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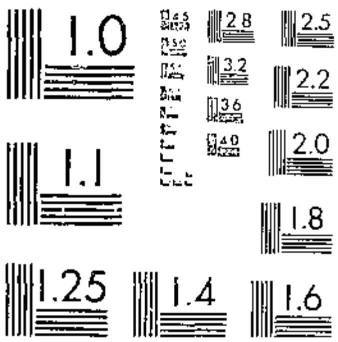

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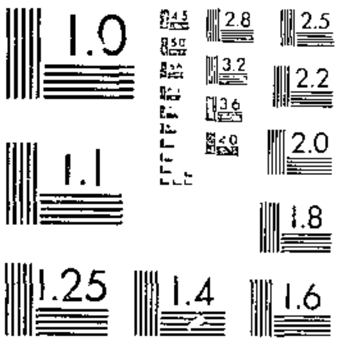

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TECHNICAL BULLETIN No. 373 — OCTOBER 1933

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STUDIES OF FLUORINE COMPOUNDS FOR CONTROLLING THE CODLING MOTH

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CONTENTS

INTRODUCTION

In the search for insecticidal materials which could be substituted for lead arsenate for the control of the codling moth, the Bureau of Entomology and the Bureau of Chemistry and Soils have studied a number of inorganic fluorine compounds. These compounds, because of their availability and chemical and physical properties, seem to offer a profitable field for investigation. This bulletin reports results of insecticidal tests made at the Yakima (Wash.) laboratory of the Bureau of Entomology. The experiments were all conducted under arid conditions. This fact is emphasized, as it is of special significance in interpreting the results obtained. Effective control or freedom from plant injury was not secured in similar experiments conducted under more humid conditions by other investigators of the Bureau of Entomology.

Our knowledge of the effect of fluorine compounds on human beings is limited. Available information, however, indicates that they are not more toxic than arsenic and that the fluorine residue on the fruit at harvest can be removed as easily as can either arsenic or lead residues. Information as to the removal of the metallic element of the fluorine compound is, however, not available.

[1] The writers are indebted to M. A. Yothers, associate entomologist, and F. P. Dean and A. R. Rolfs, junior entomologists, who assisted with many of the experiments

The toxicity of certain fluorine compounds to insects has been recognized for some time, and a few of them have found wide application in the control of pests such as roaches, chicken lice, etc., where foliage injury is not a factor. One of the earliest references to the insecticidal properties of fluorine compounds is contained in British patent no. 8236, entitled "An Improved Composition or Material for Destroying Insects," issued to C. H. Higbee in 1896. During the last 15 years other fluorine compounds have been tested against a number of different insects infesting growing crops. In many instances good control has been reported. The records of these tests have been reviewed by Marcovitch (*9*),[2] who has also published a comprehensive bibliography.

OCCURRENCE AND AVAILABILITY OF FLUORINE COMPOUNDS

Fluorine does not occur free in nature, but it occurs in a wide variety of combinations with other elements throughout the earth's crust. Most phosphate-rock deposits contain 3 percent or more of fluorine; calcium fluoride in the form of fluorspar is a common material; and many other combinations of fluorine have a wide geographical distribution.

Many of the fluorine compounds are stable, chemically inert, finely crystalline or amorphous powders, and relatively insoluble. These qualities make them desirable from an insecticidal standpoint, as they can be applied by dusting or spraying; they adhere to foliage without being toxic to it, and they retain their efficiency over a considerable period of time. They are also nonirritating to operators and noninjurious to machinery.

HYDROFLUORIC AND HYDROFLUOSILICIC ACIDS

Two common acids containing fluorine are easily prepared from the naturally occurring compounds. When fluorspar or any other nonsiliceous fluoride is treated with sulphuric or other nonvolatile acid and the reaction mixture is heated, hydrogen fluoride distills off and may be dissolved in water to form aqueous hydrofluoric acid or condensed to the anhydrous hydrofluoric acid. Commercial aqueous hydrofluoric acid containing 48 percent HF is available in large quantitites. The reaction involved in its manufacture is expressed by the equation:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Phosphate rock contains a double compound of calcium phosphate and calcium fluoride and in addition silicon dioxide or sand, so that when this material is heated with sulphuric acid, as in the manufacture of phosphate fertilizer, reactions take place as follows: The calcium fluoride and sulphuric acid react to form hydrofluoric acid, which in turn reacts with the silica to form silicon tetrafluoride, which is evolved as a gas. These reactions are expressed by the equations:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$
$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

When the silicon tetrafluoride is passed into water, it combines with it to form hydrofluosilicic acid (H_2SiF_6).

$$3SiF_4 + 4H_2O \longrightarrow 2H_2SiF_6 + Si(OH)_4$$

[2] Italic numbers in parentheses refer to Literature Cited, p. 23.

Commercial aqueous hydrofluosilicic acid containing about 35 percent of H_2SiF_6 is available in large quantities. Each ton of phosphate rock contains the equivalent of about 75 pounds of hydrofluosilicic acid, and, since approximately 3,000,000 tons of phosphate rock are sold or used annually in the United States, there is an ample supply of fluorine. As gaseous silicon tetrafluoride is deleterious to vegetation, most fertilizer manufacturers are required to prevent its escape into the air; so any new use for this compound is welcomed.

FLUORIDES

The fluorides, or salts of hydrofluoric acid, are the most common commercial fluorine compounds. They are represented by the general formulas MF, MF_2, MF_3, etc., where M represents mono-, di-, and tri-basic elements, respectively. Fluorides of practically all the metals have been prepared and their properties studied. In general, they are finely crystalline compounds or almost amorphous powders, stable, and with widely differing solubilities in water (*2*). Their insecticidal properties have been investigated quite thoroughly, but usually if soluble enough to have the desired toxicity to insects these compounds cause foliage injury. Most fluorides are dense powders which are not suitable for dusting purposes and do not adhere well to foliage.

FLUOSILICATES

The fluosilicates, or salts of hydrofluosilicic acid, are another important class of fluorine compounds. They are also sold and advertised commercially as silicofluorides, but the American Chemical Society recognizes only the term "fluosilicate." They are represented by the general formulas M_2SiF_6, $MSiF_6$, $M_2(SiF_6)_3$, etc., where M represents mono-, di-, and tri-basic elements, respectively.

The fluosilicates of most of the metals have been prepared and their properties determined. They are finely crystalline or amorphous powders or well-defined crystalline compounds, some with and some without water of crystallization. They are usually much more soluble than the corresponding fluorides (*2*, *4*), and in solution they give an acid reaction. Sodium fluosilicate, for example, reacts with water according to the equation:

$$3Na_2SiF_6+4H_2O \rightleftharpoons 6NaF+2H_2SiF_6+Si(OH)_4$$

The titration of the liberated acid in a fluosilicate solution with standard alkali is often employed as an analytical procedure:

$$Na_2SiF_6+4NaOH \longrightarrow 6NaF+SiO_2+2H_2O$$

There are only three fluosiliates whose solubility is low enough to permit of their use as insecticides on field crops. They are the fluosilicates of barium, potassium, and sodium. These compounds are available commercially both in the pure form and mixed with diluents to improve their physical condition for dusting purposes.

Sodium fluosilicate is available commercially in large quantities. It can be obtained easily in a high degree of purity, commercial samples in many cases showing by analysis a purity of more than 99 percent. In order to improve its physical condition for dusting purposes it is also mixed with diluents and sold as a dusting material. Diatomaceous earth, talc, silica, sulphur, hydrated lime, and other finely divided materials are used for this purpose.

Potassium fluosilicate is less soluble than sodium fluosilicate and has received less attention as an insecticide, probably on account of its greater cost. It is a white, very finely divided powder suitable for application by spraying or dusting. It can be obtained easily in a high state of purity and can be mixed with diluents similarly to sodium fluosilicate.

