray or the time of spraying are not of the same order as those obtained by increasing the concentration and introducing deposit building materials such as Washington State College "dynamite". Our chief dependence has, therefore, been on the two latter, although the necessity for good spraying and complete coverages is fully recognized.

Hamilton (1930) and others have shown that excessive amounts of spreaders with an accompanying depression of surface tension lowered the deposit. Hensill and Hoskins (1935; Fig. 140) showed very definitely the same phenomenon. Our investigations have extended this to adhesiveness and indicate that there may sometimes be an optimum sticker concentration very similar to the described spreader optimums in relation to deposit.

To summarize: From previous work it becomes evident that what is needed in spray schedule reduction program is

(1) A material with positive charge, which will impart such a charge to, or counterbalance any charge carried by, other spray ingredients, thereby improving adhesion.

(2) A material that will provide increased safety for the tree because of the heavier doses which could conceivably be used and the long period of time which they might be required to remain on the foliage and fruit.

(3) A material that will increase deposit so that heavy loads could be easily placed on the tree at the desired time, i. e., early in the season.

(4) A material that will provide reasonable coverage without reaching a point where deposit is lowered or adhesiveness impaired as indicated by laboratory experiments.

As finally developed, these requirements have been met by the following: (1) Aluminum hydroxide gels, including bentonite, for increased adhesions. (2) Oils for increased deposit and increased adhesion. Increased concentration of lead arsenate for increased deposit. (3) Ferric dimethyl dithio carbamate as the fungicide and lead arsenate as the insecticide. (4) Addition of skim milk or casein in small amounts to increase the spread.

The value of the ingredients mentioned has been fully demonstrated in laboratory experiments.

Results of Field Experiments.

Preliminary small scale tests for adhesion.

Two types of field experiments were conducted, the first with a view to learning what materials adhered well to foliage and fruit, and the second designed to give evidence regarding insect and disease control. Work was begun with stickers for special curculio sprays. These tests indicated a definite increase in adhesion for oils such as fish, perilla, and soybean oil, but there was no apparent advantage in the use of oils over aluminum sulfate. In 1942 we tested for adhesion (1) lead arsenate and flotation sulfur, (2) lead arsenate and oil, (3) lead arsenate-oil-talc-lime, and (4) lead arsenate-aluminum aceto-formate-manganese borate and oil. Adhesion of all oil-containing mixtures was much better than was obtained with lead arsenate-flotation sulfur, and the residues on fruit and foliage were higher

TABLE 13. LOSS OF ARSENIC WITH DIFFERENT STICKERS

Sticker	Dates of experiment	Percentage lost As_2O_3	Percentage lost Lead	Rainfall
Perilla oil	June 8–July 8	72	62	4.09 inches
Fish oil	" "	78	62	
Soybean oil	" "	79	69	
Commercial spreader and sticker	" "	83	74	
Aluminum sulfate-lime	" "	75	67	
No sticker	" "	86	75	
Perilla oil	July 11–Aug. 11	35	39	2.14 inches
Fish oil	" "	49	31	
Soybean oil	" "	40	43	
Commercial spreader and sticker	" "	62	51	
Aluminum sulfate-lime	" "	39	28	
No sticker	" "	65	42	

Spray formulae for 100 gallons:

Lime 10 lbs., lead arsenate 3 lbs., plus one of the following stickers—

Soybean oil	1 quart
Perilla oil	1 quart
Fish oil	1 quart
Aluminum sulfate and lime	3 lbs. each
Commercial spreader and sticker	1 pint

TABLE 14. COMPARISON OF STICKERS FOR LIME-LEAD ARSENATE

Year	Sticker	Per cent As_2O_3[1] remaining after 1 month	Year		Per cent As_2O_3 remaining after 1 month	Per cent gain for sticker
1940	Fish oil	25.7	1940	Check	22.8	2.9
1940	Fish oil	45.8	1940	"	45.7	.1
1939	Fish oil	22.0	1939	"	14.0	8.0
1939	Fish oil	51.0	1939	"	35.0	16.0
1938	Fish oil	25.4	1938	"	13.6	11.8
1938	Fish oil	47.4	1938	"	25.4	22.0
1939	Perilla oil	28.0	1939	"	14.0	14.0
1939	Perilla oil	65.0	1939	"	35.0	30.0
1939	Soybean oil	21.0	1939	"	14.0	7.0
1939	Soybean oil	60.0	1939	"	35.0	25.0
1939	Aluminum sulfate	25.0	1939	"	14.0	11.0
1939	Aluminum sulfate	61.0	1939	"	35.0	26.
1940	Aluminum acetate	48.0	1940	"	45.7	2.3
1940	Aluminum acetate	28.1	1940	"	22.8	5.3

[1] Analyses made immediately following sprays and again at the end of one month. Spray formulae as in preceding table.

TABLE 15. COMPARISON OF ADHESIVENESS FOR SEVERAL SPRAY MIXTURES IN 1942

Treatment	Dates of examination 6/16	7/3	8/1	9/1	Residue on fruit at harvest
	Micrograms As_2O_3 per 100 sq. cm.				Grams per lb. As_2O_3
(1) Lead arsenate 3 lbs., flotation sulfur 5 lbs. per 100 gallons	984	703	669	564	.008
(2) Lead arsenate 3 or 6 lbs. (calyx), oil ½ gal. to 100 gallons	2,838	2,312	1,548	1,053	.014
(3) Lead arsenate 3 lbs., talc 3 lbs., lime 3 lbs., oil ½ gal. to 100 gallons	2,264	1,613	952	614	.010
(4) Lead arsenate 3 or 6 lbs. (calyx), aluminum aceto-formate 1 pint, manganese borate 4 oz., oil ½ gal. to 100 gallons	3,089	2,442	1,722	1,087	.013

Applications: No. 1—May 1, 16, 27, June 9, July 7.
Nos. 2-4—May 1, 15, June 8-9.

throughout the season in spite of fewer sprays. A comparison was also made between western "dynamite" and aluminum aceto-borate-oil mixtures. They appeared to be approximately equal, with the advantage in favor of the aluminum aceto-borate-oil combination because of better foliage at the end of the season.

In the hope of verifying some of our laboratory results, another series of materials was tested for adhesion in 1943. All sprays were applied with a hand sprayer to small Wealthy trees. They were as follows:

1. Lead arsenate alone.
2. Lead arsenate plus flotation sulfur.
3. Lead arsenate plus Orthex (three concentrations).
4. Lead arsenate plus Kolofog-lime (three concentrations).
5. Lead arsenate plus aluminum hydroxide gel (three concentrations).
6. Lead arsenate plus lime sulfur (three concentrations).
7. Lead arsenate plus bentonite, oil and Ultrawet.

Results obtained in these tests were not completely consistent, but chemical analysis and visual examination at the end of the season showed that the tenacity of Number 7 was much better than any of the others. The amount of lead arsenate remaining on the foliage, as determined by chemical analysis after one month, was also much greater in test Number 7 than in any of the others. In the series of concentrations there appeared to be a gradual rise in adhesion as the sticker amounts were increased, especially with aluminum hydroxide gel and Kolofog-lime—very similar to laboratory slide and foliage results. Adhesion after one month was approximately equal for 40 per cent Orthex (2 pounds per 100 gallons) and aluminum hydroxide gel at the same concentration.

A somewhat similar experiment in 1944 confirmed in general what was apparent from the 1943 tests. Those mixtures containing oil were much better, as regards the amount of residue on the foliage at the end of the season. The next best appeared to be those containing bentonite or aluminum gel and skim milk powder. A commercial deposit builder did not equal the best mixtures listed. Table 16 gives a general picture of 1944 results.

TABLE 16. RESULTS OF SMALL SCALE FIELD STICKER TESTS ON WEALTHY FOLIAGE—1944. SPRAYS APPLIED JUNE 22 WITH POWER SPRAYER

Materials and amounts per 100 gallons		Condition on August 30
Lead arsenate	6 lbs.	
Dry flotation sulfur	5 lbs.	All washed off
Lead arsenate	6 lbs.	
Dry flotation sulfur	5 lbs.	
Skim milk powder	½ lb.	All washed off
Lead arsenate	6 lbs.	
Fermate	2 lbs.	All washed off
Lead arsenate	6 lbs.	
Dry flotation sulfur	5 lbs.	
Skim milk powder	½ lb.	
Bentonite	3 lbs.	Some visible residue
Lead arsenate	6 lbs.	
Dry flotation sulfur	5 lbs.	
Aluminum hydroxide gel	3 lbs.	
Skim milk powder	½ lb.	Some visible residue
Lead arsenate	6 lbs.	
Fermate	2 lbs.	
Bentonite	3 lbs.	
Ultrawet	¼ lb.	
White oil	1 qt.	Some visible residue
Lead arsenate	6 lbs.	
Fermate	2 lbs.	
Bentonite	3 lbs.	
Skim milk powder	½ lb.	
Soybean oil	1 qt.	Conspicuous residue
Lead arsenate	6 lbs.	
Dry flotation sulfur	5 lbs.	
Bentonite	3 lbs.	
Skim milk powder	½ lb.	
Soybean oil	½ gal.	Very conspicuous residue

Comparison of pest control with short schedules having few sprays and high concentrations plus stickers, and longer schedules carrying lower concentrations and no sticker.

Having studied the adhesive properties of materials commonly used in sprays, it was decided to start programs of a kind which would be likely to give the necessary disease and insect control with the fewest number of applications. As explained previously, the idea involves the use of equal or approximately equal amounts of insecticides during the summer, in one case applied with three or four sprays, in the other with seven or eight. The materials and reasons for selecting them have been given in the general discussion.

Several of the major apple pests were considered separately and comparisons secured with full and reduced programs. A power sprayer and multiple nozzle or single guns were used with sufficient pressure to drive the spray into the trees and over the tops. For very large trees a tower was used in some of the sprays. Each application was made as thoroughly as possible, and comparisons of short and extended schedules were possible in several different locations within the various orchards. Three orchards in all were used.

Curculio control.

A comparison of special curculio sprays was made first in 1940. Lime, lead arsenate and fish oil, and lime, lead arsenate and aluminum sulfate gave equal control in a bad year for curculio. Neither was