Barium fluosilicate is the least soluble of the fluosilicates. It is available commercially in large quantities either in the pure form or mixed with diluents, as in the case of sodium fluosilicate. A special light form claimed to contain 80 percent $BaSiF_6$ and 20 percent fluffing agent is also available. It is a white, very finely divided powder suitable for application by spraying or dusting, and it adheres well to foliage.

It should be remembered that all fluosilicates give an acid reaction in solution and that mixtures with basic materials such as hydrated lime react, neutralizing part of the fluosilicate, to form a fluoride. Barium fluosilicate in particular is also not compatible with nicotine sulphate, Bordeaux mixture, lime-sulphur, or spreaders containing a high percentage of calcium compounds, sodium sulphate, or other soluble sulphates.

FLUOALUMINATES

Other fluorine compounds that appear promising are the fluoaluminates, or salts of the hypothetical acid H_3AlF_6. If aluminum oxide or hydroxide is treated with hydrofluoric acid in excess, the aluminum fluoride first formed is soluble in the excess acid so that in effect we have a solution of H_3AlF_6:

$$Al(OH)_3 + 6HF \rightleftharpoons H_3AlF_6 + 3H_2O$$

Salts of this acid may be formed in the same way as with any other acid—viz, by treatment with a base or a solution of another more soluble salt.

The natural mineral cryolite, or sodium fluoaluminate, is an example of this class of compounds. It occurs in nature in well-defined crystalline form. The other alkali-metal salts of this class are described by Carter (*5*). Little has been published on the preparation and properties of the fluoaluminates of the other metals, but considerable work is now in progress.

In general, the fluoaluminates are finely crystalline or amorphous powders, stable, relatively insoluble, and since they are not easily hydrolyzed by water their solutions or suspensions in water are practically neutral. They should therefore be safe for use on field crops. These compounds are also stable in the presence of moisture and are not appreciably decomposed by hard water. However, they should not be mixed with lime-sulphur or other materials of high calcium content.

Synthetic cryolite, or sodium fluoaluminate, of a high degree of purity is available commercially. This is a white, very finely divided powder, relatively insoluble, and suitable for spraying and dusting purposes. Its refractive index is close to that of water, so that concentrations of 4 pounds to 100 gallons appear almost clear, although only a small percentage is really in solution. There is also available commercially a special form of natural cryolite, which is finely powdered, suspends well in water, and seems to be as suitable as the synthetic material.

Potassium fluoaluminate has been made commercially and is a white, finely crystalline or amorphous powder of low solubility, suitable for spraying purposes but not quite so suitable for dusting. Its dusting properties can probably be improved, however. The refractive index of this compound is likewise low, and suspensions of it are nearly transparent, but only a small percentage actually goes into solution.

ANALYSES OF MATERIALS USED

Most of the compounds used for the experimental work reported in this bulletin were analyzed to determine the percentage purity, and these analyses are given below:

	Percent
Barium fluosilicate no. 1:	
Barium fluosilicate ($BaSiF_6$)	74. 5
Other material	25. 5
Barium fluosilicate no. 2:	
Barium fluosilicate ($BaSiF_6$)	66. 5
Barium fluoride (BaF_2)	22. 4
Moisture	0. 2
Other material	10. 9
Barium fluosilicate no. 3:	
Barium fluosilicate ($BaSiF_6$)	95. 0
Inert ingredients	5. 0
Barium fluosilicate no. 4:	
Barium fluosilicate ($BaSiF_6$)	95. 4
Barium fluoride (BaF_2)	1. 5
Inert ingredients	3. 1
Barium fluosilicate no. 5:	
Barium fluosilicate ($BaSiF_6$)	74. 1
Barium fluoride (BaF_2)	2. 7
Undetermined (mostly silica)	23. 2
Potassium fluosilicate no. 1:	
Potassium fluosilicate (K_2SiF_6)	96. 7
Potassium fluoride (KF)	2. 7
Moisture	0. 2
Other material	0. 4
Sodium fluosilicate no. 1:	
Sodium fluosilicate (Na_2SiF_6)	98. 1
Iron and aluminum oxides (Fe_2O_3 and Al_2O_3)	0. 6
Other material	1. 3
Potassium fluoaluminate no. 1:	
Potassium fluoaluminate (K_3AlF_6)	96. 6
Iron and aluminum oxides, etc. (Fe_2O_3 and Al_2O_3)	3. 4
Sodium fluoaluminate (synthetic cryolite) no. 1:	
Sodium fluoaluminate (Na_3AlF_6)	79. 8
Undetermined	20. 2
Sodium fluoaluminate (synthetic cryolite) no. 2:	
Sodium fluoaluminate (Na_3AlF_6)	91. 0
Alumina (Al_2O_3)	6. 0
Undetermined	3. 0

The fish oils employed were salmon oils, which are obtainable on the Pacific coast. The physical and chemical constants of two of these oils were determined:[3]

	No. 1	No. 2
Specific gravity at 15°/4° C	0. 922	0. 932
Viscosity, seconds, Saybolt Universal at 100° F	165	132
Saponification number	191	194
Unsulphonated residue (A.O.A.C. method)	None.	None.
Iodine number (Hanus)	125	180
Acetyl value, mg KOH per gram acetylated oil	24	12
Free fatty acids (calculated as oleic acid), percent	7. 5	. 7
Water-soluble acids (calculated as oleic acid), percent	. 14	. 08
Volatile fatty acid number, mg KOH per 5 g of oil	. 52	. 23
Insoluble fatty acids (Hehner), percent	96. 6	96. 1

[3] These analyses were made by F. E. Dearborn, of the Bureau of Chemistry and Soils.

These constants correspond quite well with those given by Hood (*8*), except that sample no. 1 had a rather high free-fatty-acid content. No injury resulted from the use of this oil, however.

METHODS OF MAKING TESTS

Most of the laboratory experiments were made in the manner already used by Newcomer (*11*). Carefully selected apples of one variety were suspended by their stems in an outdoor shelter and sprayed or dusted uniformly with the material to be tested. When they were thoroughly dry, 10 newly hatched larvae were placed on each apple, five apples being used for each test. In 1929 and 1930 tests were also made in which larvae were placed on the fruit several days after it had been sprayed. In order to have the fruit in a normal condition, it was sprayed while hanging on the tree, and picked just before the larvae were placed on it. Care was taken to remove adjacent leaves, so that the spray material would not be rubbed off by them. In 1930, also, small pieces of paraffined paper on which were 10 eggs almost ready to hatch were attached to the stems by means of paper clips. The resulting larvae readily found their way to the apples.

The results of the laboratory experiments are given in terms of percentage of worms entering the fruit, percentage causing only stings, percentage causing total blemishes, and, in most instances, percentage of control. The last-mentioned figure has been obtained by the method of Abbott, Culver, and Morgan (*1, p. 6*), who used the following formula:

$$\frac{(\text{Percentage of worms entering fruit in check}) - (\text{percentage of worms entering treated fruit})}{(\text{Percentage of worms entering fruit in check})} \times 100 = \text{percent control}$$

Many of the experiments reported are averages of two or more tests made during the same season. When this was done, the same number of tests, made on the same dates, are used for each experiment in the table. No attempt has been made to compare one series of experiments with another, for variations due to differences in temperature and humidity, condition of the larvae, and variety and degree of ripeness of the fruit would make such a comparison of little or no value.

For the orchard experiments plots containing 8 to 16 trees were used. The spraying was done with a gasoline power sprayer maintaining 300 to 350 pounds pressure and using spray guns and two lines of hose. Very wormy orchards were selected for all the tests in order to give a fair comparison. Tests in which the infestation is less than 5 percent are not dependable, as experimental error may overshadow any differences caused by variations in the treatment.

The results of the orchard experiments are given in terms of percentage of fruit wormy, percentage stung, percentage of sound fruit—that is, fruit that is neither wormy nor stung—and ratio of stings to total blemishes. Fruit that was both wormy and stung is recorded under both headings.