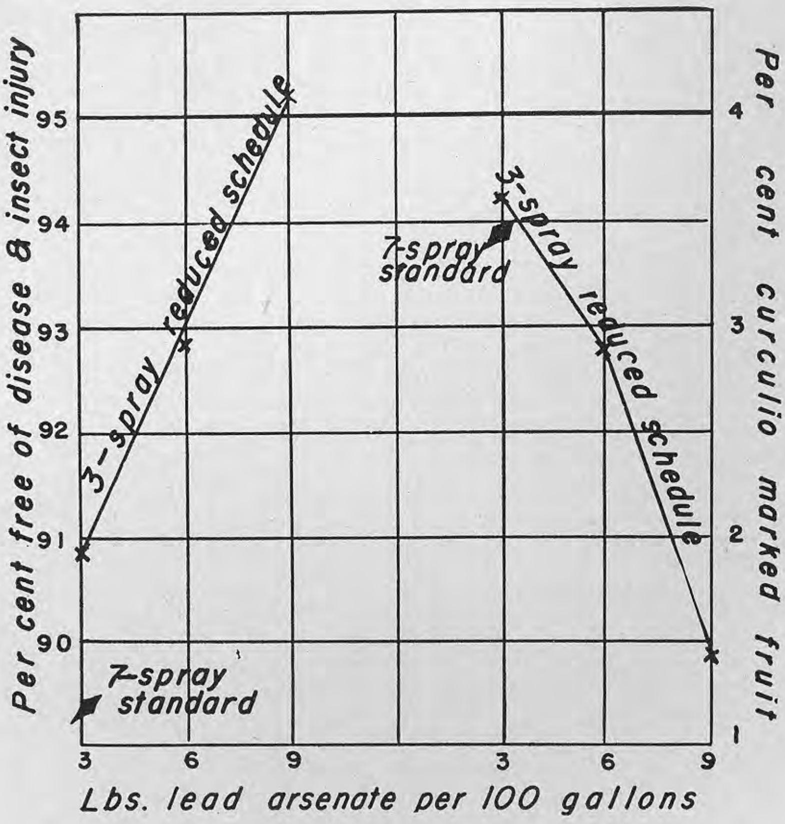

FIGURE 19. Graphic representation of data in Table 29. Shows the relative amounts of clean and curculio free fruit in our 1944 reduced schedule plots. Diamond-shaped marks give control from a 7-spray program.

significantly better than flotation sulfur and lead arsenate. This could possibly have been forecast had we known more in regard to the sticking properties of the mixtures.

The next year, a light season for curculio damage, four different mixtures were compared, two of them on a reduced schedule (Table 17). Curculio control was approximately the same in all, but there was a slight advantage for the four-spray schedule over the three-spray schedule with special stickers. In 1943, another bad year for curculio, control with reduced schedules was slightly inferior to the more extended program (four versus six sprays). There was, however, a marked difference between sprays containing soybean flour and manganese borate and those which contained none. Those without soybean flour were about equal to the reduced schedule. This was apparent in two different orchards (Table 18). There was, then, an apparent advantage in the addition of the soybean flour for curculio control which had not been recognized by us up to that point. In 1944, a year in which curculio was fairly easy to control, comparison of a number of treatments in the Burton orchard showed equal control for a three-spray as compared with a seven-spray program, where the amounts of lead arsenate were increased to 6 and 9 pounds per 100 gallons in the reduced programs, as indicated in Tables 19-21 and

TABLE 17. COMPARISON OF CURCULIO CONTROL, 1941
Percentages of Marked Fruit at Harvest

	Treatments[1]				
Trees compared	(1)	(2)	(3)	(4)	Differences
A 4 and A 5	14.01			38.02	+24.01
A 10 and A 11		8.03		11.07	+ 3.04
A 12 and A 13		2.31	5.84		+ 3.53
A 14 and A 15	2.52		17.18		+14.66
B 10 and B 11		2.50		4.31	+ 1.81
D 2 and C 2		5.26	5.87		+ .61
D 3 and C 3	6.47			3.32	— 3.15
C 4 and C 5	3.13			4.44	+ 1.31
D 6 and C 6		2.55		5.21	+ 2.66
D 7 and C 7	2.38		1.04		— 1.34
D 8 and D 9	1.04		1.25		+ .21
D 10 and D 11	1.82		1.89		+ .07
C 10 and C 11		1.40		1.47	+ .07
B 14 and B 15	10.34		5.66		— 4.68
E 14 and E 15		2.64		8.87	+ 6.23
E 4 and E 5		8.90		4.46	— 4.44

[1] Explanation of treatments:
(1) Flotation sulfur and lead arsenate—4 sprays.
(2) Lime sulfur, manganese sulfate, lead arsenate and soybean flour—4 sprays.
(3) Aluminum aceto-borate, lead arsenate, oil and "Spergon"—3 sprays.
(4) Aluminum aceto-borate, lead arsenate and oil—3 sprays.

Amounts in 100 gallons

Flotation sulfur	8 lbs.
Lead arsenate	3 lbs.
Lime sulfur	1 1/4 gals.
Manganese sulfate	2 oz.
Soybean flour	1/2 lb.
Aluminum aceto-borate	2 lbs.
"Spergon"	1 lb.

29. Up to 1943 it was apparent that the longer schedules gave better control of curculio than the short, but it was evident in 1944 that equal control could be had by increasing the amounts of lead arsenate used in the shorter schedules. Thus, 6 and 9 pounds of lead arsenate per 100 gallons in three sprays was equal or better than seven sprays using 3 pounds of lead arsenate in a standard program (Figure 19).

Apple maggot control.

It was apparent early in the experiments that sprays which deposited heavy loads of lead arsenate on the foliage and held it there gave the best protection (Tables 22 and 23). All reduced schedule experiments gave a decided improvement in maggot control, evidently because there was more arsenic on the leaves throughout the season.

TABLE 18. ADVANTAGE OF ADDING SOYBEAN FLOUR-MANGANESE BORATE SAFENER AND SPREADER TO FLOTATION SULFUR AND LEAD ARSENATE FOR CURCULIO

Burton and Connecticut Agricultural Experiment Station Orchards, 1943

Trees compared	Per cent in favor of spreader-safener	Trees compared	Per cent in favor of spreader-safener
D 7 and D 6	+13.09	D 33 and C 34	+17.13
D 8 and D 13	+ 4.03	D 33 and C 32	— .32
D 5 and D 9	+22.50	F 12 and F 16	+12.32
D 9 and D 11	+ 5.65	F 14 and F 16	+ 2.92
E 15 and F 16	+ .43	E 9 and D 9	+24.47
E 17 and E 18	+12.43	E 11 and D 11	+ 6.78
C 24 and C 32	+15.83		

Average difference in favor of spreader-safener 9,89

Amounts in 100 gallons

Lead arsenate ....3 lbs.
Dry flotation sulfur ....5 lbs.

Lead arsenate ....3 lbs.
Dry flotation sulfur ....5 lbs.
Manganese borate ....1/4 lb.
Soybean flour ....1/2 lb

TABLE 19. SUMMARY OF CURCULIO CONTROL — 1944

Burton Orchard

McIntosh

Trees compared	Per cent curculio I Black and white	Per cent curculio II Yellow	Increased control for I
C 20 and C 26	3.40	7.28	+3.88
D 25 and F 22	3.15	3.55	+ .40
D 27 and C 26	1.55	7.28	+5.73
F 32 and C 34 } F 34 and C 34 }	5.38	6.25	+ .87
E 4 and G 5	2.08	4.26	+2.18

Treatment I—Black and white, standard, 7 sprays. 3 lbs. lead arsenate per 100 gallons.
II—Yellow, reduced, 3 sprays. 3 lbs. lead arsenate per 100 gallons.

TABLE 20. SUMMARY OF CURCULIO CONTROL — 1944
Burton Orchard
McIntosh

Trees compared	Per cent curculio I Black and white	Per cent curculio II Red	Gain for II
C 13 and C 12	7.46	.61	+6.85
C 20 and E 19-23	3.40	1.20	+2.20
D 25 and D 29	3.15	2.49	+ .66
D 27 and E 25	1.55	1.08	+ .47
F 32 and D 31	4.23	4.69	— .46
F 34 and D 31	6.54	4.69	+1.85
G 3 and F 3	1.78	5.18	—3.40
F 5 and G 5	2.08	1.36	+ .72
F 33 and G 28	3.95	3.00	+ .95

Treatment I—Black and white, standard, 7 sprays. 3 lbs. lead arsenate to 100 gallons.
II—Red, reduced, 3 sprays. 6 lbs. lead arsenate to 100 gallons.

TABLE 21. SUMMARY OF CURCULIO CONTROL — 1944
Burton Orchard
McIntosh

Trees compared	Per cent curculio I Black and white	Per cent curculio II Green	Gain for II
C 13 and E 15	7.46	4.18	+3.28
C 20 and C 22	3.40	.00	+3.40
D 25 and F 26	3.15	.00	+3.15
D 27 and C 24	1.55	1.18	+ .37
F 32 and F 30	4.23	.31	+3.92
F 34 and F 30	6.54	.31	+6.23
G 33 and F 33	3.95	3.73	+ .22

Treatment I—Black and white, standard, 7 sprays. 3 lbs. lead arsenate per 100 gallons.
II—Green, reduced, 3 sprays. 9 lbs. lead arsenate per 100 gallons.

In 1944, we made a comparison of a seven-spray schedule and a three-spray reduced program. Again the maggot control appeared to be better in the short schedules, but the general level of infestation was so low that no critical comparisons were made. It seems probable that in bad years for maggot infestations it will be advisable to supplement the short schedules with sprays or dusts about the first of August. Non-arsenicals, such as rotenone or DDT, may possibly fill the need for August treatments in Connecticut.

European red mite control.

Because of the striking differences obtained between sulfured and unsulfured plots during the last six to eight years, observations were made at different times to determine the value of reduced schedules for mite control. Counts made in 1942 are shown in Table 24. In

1943 the extended schedules with sulfur fungicides were so effective in building up populations of mites that a distinct line of demarkation could be seen between those plots and the reduced schedule plots.

TABLE 22. COMPARISON OF MAGGOT CONTROL — 1941

Variety	No. trees	No. fruits	Maggoty in treatments[1] III and IV Per cent	No. trees	No. fruits	Maggoty in treatments[1] I and II Per cent	Differences Per cent
Greening	6	13,646	1.60	6	22,425	6.54	4.94
King	2	3,606	6.21	2	4,746	25.81	19.60
Spy	2	11,447	5.39	2	6,858	22.31	16.92
Pippin	2	4,031	.72	2	2,929	22.94	22.22
Sutton	2	6,924	1.90	2	1,486	3.53	1.63
Russet	4	11,604	2.56	4	7,459	6.98	4.42

[1] Explanation of treatments: (See Table 17 for amounts per 100 gallons)

I Flotation sulfur and lead arsenate—4 sprays.
II Lime sulfur, manganese sulfate, lead arsenate and soybean flour—4 sprays.
III Aluminum aceto-borate, lead arsenate, oil and "Spergon"—3 sprays.
IV Aluminum aceto-borate, lead arsenate and oil—3 sprays.

TABLE 23. MAGGOT CONTROL — 1943

Greening and King

Trees compared	Per cent maggot I	Per cent maggot II	Per cent gain for I
D 3 and D 6	10.3	22.6	12.3
D 4 and D 7	21.2	35.0	14.0
D 14 and D 15	8.9	34.0	25.1
D 13 and D 16	21.2	33.6	12.4
C 9 and C 10	15.5	46.6	31.1

Amounts in 100 gallons:

I Lead arsenate 3 pounds (pink), 6 pounds calyx and 1st cover.
Aluminum hydroxide gel 1 1/2 pounds.
Fermate 3/4 pounds.
White oil 1/2 gallon. (3 sprays)

II Lead arsenate 3 pounds.
Dry flotation sulfur 5 pounds. (5 sprays)

The difference in color of the foliage during 1943 was so pronounced that kodachrome pictures of the differences were easily obtained about the first of September. In only one of three experimental orchards did mites assume outbreak proportions in 1944. At the Townsend orchard an area dusted with sulfur and cryolite (25 per cent) became so heavily infested by mites that the leaves turned brown in midsummer and remained brown until the end of the summer. The contrast between this block and the short schedule plots was great, indicating good mite control for the formula used in the reduced schedule. However, it was not possible in this orchard to determine the actual effect of oil in the mixture or to make counts as anticipated.