LABORATORY EXPERIMENTS

EXPERIMENTS IN 1925 AND 1926

The first work done with fluorine compounds at Yakima, Wash., was in 1925, when a barium fluosilicate (no. 1) was available for laboratory experiments. It was tested at dilutions of 2 and 4 pounds to 100 gallons of water, without fish oil, in comparison with lead arsenate at 2 pounds to 100 gallons (table 1). The results were nearly as good as those obtained with lead arsenate.

TABLE 1.—*Toxic effect of barium fluosilicate, as compared with that of lead arsenate, on the larvae of the codling moth: Laboratory experiments, 1925*

[4 tests averaged for each experiment]

Experiment no.	Material [1]	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes	Control
		Pounds	*Number*	*Percent*	*Number*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no. 1	2	17	8.5	48	24.0	32.5	74.6
2	do	4	16	8.0	49	24.5	32.5	76.1
3	Lead arsenate	2	13	6.5	46	23.0	29.5	80.6
4	Check (unsprayed)		67	33.5	42	21.0	54.5	

[1] Analyses of most of the fluorine compounds mentioned in this and following tables are given under Analyses of Materials.

In 1926 a sodium fluosilicate was tested, both as a spray and as a dust, being diluted with lime in the latter case, as indicated in table 2. The results were relatively poor.

TABLE 2.—*Toxic effect of sodium fluosilicate, as compared with that of lead arsenate, with and without the addition of hydrated lime, on the larvae of the codling moth: Laboratory experiments, 1926*

[4 tests averaged for each experiment]

Experiment no.	Material	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes	Control
		Pounds	*Number*	*Percent*	*Number*	*Percent*	*Percent*	*Percent*
1	Sodium fluosilicate no. 1	2	80	40.0	21	10.5	50.5	31.0
2	do	4	60	30.0	28	14.0	44.0	48.3
3	Lead arsenate	2	35	17.5	29	14.5	32.0	69.8
		Percent [1]						
4	Sodium fluosilicate no. 1 Hydrated lime	16.7 83.3	38	19.0	18	9.0	28.0	67.2
5	Lead arsenate Hydrated lime	15 85	9	4.5	26	13.0	17.5	92.2
6	Check (not sprayed or dusted)		116	58.0	5	2.5	60.5	

[1] By weight.

EXPERIMENTS IN 1927

In 1927 the fluosilicates of barium, sodium, magnesium, and zinc and sodium fluoaluminate (synthetic cryolite) were tested at dilutions of 4 and 8 pounds per 100 gallons of water in comparison with lead arsenate at 2 and 4 pounds, respectively. The results obtained with the barium fluosilicate no. 2 and sodium fluosilicates were very good, as shown in table 3. The soluble zinc and magnesium fluosilicates were of little value. The zinc fluosilicate also caused the apples to turn brown wherever it entered the fruit through holes in the skin made by the codling-moth larvae. This suggests that it might burn the fruit and foliage if used in the orchard. The sodium fluoaluminate, which was rather impure and dense, did not give good control.

TABLE 3.—*Toxic effect of various fluorine compounds, as compared with that of lead arsenate, on the larvae of the codling moth: Laboratory experiments, 1927*

[2 tests averaged for each experiment]

Experiment no.	Material	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes	Control
		Pounds	*Number*	*Percent*	*Number*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no. 2	4	24	24	5	5	29	68.4
2	Sodium fluosilicate no. 1	4	31	31	11	11	42	59.2
3	Magnesium fluosilicate	4	57	57	4	4	61	25.0
4	Zinc fluosilicate	4	53	53	2	2	55	30.3
5	Sodium fluoaluminate no. 1	4	51	51	5	5	56	32.0
6	Lead arsenate	2	40	40	3	3	43	47.4
7	Barium fluosilicate no. 2	8	18	18	13	13	31	76.3
8	Sodium fluosilicate no. 1	8	17	17	11	11	28	77.6
9	Magnesium fluosilicate	8	46	46	4	4	50	39.5
10	Zinc fluosilicate	8	49	49	7	7	56	35.5
11	Sodium fluoaluminate no. 1	8	37	37	3	3	40	51.3
12	Lead arsenate	4	28	28	8	8	36	63.2
13	Check (unsprayed)		76	76	0	0	76	

EXPERIMENTS IN 1928

It was thought that these materials might not adhere so well as lead arsenate, and therefore fish oil, in the quantity suggested by Hood (*8*) for use with lead arsenate, was added to them in the tests made in 1928. The degree of control obtained with all the fluorine compounds was higher than with lead arsenate, when compared with half the quantity of the latter, used without fish oil, as shown in table 4. This was in spite of the fact that the barium fluosilicate and sodium fluoaluminate were not very pure, being the same as were used in 1927. The addition of fish oil (no. 1) to the lead arsenate resulted in somewhat better control than was obtained with the fluorine compounds.

TABLE 4.—*Toxic effect of various fluorine compounds plus fish oil, as compared with that of lead arsenate, with and without the addition of fish oil, on the larvae of the codling moth: Laboratory experiments, 1928*

[3 tests averaged for each experiment]

Experiment no.	Material	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes	Control
			Number	*Percent*	*Number*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no. 2 Fish oil no. 1	4 pounds 1 pint	24	16.0	24	16.0	32.0	70.4
2	Potassium fluosilicate no. 1 Fish oil no. 1	4 pounds 1 pint	18	12.0	30	20.0	38.0	77.8
3	Sodium fluoaluminate no. 1 Fish oil no. 1	4 pounds 1 pint	25	16.7	23	15.3	32.0	69.1
4	Lead arsenate Fish oil no. 1	2 pounds 1 pint	16	10.7	35	23.3	34.0	80.2
5	Lead arsenate	2 pounds	30	20.0	31	20.7	40.7	63.0
6	Check (unsprayed)		81	54.0	9	0.0	60.0	

EXPERIMENTS IN 1929

The compounds tested in 1929 were the same as those used in 1928. Tests were made 1 day and 7 days after spraying. Inasmuch as it was necessary to spray the apples while they were still on the trees, it was impossible to spray them so evenly and thoroughly as when they can be revolved while being sprayed. However, the results are interesting (table 5). The barium fluosilicate gave, on the whole, slightly better control than the potassium fluosilicate, possibly because of better adhesive power. The sodium fluoaluminate was the best of the three in the 1-day test, but at the end of 7 days the control was not quite so good as with the other materials. In most instances the addition of fish oil improved the degree of control in the 1-day test, but this improvement was not evident in the 7-day test.

TABLE 5.—*Toxic effect of various fluorine compounds, as compared with that of lead arsenate, with and without the addition of fish oil, on the larvae of the codling moth: Laboratory experiments, 1929*

Experiment no.	Material	Dilution (per 100 gallons)	1 day after spraying				7 days after spraying			
			Worms entering fruit	Worms causing stings	Worms causing total blemishes	Control	Worms entering fruit	Worms causing stings	Worms causing total blemishes	Control
			Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no. 2	2 pounds	20	14	34	64.3	12	8	20	80.0
2	do Fish oil no. 1	do 1 pint	14	20	34	75.0	24	10	34	60.0
3	Barium fluosilicate no. 2	4 pounds	12	12	24	78.6	14	6	20	76.7
4	Potassium fluosilicate no. 1	2 pounds	24	20	44	57.1	24	8	32	60.0
5	do Fish oil no. 1	do 1 pint	12	30	42	78.6	32	6	38	46.7
6	Potassium fluosilicate no. 1	4 pounds	18	20	38	67.9	22	6	28	63.3
7	Sodium fluoaluminate no. 1	2 pounds	8	32	40	85.7	28	20	48	53.3
8	do Fish oil no. 1	do 1 pint	10	26	36	82.1	28	14	42	53.3
9	Sodium fluoaluminate no. 1	4 pounds	10	24	34	82.1	44	18	62	26.7
10	do Fish oil no. 1	do 1 pint	2	22	24	96.4	18	16	34	70.0
11	Lead arsenate	2 pounds	18	8	26	67.9	14	22	36	76.7
12	do Fish oil no. 1	do 1 pint	24	16	40	57.9	26	10	36	56.7
13	Check (unsprayed)		56	2	58		60	0	60	

In an additional test made with sodium fluoaluminate and fish oil, the control was very good, as shown in table 6. This table also gives the results of a preliminary test with potassium fluoaluminate, which indicates that this compound may be of some value.

TABLE 6.—*Toxic effect of sodium fluoaluminate and potassium fluoaluminate, as compared with that of lead arsenate, on the larvae of the codling moth: Laboratory experiments, 1929*

Experiment no.	Material	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes	Control
			Number	*Percent*	*Number*	*Percent*	*Percent*	*Percent*
1	Sodium fluoaluminate no. 1 Fish oil no. 1	2 pounds 1 pint	4	8	21	42	50	81.0
2	Sodium fluoaluminate no. 1 Fish oil no. 1	4 pounds 1 pint	6	12	19	38	50	71.4
3	Lead arsenate	2 pounds	13	26	14	28	54	38.1
4	Check (unsprayed)		21	42	6	12	54	
5	Potassium fluoaluminate no. 1	do	24	48	10	20	68	38.5
6	Lead arsenate	do	26	52	6	12	64	33.3
7	Check (unsprayed)		39	78	0	0	78	

EXPERIMENTS IN 1930

Experiments were made in 1930 with barium fluosilicate and sodium fluoaluminate from several sources and with a series of 17 fluorine compounds prepared by Carter. The five fluorine compounds included in table 7, when used at the rate of 3 pounds to 100 gallons of water, with fish oil, all resulted in a control equal to or better than that with lead arsenate used at the rate of 2 pounds per 100 gallons, without fish oil. This was true both 1 day after spraying and 5 days after spraying.

TABLE 7.—*Toxic effect of various fluorine compounds, as compared with that of lead arsenate, with and without the addition of fish oil, on the larvae of the codling moth: Laboratory experiments, 1930*

[2 tests averaged for each experiment]

Experiment no.	Material	Dilution (per 100 gallons)	1 day after spraying				5 days after spraying			
			Worms entering fruit	Worms causing stings	Worms causing total blemishes	Control	Worms entering fruit	Worms causing stings	Worms causing total blemishes	Control
			Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no 2 Fish oil no. 2	3 pounds 1 quart	45.6	21.2	66.8	52.5	68.9	21.2	90.1	29.0
2	Barium fluosilicate no. 3 Fish oil no. 2	3 pounds 1 quart	53.3	22.3	75.6	44.5	68.4	22.3	90.7	29.5
3	Sodium fluoaluminate no. 1 Fish oil no. 2	3 pounds 1 quart	59.9	19.8	79.7	37.6	67.3	15.4	82.7	30.6
4	Sodium fluoaluminate no. 2 Fish oil no. 2	3 pounds 1 quart	40.0	31.0	71.0	58.3	47.1	34.8	81.9	51.4
5	Potassium fluoaluminate no. 1	2 pounds	76.0	11.0	87.0	20.8	73.5	14.3	87.8	24.2
6	do	3 pounds	57.5	15.2	72.7	40.1	73.9	17.1	91.0	23.8
7	do Fish oil no 2	do 1 quart	52.7	18.2	70.9	45.1	61.8	28.4	90.2	36.3
8	Potassium fluoaluminate no. 1	4 pounds	50.3	29.0	79.3	47.0	58.0	27.8	85.8	40.2
9	Lead arsenate	2 pounds	60.0	18.0	78.0	37.5	73.6	9.0	82.0	24.1
10	Check (unsprayed)		96.0	0	96.0		97.0	0	97.0	

In another series of experiments a barium fluosilicate over 95 percent pure (no. 4) was compared with a material containing only about 74 percent barium fluosilicate (no. 5). The former material was somewhat better than the latter both 1 day and 5 days after application, as shown by comparing experiments nos. 1, 2, and 3 with nos. 4, 5, and 8 in table 8. Even when used at the rate of 4 pounds to 100 gallons (experiment no. 9), the compound containing 75 percent barium fluosilicate was not much better than the other material at 3 pounds. Variations in the method of using the fish oil were also tried. It was used without emulsification, and emulsified with the fluosilicate and with casein-lime spreader (experiments nos. 5, 6, and 7). No great difference in control resulted.

TABLE 8.—*Toxic effect of barium fluosilicate, as compared with that of lead arsenate, with and without the addition of fish oil or summer-oil emulsion, on the larvae of the codling moth: Laboratory experiments, 1930*

[2 tests averaged for each experiment]

Experiment no.	Material	Dilution (per 100 gallons)	1 day after spraying: Worms entering fruit	1 day after spraying: Worms causing stings	1 day after spraying: Worms causing total blemishes	1 day after spraying: Control	5 days after spraying: Worms entering fruit	5 days after spraying: Worms causing stings	5 days after spraying: Worms causing total blemishes	5 days after spraying: Control
			Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Barium fluosilicate no. 4	3 pounds	60.7	19	79.7	35.4	59.5	10.1	60.6	26.4
2	do; Fish oil no. 2	do; 1 quart	50.9	17.6	68.5	45.9	61	25	86	24.5
3	Barium fluosilicate no. 4; Summer-oil emulsion	3 pounds; 1 gallon	47.0	23.3	70.9	49.4	65.5	7	72.5	18.9
4	Barium fluosilicate no. 5	3 pounds	67	15	82	28.7	68.8	10	78.8	14.9
5	do; Fish oil no. 2	do; 1 quart	64.7	10.2	74.9	31.2	63.8	14.2	78	21
6	Barium fluosilicate no. 5; Fish oil no. 2, emulsified with the fluosilicate	3 pounds; 1 quart	61.2	10.9	72.1	34.9	66.7	11.2	77.9	17.5
7	Barium fluosilicate no. 5; Fish oil no. 2, emulsified with casein-lime spreader	3 pounds; 1 quart	60	12	72	30.2	63.2	10.4	73.6	21.8
8	Barium fluosilicate no. 5; Summer-oil emulsion	3 pounds; 1 gallon	58.4	13.4	71.8	37.9	73.2	4	77.2	9.4
9	Barium fluosilicate no. 5	4 pounds	55.3	19.3	74.6	41.2	59.4	7.1	66.5	26.5
10	Lead arsenate	2 pounds	65.6	9.7	75.3	30.2	71	8	79	12.1
11	Check (unsprayed)		94	1	95		80.8	0	80.8	

The two sodium fluoaluminates (nos. 1 and 2) shown in table 9 were tested at the rate of 4 pounds to 100 gallons, with and without fish oil, and also with mineral oil and with a small quantity of mineral-oil emulsion. Unfortunately there was no unsprayed check with this series, so that the percentage of control cannot be given. However, by examining the percentage of worms entering the fruit and the percentage causing the total blemishes, as given in table 9, it will be evident that sodium fluoaluminate no. 2, which was the purer of the two, gave the better control. This was also shown in experiments nos. 3 and 4, table 7. It is apparent also that, with sodium fluoaluminate no. 2 at least, there is an advantage in adding a fish oil or mineral oil.