TABLE 24. EUROPEAN RED MITE POPULATION STUDIES — 1942

Variety, Baldwin

20 Leaf Samples — Adult Females

Treatment	June 3	June 11	June 26	July 7	July 16	July 29	Aug. 6	Totals
Sulfur–lime–lead arsenate (five sprays)[1]	76	2,054	1,245	1,052	27	0	0	4,454
No sulfur Oil–aluminum acetato–formate manganese borate–lead arsenate (three sprays)	116	1,024	419	388	0	2	0	1,949
No sulfur Oil–lead arsenate (three sprays)	139	1,050	408	1,213	51	0	0	2,861
No sulfur Oil–lime–talc–lead arsenate (three sprays)	118	1,114	615	649	387	3	0	2,886

[1] Amounts for 100 gallons given in Table 15.

Scab control.

Prior to 1943, only partial success in handling diseases with reduced programs could be noted. Spergon[1] gave some promise. Experiments were begun with Fermate in the reduced schedules during 1943, and in general the results were much more encouraging than any previously obtained. It will be seen from Table 25 that scab control on McIntosh and Romes was just as good with the four-spray schedule as with the six. The latter half of our 1943 summer was, however, dry, so that the comparison may not have been critical enough. It is interesting to note that in spite of a dry, late season the scab control was here obtained with a reduced number of sprays *when the weather was wet*, and in an orchard where scab was difficult to control. Apples from nearby unsprayed McIntosh trees were heavily infected with scab, estimated at 97 to 100 per cent. Scab control was even better in 1944. So far, however, the short schedules have not been tested for scab control in seasons producing rainfall approaching normal for this area (four inches or thereabouts per month). The closest approach was the 1943 season. It is interesting to observe that during 1943 and 1944 the comparisons did not show any advantage whatever for the extended schedule over the reduced, and it is evident that scab control, for some seasons at least, is satisfactory with fewer sprays.

[1] Chloranil.

TABLE 25. SCAB AND INSECT CONTROL IN TOWNSEND ORCHARD
With Reduced Schedules—1943

Treatment		McIntosh			Romes	
Amounts per 100 gals.	Tree No.	Good[1] Per cent	Scab Per cent	Tree No.	Good Per cent	Scab Per cent
Lead arsenate, 3 lbs. at pink,	I 12	44.45	9.21	P 23	54.16	16.66
6 lbs. at calyx and only cover	G 21	19.52	41.71	P 25	66.42	2.14
Fermate, ¾ lb., plus aluminum	G 18	31.99	11.01	P 27	84.00	1.33
gel or bentonite, and oil	H 20	35.08	8.85	P 19	59.82	3.57
4 sprays (at prepink, Fermate only)				D 15	58.93	7.83
Averages		41.29	29.84		65.01	5.46
Lead arsenate, 3 lbs. at pink,	K 20	53.69	.18	P 29	86.11	2.77
6 lbs. at calyx and only cover	M 40	59.13	3.19	P 31	90.56	0.00
Fermate, 1½ lbs.	E 27	21.14	1.14	P 33	66.37	2.62
Aluminum gel or bentonite, and	H 27	24.53	4.69	I 20	93.68	.75
oil	O 32	37.32	1.67	J 17	84.87	3.36
4 sprays (at prepink,	M 14	55.48	4.20	J 19	87.33	2.00
Fermate only)	O 30	80.14	2.36			
Averages		60.79	2.65		84.84	1.72
Lead arsenate, 3 lbs.	D 3	49.18	9.05	H 11	91.46	5.99
Dry flotation sulfur, 5 lbs.	E 4	42.02	34.43	H 17	82.06	3.58
6 sprays (At prepink,	K 25	81.52	7.60	F 11	94.80	2.59
flotation sulfur only)	K 24	43.90	32.07	J 21	87.45	5.78
				F 7	66.72	12.99
				J 27	87.70	2.15
				H 5	73.60	3.43
Averages		57.59	19.22		81.57	6.34

[1] Free of external insect marks.

Spray russet.

Reduction of spray russet on apples has been an important problem for many years. With the change from sulfur to other fungicides and the incorporation of safeners in the mixture, we began to look for improvement in the smoothness of the fruit at harvest. A comparison of several different treatments in 1942 showed a pronounced difference between the plots, especially in the Baldwin variety. The data are given in Table 26. In 1943 continued observations showed similar results and counts confirmed previous conclusions. Apparently Fermate did not increase the amount of russet, since, in all cases, russetting was much less in plots where it was used (Table 27).

TABLE 26. COMPARISON OF STANDARD SPRAY SCHEDULE WITH 3-SPRAY PROGRAM
Effect of Sprays on Fruit Russetting and Foliage Burn, 1942

	Treatment	Per cent conspicuous russet on Baldwin	Foliage burn
I	Lead arsenate-aluminum aceto-formate-oil; 3 sprays[1]	8.91 7.76	Slight
II	Lead arsenate-flotation sulfur; 5 sprays	40.40 34.74	None to slight
III	Lead arsenate-oil; 3 sprays	21.41 14.85	Moderate
IV	Lead arsenate-lime-talc-oil; 3 sprays	8.04 8.57	Heavy (some defoliation)

[1] Formulae as in Table 15.

TABLE 27. EFFECT OF DIFFERENT TREATMENTS ON SPRAY RUSSET
Baldwins — 1943

Treatments—amounts in 100 gallons	Per cent fruit with conspicuous russet
1. Lead arsenate 3 lbs., dry flotation sulfur 5 lbs., soybean flour ½ lb., manganese borate ¼ lb. *Five sprays*	29.36
2. Lead arsenate 3 lbs., dry flotation sulfur 5 lbs., soybean flour ¼ lb., manganese borate ⅛ lb. *Five sprays*	31.62
3. Lead arsenate 3 lbs., dry flotation sulfur 5 lbs. *Five sprays*	35.51
4. Lead arsenate 3 - 6 lbs., aluminum gel 3 lbs., Spergon ¼ lb., white mineral oil ½ gallon. *Three sprays*	6.88
5. Lead arsenate 3 lbs., aluminum gel 3 lbs., Spergon ¼ lb. *Three sprays*	7.18

Arsenical load carried on the leaves during the season in increased-dose, reduced-schedule experiment.

It has been our observation that schedules of three or four sprays with stickers and double lead arsenate dosages, such as were employed in 1943 and 1944 (last spray not later than June 10), provide a very heavy arsenical deposit on the leaves throughout the season. Analyses by Mr. Shepard proved that the residues were in fact considerably heavier than were found on leaves sprayed by the more extended schedules. Every year that we have used such schedules, the arsenical load on the leaves appeared to be greater than on the fruit. In 1944 comparisons of leaves from seven- and three-spray schedules, made about the first of September, showed greater deposits for the three-spray programs wherever concentrations as high as six pounds of lead arsenate per 100 gallons were employed (Table 28).

TABLE 28. ANALYSES BY C. E. SHEPARD FOR ARSENICAL RESIDUES ON FRUIT AND FOLIAGE

Burton Orchard, 1944

Treatment	and variety	Date sampled	Grains[1] As_2O_3 per lb. of fruit	Micrograms $PbHAsO_4$ per 200 sq. cm. discs
7 sprays	Gravenstein	August 22	.038	
3 lbs. lead			.026	
arsenate per	McIntosh	September 9	.027	8,269 (August 30)
100 gallons.			.032	
Formula 4[2]	Baldwin	September 29	.024	
			.035	
3 sprays	Gravenstein	August 22	.032	
9 lbs. lead			.026	
arsenate per	McIntosh	September 9	.022	17,756 (August 30)
100 gallons.			.028	
Formula 3	Baldwin	September 29	.019	
			.026	
3 sprays	Gravenstein	August 22	.018	
6 lbs. lead			.018	
arsenate per	McIntosh	September 9	.015	9,381 (August 30)
100 gallons.			.020	
Formula 2	Baldwin	September 29	.015	
			.016	
3 sprays	Gravenstein	August 22	.018	
6 lbs. lead			.020	
arsenate per	McIntosh	September 9	.014	12,277 (August 30)
100 gallons.			.013	
	Baldwin	September 29	.018	
			.016	
3 sprays	Gravenstein	August 22	.013	
3 lbs. lead			.010	
arsenate per	McIntosh	September 9	.014	14,408 (August 30)
100 gallons.			.013	
Formula 1	Baldwin	September 29	.012	
			.011	
3 sprays	Gravenstein	August 22	.013	
3 lbs. lead			.011	
arsenate per	McIntosh	September 9	.012	4,449 (August 30)
100 gallons.			.011	
	Baldwin	September 29	.007	

[1] U. S. tolerance .025 grains As_2O_3 per pound.
[2] See page 156 for explanation of formulae and dates of application.

TABLE 29. PERCENTAGES OF SOUND AND CURCULIO-MARKED FRUIT FROM BURTON'S ORCHARD IN 1944

Figures Are Averages of All Trees Examined
Varieties—Baldwin, McIntosh and Gravenstein

Treatment		Amounts in 100 gals.	Per cent clean fruit	Per cent curculio	Number of trees
(1)[1]	Reduced	3 lbs. lead arsenate ¾ lb. Fermate[2]	90.94	3.62	14
(2)	Reduced	6 lbs. lead arsenate 1½ lbs. Fermate[2]	92.88	2.87	19
(3)	Reduced	9 lbs. lead arsenate 3 lbs. Fermate[2]	95.21	1.42	15
(4)	Standard	3 lbs. lead arsenate 8 lbs. flotation sulfur paste[3]	89.35	3.43	12

[1] See next page for formulae used and dates of treatment.
[2] Plus aluminum hydroxide gel 3 lbs., white mineral oil 1/2 gal.
[3] No sticker added.

TABLE 30. COMPARISON OF THE DIFFERENT TREATMENTS GIVEN IN TABLE 29 SHOWING SIGNIFICANCE OF THE TREATMENTS AS COMPUTED BY STATISTICAL METHODS

Data Figured from Individual Tree Comparisons, Not Directly from Table 29

Treatments compared	Clean fruit	Curculio
1 and 4[1]	Not significant	Not significant
1 and 2	Not significant	Not significant
1 and 3	Significant	Significant
2 and 3	Significant	Significant
2 and 4	Significant	Not significant
3 and 4	Significant	Significant

[1] See next page for formulae used and dates of treatment.

Spray residues on the fruit at harvest.

So far none of the fruit receiving the heavy dose-reduced schedule have been over tolerance except for the dry season of 1944 (Table 28). Apples from Gravenstein trees, picked during the last 10 days of August 1944, showed an excess of residue over tolerance where the lead arsenate had been increased to 9 pounds per 100 gallons, and the last spray applied June 9. Analyses from random samples were only slightly over the tolerance, however, and samples from Baldwins, picked later, were on the line or below. The apples from three 9-pound treatments showed almost exactly the same amount of arsenic oxide per pound as apples from trees sprayed seven times with 3 pounds of lead arsenate per 100 gallons, the last spray July 25 (Table 28). McIntosh apples picked September 9 carried more grains of As_2O_3 per pound of fruit from the standard seven-spray program than those sprayed with the reduced schedules, wherever the arsenical dose was 6 pounds or less per 100 gallons. There seems to be little danger, therefore, from excessive residues in the reduced schedules as employed in these experiments except on early varieties rceiving at least 9 pounds per 100 gallons.