TABLE 9.—*Toxic effect of sodium fluoaluminate, as compared with that of lead arsenate, with and without the addition of fish oil, summer oil, or summer-oil emulsion, on the larvae of the codling moth: Laboratory experiments, 1930*

Experiment no.	Material	Dilution (per 100 gallons)	Wormholes	Worms entering fruit	Stings	Worms causing stings	Worms causing total blemishes
			Number	*Percent*	*Number*	*Percent*	*Percent*
1	Sodium fluoaluminate no. 1	4 pounds	19	38	12	24	62
2	do. Fish oil no. 2	do. 1 quart	16	32	19	38	70
3	Sodium fluoluminate no. 1 Summer-oil emulsion	4 pounds 1 quart	22	44	12	24	68
4	Sodium fluoaluminate no. 1 Summer oil	4 pounds 1 quart	23	46	11	22	68
5	Sodium fluoluminate no. 2	4 pounds	19	38	4	8	46
6	do. Fish oil no. 2	do. 1 quart	15	30	11	22	52
7	Sodium fluoaluminate no. 2 Summer-oil emulsion	4 pounds 1 quart	12	24	11	22	46
8	Sodium fluoaluminate no. 2 Summer oil	4 pounds 1 quart	17	34	4	8	42
9	Lead arsenate	2 pounds	34	68	5	10	78

In the tests made in 1930 fish oil was used at the rate of 1 quart to 100 gallons, instead of 1 pint. Analyses of apples sprayed with barium fluosilicate alone and with the addition of 0.5, 1, and 2 pints of fish oil (table 10) indicated that increasing the quantity of fish oil did not increase the quantity of barium fluosilicate placed on the apples but did increase the residue remaining after an interval of 10 days. Marcovitch and Stanley (*10*) had shown increased adhesiveness of barium fluosilicate during rains when fish oil was added. In this case a slight rain, amounting to 0.15 inch, occurred in the 10-day interval. Fish oil no. 2 was used in these tests.

TABLE 10.—*Effect of addition of different quantities of fish oil on adherence of barium fluosilicate* [1] *sprayed on apples*

Fish oil per 100 gallons of spray	Barium fluosilicate on apples		
	Sprayed in insectary; analyzed immediately	Sprayed in orchard	
		Analyzed immediately	Analyzed after 10 days
Pints	*Grain per pound*	*Grain per pound*	*Grain per pound*
None.	0.173	0.116	0.078
0.5	.093	.117	.080
1	.143	.119	.107
2	.107	.115	.114

[1] 4 pounds of barium fluosilicate used per 100 gallons.

The results of the toxicity tests (tables 5, 7, and 8) are not what would be expected from the analyses in table 10, the percentages of control decreasing about as much during the interval in the tests with fish oil as in those without it. Rain amounting to 0.3 inch fell during the interval of the test of 1929 and a smaller quantity fell during one of the two series of tests included in table 8, but no correlation between the rainfall and the results is evident. Further work is necessary before the value of the fish oil and the optimum quantity that should be used can be determined.

Table 11 gives tests of 17 fluorine compounds, all of which were laboratory preparations purified with a reasonable degree of care and may be considered as being at least 90 percent pure in all cases. Their solubilities were in every case less than that of sodium fluosilicate. The compounds were used at the rate of 4 pounds to 100 gallons, and compared with lead arsenate at the rate of 2 pounds to 100 gallons, no fish oil being used. In these tests five compounds—manganese fluoride, barium fluosilicate, potassium fluosilicate, magnesium fluoaluminate, and potassium fluoaluminate—were distinctly superior to lead arsenate, as indicated by the relative percentages of worms entering the fruit. Three others—sodium fluosilicate, ammonium fluoaluminate, and sodium fluoaluminate—were approximately equal to lead arsenate. Of these 8 compounds, 3—manganese fluoride, magnesium fluoaluminate, and ammonium fluoaluminate—had not been tried before.

TABLE 11.—*Toxic effect of various fluorine compounds and of lead arsenate on the larvae of the codling moth: Laboratory experiments, 1930*

Experiment no.	Material [1]	Worms entering fruit	Worms causing stings	Worms causing total blemishes
		Percent	*Percent*	*Percent*
1	Barium fluoride (BaF_2)	72	9	81
2	Lead fluoride (PbF_2)	61	15	76
3	Magnesium fluoride (MgF_2)	74	5	79
4	Manganese fluoride (MnF_2)	41	23	64
5	Barium fluosilicate ($BaSiF_6$)	42	32	74
6	Potassium fluosilicate (K_2SiF_6)	39	31	70
7	Sodium fluosilicate (Na_2SiF_6)	54	24	78
8	Ammonium fluoaluminate [$(NH_4)_3AlF_6$]	47	27	74
9	Barium fluoaluminate ($BaAlF_5$)	77	15	92
10	Calcium fluoaluminate ($CaAlF_5$)	66	15	81
11	Magnesium fluoaluminate ($MgAlF_5$)	39	31	70
12	Potassium fluoaluminate (K_3AlF_6)	33	37	70
13	Potassium fluoaluminate (K_3AlF_6)+SiO_2	50	23	73
14	Sodium fluoaluminate (Na_3AlF_6)	52	23	75
15	Sodium fluoaluminate (Na_3AlF_6)+SiO_2	74	9	83
16	Strontium fluoaluminate ($SrAlF_5$)	60	4	64
17	Zinc fluoaluminate ($ZnAlF_5$)	66	16	82
18	Lead arsenate ($PbHAsO_4$)	49	15	64

[1] The fluorine compounds were used at the rate of 4 pounds to 100 gallons and the lead arsenate at 2 pounds to 100 gallons. No fish oil was used.

The results of these laboratory experiments are somewhat variable, probably on account of the rather large experimental error which must exist in tests of this nature. Moreover, for the most part they show only the toxicity of the materials immediately after application. Nevertheless, they are valuable in giving preliminary indications of what may be expected from these compounds. The practical value of a new material can be determined only by orchard experiments. Such factors as durability of the material and its effect on the tree and the fruit do not enter into laboratory experiments.

ORCHARD EXPERIMENTS

EXPERIMENTS IN 1926 AND 1927

In 1926 some dusting experiments were made in two orchards, in which a sodium fluosilicate dust was compared with a lead arsenate dust and with a lead arsenate spray. The same dilutions were used as in the laboratory tests (table 2, experiments nos. 3, 4, and 5). In one orchard the fluosilicate dust resulted in poorer control than the lead arsenate dust, and in the other orchard it was somewhat better. In both orchards the lead arsenate spray controlled the worms much better than either of the dusting treatments. Tests with barium fluosilicate and sodium fluosilicate used as sprays were made in 1927, but the crop on the trees used was so much smaller than that on the trees sprayed with lead arsenate that a fair comparison could not be made.

EXPERIMENTS IN 1928

In 1928 an orchard of Jonathan apple trees was selected that had not been sprayed the previous season and was therefore very heavily infested. The fluorine compounds were used at the rate of 4 pounds to 100 gallons, and compared with lead arsenate used at the rate of 2 pounds to 100 gallons. These fluorine compounds were made especially for the experiment, but they were quite dense, and the barium fluosilicate and sodium fluoaluminate were not especially pure. In order to increase the adhesiveness of the fluorine sprays, fish oil was added at the rate of 1 pint to 100 gallons. It was usually emulsified first with some of the fluorine compound, as suggested by Porter and Sazama (*12*). The crop was good, although somewhat smaller on the trees sprayed with fluorine compounds than on those sprayed with lead arsenate. Eight trees were used for each test, and the apples from the two most nearly uniform trees in each plot were examined.

As shown in table 12, the percentages of wormy apples on the trees sprayed with potassium fluosilicate and with sodium fluoaluminate were not materially higher than on the trees sprayed with lead arsenate, and the percentages of stung apples were somewhat lower; consequently a slightly larger percentage of the apples were sound. The barium fluosilicate was rather impure, and the results with it were poorer than when potassium fluosilicate was used.

TABLE 12.—*Effectiveness of various fluorine compounds, as compared with lead arsenate, in controlling the codling moth: Orchard experiments, 1928*

Test no.	Material [1]	Dilution (per 100 gallons)	Total apples	Wormy apples		Stung apples		Sound apples	Ratio of stings to total blemishes
		Pounds	*Number*	*Number*	*Percent*	*Number*	*Percent*	*Percent*	
1	Barium fluosilicate no. 2	4	2,698	718	26.6	524	19.4	59.1	0.40
2	Potassium fluosilicate no. 1	4	3,950	943	23.9	787	19.9	61.0	.45
3	Sodium fluoaluminate no. 1	4	4,348	1,006	23.1	873	20.1	62.1	.48
4	Lead arsenate	2	5,502	1,251	22.7	1,333	24.2	60.1	.49

[1] Fish oil, 1 pint to 100 gallons, used with all fluorine sprays.