Burton Orchard — Description of Treatments — 1944

Number	Materials	Amounts per 100 gals.		Dates
(1)	Lead arsenate	3 lbs.	(*3 sprays*)	May 5
	Aluminum hydroxide gel	1½ lbs.		May 18
	White mineral oil	¼ gal.		June 8-9
	Fermate	¾ lb.		
(2)	Lead arsenate	6 lbs.	(*3 sprays*)	May 5
	Aluminum hydroxide gel	3 lbs.		May 18
	White mineral oil	½ gal.		June 8-9
	Fermate	1½ lbs.		
(3)	Lead arsenate	9 lbs.	(*3 sprays*)	May 5
	Aluminum hydroxide gel	4½ lbs.		May 18
	White mineral oil	¾ gal.		June 8-9
	Fermate	3 lbs.		
(4)	Lead arsenate	3 lbs.	(*7 sprays*)	May 5
	Flotation sulfur paste	8 lbs.		May 18
				May 29
				June 9
				June 20
				July 3
				July 25

GENERAL CONCLUSIONS

(1) Lead arsenate alone sticks better than lead arsenate plus dry flotation sulfur.

(2) Lead arsenate alone sticks better than lead arsenate, flotation sulfur and lime.

(3) Lead arsenate plus lime shows improvement in adhesion over lead arsenate alone on glass slides but not on foliage, especially at high concentrations.

(4) Oils are good deposit builders.

(5) Oils are good stickers, but the amounts used should be in proportion to the amount of solids in the spray mixture.

(6) Bentonite plus skim milk or casein (20 per cent skim milk or casein) is an excellent sticker, second only to the oils. In 1944, a dry season, it equalled the oils in field experiments.

(7) Aluminum gel is a good sticker, and various compounds that have been utilized in the course of these experiments evidently produce some form of aluminum gel.

(8) Aluminum gels, including bentonite, act as safeners both for oil and lead arsenate, thereby preventing foliage burn even though the arsenic is retained on the leaves in large amounts over a long period of time.

(9) By utilizing stickers that are good deposit builders and also safeners, the total number of sprays needed may be reduced considerably in seasons such as 1943 and 1944.

(10) The advantages of the reduced schedules in Connecticut appear to lie in improved control of European red mite and apple maggot, as well as reduction in spray russet and less foliage burn and drop. There is also a saving in labor which is considerable, a saving of gasoline, and a reduction in machinery depreciation.

(11) The main objections lie in the difficulty of handling the complex mixtures and the rather poor control of curculio in bad years for that insect. Supplementary treatments may be needed in certain years, but these should not detract from the value of the method. Curculio control in 1944 was just as good or better than that obtained with the standard spray schedule.

(12) Although we have had no difficulty controlling codling moth with reduced programs and increased dosages of lead arsenate, it should be understood that we do not yet recommend their use when codling moth becomes a threatening factor in Connecticut fruit production. In this connection, however, the reader should consult Frear and Worthley (1940; p. 19).

(13) It is believed that reduced programs, such as have been described, may have a definite place in Connecticut for such varieties as Baldwins, Wagners, Staymens or similar varieties. The method has not been tested sufficiently in wet years to warrant recommendation at this time for scab susceptible varieties.

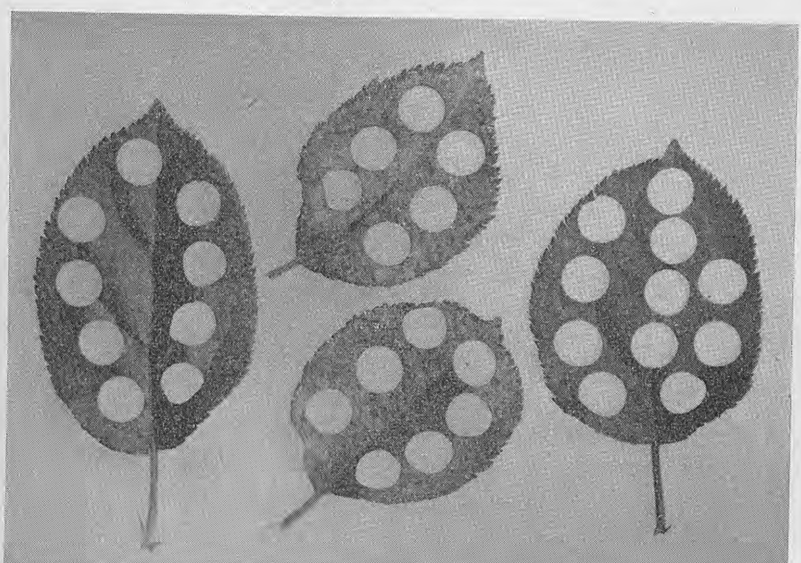

FIGURE 20. Illustrating the method of sampling for lead arsenate deposit and residue. A number of holes are punched in the leaf before washing and the discs analyzed for lead arsenate. After the wash is complete a second sample of discs is punched from between the original holes in the leaf.

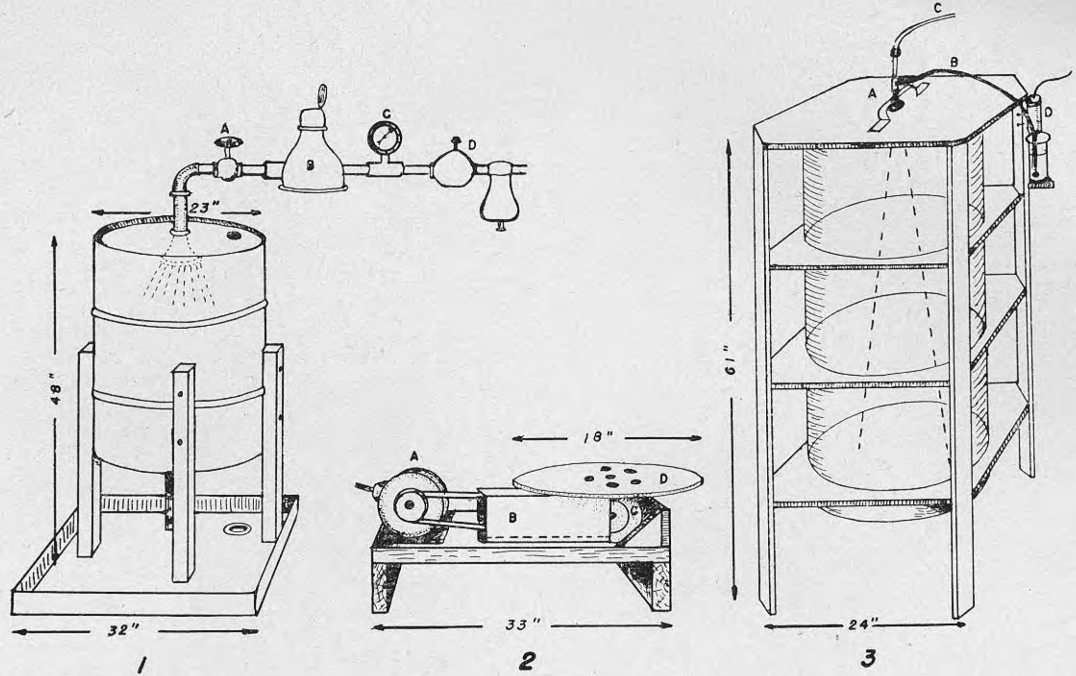

FIGURE 21. (1) Washer for sprayed leaves constructed from oil drum with bottom cut out and mounted on stilts. In operation, turntable (2) is placed beneath drum, centered, and sprayed plants or parts thereof put on the platform. A, shut off; B, meter; C, pressure gauge; D, pressure reducer. (2) Turntable construction. A, electric motor; B, tin protector for belt; C, speed reducer; D, platform of turntable. (3) Spray tower with fixed atomizer for spraying foliage. No attempt is made to spray the undersides of the leaves. In operation, turntable (2) is placed beneath the tower. A, atomizer; B, supply line to spray solution; C, air line connected with constant pressure flow meter; D, mechanical stirrer.

LIST OF MATERIALS USED IN THE EXPERIMENTS DESCRIBED IN THIS PAPER[1]

(1) Acco—commercial casein lime preparation, casein 26.38 per cent.

(2) Aluminum aceto-borate—white powder, 63.52 per cent aluminum aceto-borate.

(3) Aluminum aceto-formate—liquid, 24 per cent solution.

(4) Aluminum hydroxide—gelatinous paste reported to contain 8.5 per cent Al_2O_3. Analysis showed 5.25 per cent. Condensed to Alugel in this bulletin.

(5) Aluminum magnesium silicate—jelly—trade name "Veegum". Contains on a dry basis, SiO_2 56.32 per cent, Al_2O_3 8.58 per cent. As received contains 94.5 per cent water, .47 per cent Al_2O_3, 3.09 per cent SiO_2. (Manufacturer's analysis).

(6) Aluminum sulfate—technical grade.

(7) Alkote—commercial sticker—consistency of mayonnaise dressing. Aqueous suspension of nitrogen containing wax of high molecular weight. Total solids 14.08 per cent.

(8) Bentonite (Wyoming)—gray powder. Hydrated aluminum silicate. According to Wyoming Geol. Sur. Bul. 28, p. 4, 1939, contains approximately 16 per cent Al_2O_3.

(9) Benzyl-ethyl starch. White powder, evidently derived from the resin starch, benzyl ether.

(10) Casco waterproof glue. Commercial product. For composition see Conn. Agr. Expt. Sta. Circ. 36, p. 8, 1939.

(11) Fermate. Ferric dimethyl-dithio-carbamate. Black powder. 1944 product, said to carry some perry clay.

(12) Filmfast. A commercial sticker containing 45 per cent skim milk, 36 per cent bentonite, and 19 per cent starch.

(13) Fish oil. Light pressed menhaden grade.

(14) Flotation sulfur. Dry commercial wettable sulfur, 92 per cent sulfur.

(15) Grasselli Spreader-Sticker. A commercial spreader and sticker containing sodium oleyl sulfate and a synthetic resinous sticker.

(16) Kolofog. Fused bentonite sulfur—a commercial product marketed as a granular powder. 30 to 38 per cent sulfur and presumably 62 to 70 per cent bentonite.

(17) Lead arsenate. Standard acid—commercial brands.

(18) Manganese borate, white powder.

(19) Orthex. A commercial sticker paste containing 72.87 per cent mineral oil, 2.31 per cent potassium soap and 21.59 per cent water as the principle ingredients.

(20) Skim milk. Spray process—very fine powder. Some roller process grade also used.

(21) Soybean flour. Several grades used, "Spraysoy" being the commercial product.

(22) Soybean oil. A brownish yellow oil. Physical properties not determined.

(23) Spergon. Seed disinfectant containing chloranil as the active ingredient.

(24) Talc. Hydrous magnesium silicate—fine white powder.

(25) White mineral oil. Several grades of highly refined mineral oil were used. Most of the work was done with 100 viscosity industrial white oils.

(26) Ultrawet. A spreader and wetting agent in the form of a white powder reported to be a water soluble sodium sulfonate petroleum ether.

[1] All chemical determinations were made by Dr. H. J. Fisher, except as indicated.

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