Spray schedule: Calyx, May 10; first cover, May 22; second cover, June 1; third cover, June 12; fourth cover, June 22; fifth cover, July 11; sixth cover, Aug. 2.

EXPERIMENTS IN 1929

In 1929 the same materials were used at the same dilutions. Carter (*3*) had shown that these compounds were compatible with lead arsenate. Therefore, a plot was added in which lead arsenate was used for the calyx and first cover sprays, followed by sodium fluoaluminate, and another one in which half the usual quantities of lead arsenate and sodium fluoaluminate were used together for the first four applications, followed by sodium fluoaluminate alone. These experiments were made in a different orchard from the one used in 1928; it consisted of Rome Beauty apple trees which had been poorly sprayed the previous season and were consequently heavily infested. The fruit on the various trees in the orchard was nearly uniform. Each plot contained 12 trees, and the fruit from 5 of these was examined in each test.

The results of these experiments are given in table 13. As in 1928, the barium fluosilicate was poor in effectiveness. When potassium fluosilicate and sodium fluoaluminate (synthetic cryolite) were used, the percentage of wormy fruit was similar to that when lead arsenate was used, and the number of stung fruit was markedly smaller. The use of sodium fluoaluminate following lead arsenate (test no. 4) gave the lowest percentage of wormy apples but a higher percentage of stung apples than when sodium fluoaluminate was used throughout. The combination of lead arsenate and sodium fluoaluminate is not included in the table, as the portion of the orchard in which it was used happened to be particularly wormy, and therefore this treatment cannot be compared with the other treatments. There was no evidence of injury to foliage or fruit in any of the plots.

TABLE 13.—*Effectiveness of various fluorine compounds, as compared with lead arsenate, in controlling the codling moth: Orchard experiments, 1929*

Test no.	Material [1]	Dilution (per 100 gallons)	Total apples	Wormy apples		Stung apples		Sound apples	Ratio of stings to total blemishes
		Pounds	*Number*	*Number*	*Percent*	*Number*	*Percent*	*Percent*	
1	Barium fluosilicate no. 2	4	10,671	4,174	39.1	2,287	21.4	50.3	0.30
2	Potassium fluosilicate no. 1	4	12,257	3,025	24.7	2,777	22.7	59.4	.46
3	Sodium fluoaluminate no. 1	4	12,664	3,825	30.2	3,106	25.2	53.4	.43
4	Lead arsenate in calyx and first cover spray	2	10,434	2,184	20.9	2,870	27.5	59.4	.56
	Sodium fluoaluminate no. 1 in remaining cover sprays	4							
5	Lead arsenate	2	12,740	3,247	25.5	4,598	36.1	50.7	.56

[1] Fish oil, 1 pint to 100 gallons, used with all fluorine sprays.

Spray schedule: Calyx, May 20; first cover, June 1; second cover, June 12; third cover, June 24; fourth cover, July 12; fifth cover, Aug. 10.

EXPERIMENTS IN 1930

In 1930 a barium fluosilicate mixture that had been made especially for insecticidal purposes (no. 5) was used. It contained about 74 percent barium fluosilicate, a percentage somewhat higher than that of the material used in 1928 and 1929. It was much lighter and remained in suspension better, owing to the inert material added. The orchard used in 1930 had been heavily infested and consisted of alternating double rows of Jonathan and Winesap apples, making it possible to include both varieties in each plot. Three series of tests were made, in all of which lead arsenate was used for the calyx and first cover sprays.

In the second to the sixth cover sprays barium fluosilicate was used except for two applications in one series (C), where mineral-oil emulsion plus nicotine sulphate was substituted for the fluosilicate. In another series (A) mineral-oil emulsion was added to the barium fluosilicate in two applications. Fish oil (no. 2) was added to the barium fluosilicate except when the mineral-oil emulsion was used. Comparable adjacent plots sprayed with lead arsenate were provided. The treatments for all these plots are given in table 14.

TABLE 14.—*Spray schedule used in orchard experiments for control of the codling moth, 1930*

Series	Test no.	Calyx (May 1) and first cover (May 22)	Second cover, June 4	Third cover, June 14
A	1	Lead arsenate 3 pounds [1]	Barium fluosilicate 3 pounds + 0.75 percent oil emulsion.	Barium fluosilicate [2] 4 pounds.
	2	do	Lead arsenate 2 pounds + 0.75 percent oil emulsion.	Lead arsenate 2 pounds.
	3	do	Lead arsenate 2 pounds	Do.
B	1	do	Barium fluosilicate 4 pounds	Barium fluosilicate 4 pounds.
	2	do	Lead arsenate 2 pounds	Lead arsenate 2 pounds.
C	1	do	0.75 percent oil emulsion + nicotine sulphate (1-1,200).	Barium fluosilicate 4 pounds.
	2	do	do	Lead arsenate 2 pounds.

Series	Test no.	Fourth cover, June 26	Fifth cover, July 20	Sixth cover, Aug. 12
A	1	Barium fluosilicate 4 pounds.	Barium fluosilicate 3 pounds + 0.75 percent oil emulsion.	Barium fluosilicate 4 pounds.
	2	Lead arsenate 2 pounds	Lead arsenate 2 pounds + 0.75 percent oil emulsion.	Lead arsenate 2 pounds.
	3	do	Lead arsenate 2 pounds	Do.
B	1	Barium fluosilicate 4 pounds.	Barium fluosilicate 4 pounds	Barium fluosilicate 4 pounds.
	2	Lead arsenate 2 pounds	Lead arsenate 2 pounds	Lead arsenate 2 pounds.
C	1	Barium fluosilicate 4 pounds.	0.75 percent oil emulsion + nicotine sulphate (1-1,200).	Barium fluosilicate 4 pounds.
	2	Lead arsenate 2 pounds	do	Lead arsenate 2 pounds.

[1] Weights of barium fluosilicate and lead arsenate are for each 100 gallons of spray.
[2] Fish oil, 1 pint to 100 gallons, was used with all barium fluosilicate sprays except where oil emulsion was used.

In order to minimize the variation due to field heterogeneity, the schedule of barium fluosilicate and oil emulsion and the comparable schedules of lead arsenate, with and without oil emulsion, were repeated four times in the orchard, an arrangement similar to the Latin square being used. Owing to the number of experiments being made, it was not possible to do this with the other schedules. In each plot the fruit from two trees of each variety was examined. The results of all these experiments are given in table 15. In each case the percentages of wormy fruit in the comparable plots are similar, and the percentage of stung fruit is considerably more in the plots sprayed with lead arsenate; consequently the percentage of sound apples is lower than in the plots sprayed with fluosilicate.

TABLE 15.—*Effectiveness of sprays of barium fluosilicate, as compared with lead arsenate, in controlling the codling moth: Orchard experiments, 1930* [1]

Series	Test no.	Material	Total apples	Wormy apples		Stung apples		Sound apples	Ratio of stings to total blemishes
			Number	*Number*	*Percent*	*Number*	*Percent*	*Percent*	
A	1	Barium fluosilicate (no. 5)+oil emulsion	38,138	4,405	11.5	3,043	8.0	81.8	0.39
A	2	Lead arsenate+oil emulsion	28,505	3,122	10.9	3,324	11.7	79.5	.52
A	3	Lead arsenate	28,909	3,419	11.8	3,733	12.9	77.7	.52
B	1	Barium fluosilicate no. 5	9,783	972	9.9	733	7.5	83.8	.41
B	2	Lead arsenate	7,830	817	10.4	941	12.0	79.6	.53
C	1	Barium fluosilicate no. 5; oil emulsion+nicotine sulphate	8,576	895	10.4	649	7.6	83.3	.40
C	2	Lead arsenate	9,942	1,121	11.3	1,082	10.9	79.7	.48

[1] Sprays were applied according to the schedule given in table 14.

TABLE 16.—*Effectiveness of fluorine compounds, as compared with that of lead arsenate, in orchard experiments for controlling the codling moth*

EXPERIMENTS IN 1929

Experiment no.	Treatment	Trees	Wormy apples: Weighted mean	Wormy apples: Increase (+) or decrease (−) as compared with lead arsenate treatment	Wormy apples: Difference divided by error	Stung apples: Weighted mean	Stung apples: Increase (+) or decrease (−) as compared with lead arsenate treatment	Stung apples: Difference divided by error
			Percent	*Percent*		*Percent*	*Percent*	
1	Barium fluosilicate	5	39.1±0.8	+13.6±1.5	9.1	21.4±0.6	−14.7±1.6	9.2
2	Potassium fluosilicate	5	24.7±0.9	−.8±1.6	.5	22.7±0.7	−13.4±1.7	7.9
3	Sodium fluoaluminate	5	30.2±1.1	+4.7±1.7	2.8	25.2±0.7	−10.9±1.7	6.4
4	Lead arsenate followed by sodium fluoaluminate	5	20.9±0.8	−4.6±1.5	3.1	27.5±1.2	−8.6±1.9	4.5
5	Lead arsenate	6	25.5±1.3			36.1±1.5		

EXPERIMENTS IN 1930

Experiment no.	Treatment	Trees	Wormy apples: Weighted mean	Wormy apples: Increase (+) or decrease (−) as compared with lead arsenate treatment	Wormy apples: Difference divided by error	Stung apples: Weighted mean	Stung apples: Increase (+) or decrease (−) as compared with lead arsenate treatment	Stung apples: Difference divided by error
1	Barium fluosilicate + oil emulsion	16	11.8±0.9	+0.9±1.4	0.6	8.0±0.3	−3.7±1	3.7
2	Lead arsenate + oil emulsion	14	10.9±1.1			11.7±0.9		

Most of the comparable experiments made from 1928 to 1930 showed a slightly lower percentage of wormy fruit in the plots sprayed with lead arsenate than in those sprayed with the fluorine compounds, and it is desirable to know whether or not this difference is significant. This cannot be figured in some instances owing to the small number of trees examined. However, the significance of the differences in the treatments used in 1929 and 1930 may be determined from the statistical constants computed by the use of standard methods. The probable errors for individual plots were computed by the formula

$$P.E. = \pm 0.6745\sqrt{\frac{\Sigma pd^2}{p(n-1)}}$$

(p = the number of apples in each tree or plot), which is applicable to a weighted mean. This formula was used because of variations in the numbers of apples borne on the trees on which individual counts were made. The probable errors of the differences between plots were computed by the formula

$$E_{\text{diff.}} = \pm \sqrt{e_1^2 + e_2^2}$$

The results of these computations are given in table 16. If four times the probable error is used as a criterion, the differences in percentages of wormy apples are not significant except in the case of the barium fluosilicate used in 1929. On the other hand, the differences noted in the percentages of apples stung are significant in the comparisons in which the fluorine compounds were used throughout the

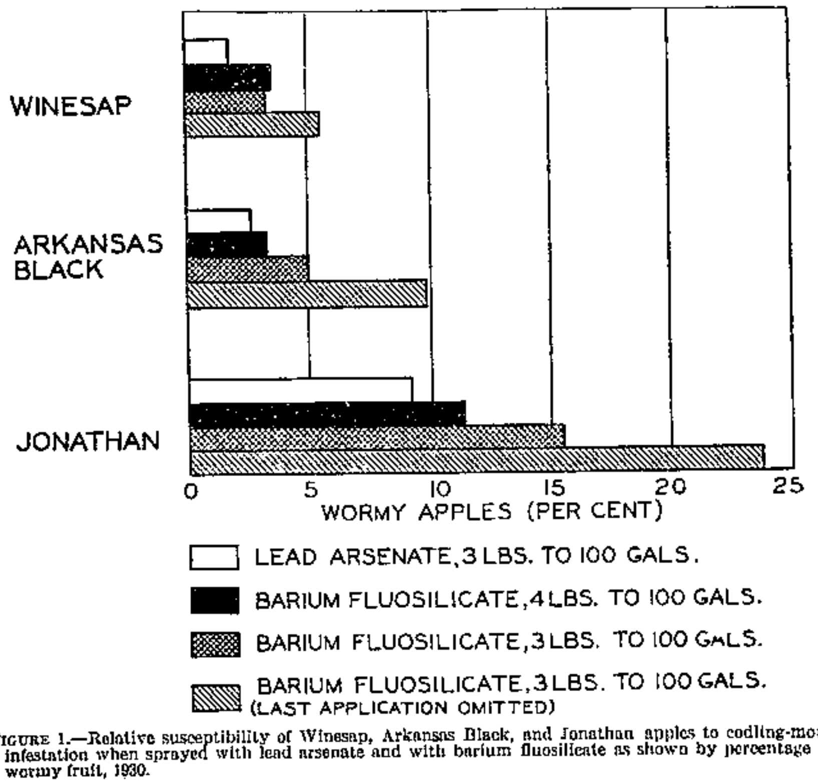

FIGURE 1.—Relative susceptibility of Winesap, Arkansas Black, and Jonathan apples to codling-moth infestation when sprayed with lead arsenate and with barium fluosilicate as shown by percentage of wormy fruit, 1930.

season, and doubtfully so in the comparisons in which the fluorine compound was used following a calyx and first cover spray of lead arsenate. It may be concluded, therefore, that under the conditions of these experiments the fluorine compounds are as effective as lead arsenate in preventing insects from infesting the fruit and that they are somewhat more effective in preventing insects from stinging it.

In 1930 two fruit growers also tested the effectiveness of barium fluosilicate as compared with lead arsenate. Apples from a number of trees in each orchard were examined. The results, which are given in table 17, are similar to those obtained in the writers' experiments, the percentage of wormy fruit being slightly higher and the percentage of stung fruit lower when barium fluosilicate was used. The results given in this table are from Jonathan and Rome Beauty apples in the first orchard (A) and from Jonathan apples in the second (B). In the latter orchard Arkansas Black and Winesap apple trees were also sprayed. The difference in the susceptibility of the three varieties is shown in figure 1. The last application of barium fluosilicate was omitted from some of the trees, and the increase in wormy apples on these trees was very marked. It should be noted that in this orchard the lead arsenate was used at the rate of 3 pounds to 100 gallons throughout the season, so that the barium fluosilicate had a more severe test than it had in the other experiments.

TABLE 17.—*Comparative effectiveness of barium fluosilicate and lead arsenate for controlling the codling moth, as shown by growers' orchard experiments, 1930*

ORCHARD A

Test no.	Material	Dilution (per 100 gallons)	Total apples	Wormy apples		Stung apples		Sound apples	Ratio of stings to total blemishes
			Number	*Number*	*Percent*	*Number*	*Percent*	*Percent*	
1	Lead arsenate calyx and fourth cover sprays. Barium fluosilicate no. 5 Fish oil, first 3 cover sprays.	2 pounds 4 pounds 1 pint	5,357	1,094	20.4	776	14.5	69.1	0.39
2	Lead arsenate calyx and 4 cover sprays.	2 pounds	4,523	840	18.6	875	19.3	66.7	.51

ORCHARD B

Test no.	Material	Dilution (per 100 gallons)	Total apples	Wormy apples		Stung apples		Sound apples	Ratio of stings to total blemishes
1	Lead arsenate calyx and first cover sprays. Barium fluosilicate no. 5 Fish oil, 4 subsequent cover sprays.	3 pounds do 1 pint	11,347	1,761	15.5	699	6.2	79.6	0.27
2	Lead arsenate calyx and first cover sprays. Barium fluosilicate no. 5 Fish oil, 4 subsequent cover sprays.	3 pounds 4 pounds 1 pint	12,542	1,431	11.4	759	6.0	83.7	.34
3	Lead arsenate, all sprays	3 pounds	14,771	1,367	9.2	857	5.8	85.8	.38

EFFECT OF FLUORINE COMPOUNDS ON FOLIAGE AND FRUIT

The possibility of injury to fruit or foliage has been considered. No foliage injury has been noted in the arid climate prevailing in the Yakima Valley, except a very little in 1927. The rainfall during the early part of September of that year was heavier than usual, and about 2 percent of the foliage sprayed with barium and sodium fluosilicate was injured. However, foliage sprayed with lead arsenate was also injured that year. All the experiments have been with apple trees, but some pear foliage has been sprayed without any injury.

There has been no apparent effect on the quality, size, or coloring of the fruit. Records have been kept of the average number of apples per box from all the trees examined. Three plots sprayed with fluorine compounds averaged 141 ± 1.3 apples per box, and three comparable plots sprayed with lead arsenate averaged 139 ± 2.5 apples per box. The difference, 2 ± 2.8, is not significant.

ACCUMULATION AND ADHERENCE OF SPRAY MATERIALS

During the summer of 1930 an attempt was made to determine the quantities of material applied by the different treatments as well as the quantities of residue remaining on the fruit over a period of time.

Samples of Winesap apples sprayed with barium fluosilicate (no. 5) in the regular orchard tests were taken before and after each spraying and analyzed for residues. No standard procedure was available as in the case of arsenical residues; so a method was developed (*6*). Briefly, the method consisted of washing samples of fruit taken before and after each spray with boiling 3 percent sodium hydroxide solution and then analyzing this solution for barium by standard procedure and calculating to barium fluosilicate. Duplicate samples of apples that had received very different treatments were selected and, judging by the agreement between the duplicate analyses, the method seemed to be fairly accurate and gave consistent results. However, it was applicable only to the barium compound.

The results, calculated in milligrams per apple and in milligrams per square centimeter of surface, are given in table 18, and are compared with similar analyses of fruit sprayed throughout with lead arsenate. The surface area was calculated in each case from the average weight of the apples. The volume was first obtained by multiplying the weight by 1.2, as the ratio of weight to volume in Winesap apples was found to be 1 to 1.2. It was determined that a sufficiently accurate estimate of the surface area could be obtained by treating the apples as spheres, and therefore the area was obtained in this way:

$$S=\sqrt[3]{36\pi V^2}=4.84\sqrt[3]{V^2}$$

in which S is surface area and V is volume in corresponding units.

Spray residues on harvested fruit are ordinarily given in terms of grains per pound of fruit. In order that the residues occurring on this fruit at harvest may be directly compared with other residues, the number of grains per pound should be stated, and are as follows: Series B, test 1, 0.124; series A, test 1, 0.152; series A, test 2, 0.089. It should be kept in mind that the barium fluosilicate found is about 74 percent of the total residue, while the arsenious oxide present is only about 28.5 percent of the total lead arsenate residue. In table 18 there are several discrepancies in the quantities of residue before and after certain sprays. This is probably due to variations in the fruit used or to errors of analysis, and these figures are given only as an indication of what residues may be expected.

TABLE 18.—*Comparison of barium fluosilicate and arsenious oxide residues on apples following spraying experiments, 1930*

BARIUM FLUOSILICATE

Treatment [1]	Quantity of residue					
	First cover, May 22		Second cover, June 4		Third cover, June 14	
	Mg per apple	*Mg per cm²*	*Mg per apple*	*Mg per cm²*	*Mg per apple*	*Mg per cm²*
Series B, test 1:						
Before spraying					0.258	0.011
After spraying					.502	.017
ARSENIOUS OXIDE						
Series A, test 2:						
Before spraying	0.032	0.005	0.094	0.006	0.174	0.007
After spraying	.160	.016	.180	.012	.300	.010

BARIUM FLUOSILICATE

Treatment [1]	Quantity of residue						
	Fourth cover, June 26		Fifth cover, July 26		Sixth cover, Aug. 12		Residue at harvest, Oct. 15
	Mg per apple	*Mg per cm²*	*Mg per apple*	*Mg per cm²*	*Mg per apple*	*Mg per cm²*	*Mg per cm²*
Series B, test 1:							
Before spraying	0.794	0.021	1.270	0.022	2.120	0.025	
After spraying	1.156	.029	1.860	.029			0.019
Series A, test 1:							
Before spraying			1.055	.027			
After spraying			1.405	.022	1.900	.022	.017
ARSENIOUS OXIDE							
Series A, test 2:							
Before spraying	0.210	0.005	0.425	0.007	0.750	0.008	
After spraying	.580	.013	.725	.011	1.100	.013	0.009

[1] For spray schedule, see table 14.

REMOVAL OF FLUORINE SPRAY RESIDUES

In 1930 some tests were made to determine the feasibility of removing residues of barium fluosilicate from the fruit by means of chemical solvents. Fruit that had had 2 applications of lead arsenate, followed by 5 applications of barium fluosilicate used at the rate of 4 pounds to 100 gallons of water with fish-oil or mineral-oil emulsion, was washed in a flood machine with 1 percent hydrochloric acid at temperatures of 75° to 110° F., and with 1 percent sodium carbonate at temperatures of 90° to 110°. Before it had been cleaned the fruit had an average deposit of 0.04 grain of fluorine per pound. Treatment with hydrochloric acid resulted in an average deposit of 0.009 grain of fluorine per pound when washed at 75° F., 0.006 grain per pound when washed at 90°, and 0.005 grain per pound when washed at 110°. Treatment with sodium carbonate at 90° and 110° resulted in an average deposit of 0.014 grain of fluorine per pound.

In March 1933 three lots of fruit that had been sprayed the previous summer two or three times with sodium fluoaluminate (cryolite) at the rate of 3 pounds to 100 gallons of water with mineral-oil emulsion were washed with 1.5 percent hydrochloric acid, with 5 percent sodium silicate, and with 18 percent sodium carbonate,[3] respectively. Fruit that has been kept in storage for several months is more difficult to clean than when freshly harvested; therefore temperatures of 110° F. were used for the acid and sodium carbonate and 120° for the sodium silicate. This fruit had a maximum deposit of 0.022 grain of fluorine per pound before it had been washed. Treatment with hydrochloric acid resulted in an average deposit of 0.004 grain of fluorine per pound; with sodium silicate, of 0.007 grain per pound; and with sodium carbonate, of 0.015 grain per pound.

Since methods of analyses for fluorine have not yet been perfected, these results are only preliminary, but they indicate the quantity of fluorine residue that it may be possible to remove by suitable washing with a solution of hydrochloric acid, sodium silicate, or sodium carbonate.

SUMMARY

This bulletin records the results of experiments conducted under arid conditions at Yakima, Wash., to determine whether certain fluorine compounds could be used as substitutes for lead arsenate for the control of the codling moth.

The fluorine compounds studied are apparently not so toxic as lead arsenate on the basis of equal weight. This may be due in part to a lack of adhesiveness. Because of their cheapness, however, larger quantities may be used without increasing the cost. The lack of adhesiveness may be overcome by using fish-oil sticker or a mineral-oil emulsion with them.

Tests of barium fluosilicate, potassium fluosilicate, and sodium fluoaluminate (cryolite) at the rate of 3 or 4 pounds to 100 gallons of water, plus 1 pint of fish oil or ¾ gallon of emulsified mineral oil, reduced the wormy fruit in about the same percentage as lead arsenate did at the rate of 2 pounds to 100 gallons of water, without a sticker except in one experiment, and reduced the quantity of stung fruit by a greater percentage.

Except in some of the tests conducted in 1927, no fruit or foliage injury resulted from any of the experiments. In the limited number of analyses made to determine the residue on the fruit at the time of harvest, the residue from these materials was less than that left by lead arsenate and was as easily removed.

The fluorine compounds should not be used with lime-sulphur or with spreaders containing lime.

[3] These tests were made by A. L. Ryall, assistant pomologist, Bureau of Plant Industry, and the analyses were made by the junior author.

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