INVERTED SPRAY MIXTURES AND THEIR DEVELOPMENT WITH REFERENCE TO CODLING MOTH CONTROL

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TO CODLING MOTH CONTROL

by

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I. INTRODUCTION

Adequate control of the codling moth[1] in the apple orchards of central Washington has become more difficult in recent years than ever before, in spite of improved spraying equipment and increased attention to control measures other than spraying.

The work discussed herewith was begun in 1933 as a continuation of previous efforts of the Washington Experiment Station to improve chemical methods of codling moth control, and in addition, to alleviate the difficulty of removing spray residues at harvest. Most of the experiments were carried on at Wenatchee, Washington, but the analyses of materials as well as some of the arsenical deposit determinations were made at the main station at Pullman, Washington.

Since the most significant outcome of this work has been the development of the inverted spray mixture, in principle an innovation for the insecticide field, it appears to merit considerable discussion. The account which follows, therefore, in addition to a brief review of the literature concerning the materials in question, presents in some detail certain of the methods and results of the Wenatchee investigations.

Because of the immediate need for practical information on the part of the Washington apple industry, it has not been possible to devote sufficient time to the laboratory part of the work. Some of the experiments

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[1] _Carpocapsa pomonella L._

could well bear repetition, and repetition might alter present concepts. Much is yet to be done, and it is hoped that other investigators will soon become sufficiently interested in this problem to subject it to more careful investigation.

II. DEFINITIONS

In the pages which follow, certain terms are used that should be defined.

1. Inverted Mixture. An inverted spray mixture is one in which a suspended solid initially wetted by water becomes wetted by oil prior to, or at the moment of impact upon a sprayed surface.

2. Stable and Unstable. The terms stable and unstable are used to denote the physical condition of spray mixtures containing water, oil, finely divided solids, and perhaps other substances. A stable combination is one in which under moderate agitation, solid and oil remain well dispersed in the aqueous medium and show little disposition to adhere to the spray tank, even when subjected to passage through the release valve of the pump. An unstable combination is one in which either the oil, or the oil and finely divided solid, tend to separate from the aqueous medium. Separation may result in a floating scum of oil or curded matter, or in settling of curded matter to the bottom of the spray tank.

3. Combination. The use of the words "combined" or "combination" in connection with spray mixtures implies merely the bringing together of different substances in a spray tank. Chemical combination, or reaction, is stated as such.

III. HISTORICAL

"It is a well known fact that the vast literature on codling moth spraying is replete with contradictory experimental data and discordant opinions and beliefs." Thus ran Smith's remarks in 1926. The situation today, because of a great increase in published matter with but slight improvement in experimental methods, is not susceptible to concise summary.

For the purpose of this account, it will serve no point to trace in detail the development of present day principles of codling moth control; nor will it be necessary to discuss the rise and fall of the numerous materials that have been advocated as substitutes for arsenicals. Brief mention will be made of the more important references dealing with arsenicals in general as applied to codling moth control, of spreaders and adhesives for arsenicals, and of oil emulsions.

A. The Use of Arsenicals

Slingerland (1878) wrote that E. P. Haynes, a fruit grower in New York State, discovered that an application of Paris green for canker worm incidentally lessened codling moth damage. This marked the beginning of a period lasting until about 1905 when Paris green and London purple were almost universally used on this continent for controlling the codling moth.

The report of the Massachusetts State Board of Agriculture (1893) mentions the use of acid lead arsenate for various leaf eating insects, and the same publication (1895) recommends its use for codling moth control. According to Sanderson (1902), Craig of the Central Experimental Farms, Ottawa, Canada, reported the experimental use of lead arsenate for codling moth control in 1895. He obtained satisfactory results when it was applied with Bordeaux as well as alone in water. Webster (1903) gave an account of successful and more detailed experiments with lead arsenate which were begun in 1900, and shortly thereafter lead arsenate became the most widely used insecticide for the codling moth. This is the position it still holds.

Calcium arsenate is said by Paillot (1931) to have been first used about 1910, and according to Sanders and Kelsall (1918) it was being commonly employed as an orchard insecticide in Nova Scotia eight years later. However, referring particularly to codling moth control, Spuler (1929) stated, "It would seem . . . that neither calcium arsenate or magnesium arsenate can be used in a codling moth program." Spuler was writing of conditions in central Washington.

B. Spreaders and Adhesives for Arsenicals

1. Soaps

Among the abundance of published material dealing with spreaders and adhesives, a few of the most significant articles are noted. Gillette (1890) was one of the first to attempt to improve the physical condition of arsenical suspensions, by the addition of a material designed to lower the surface tension of the spray liquid. He reported an experiment in which whale-oil soap was added to Paris green and London purple suspensions, and from which he concluded that injury to plants was likely to occur with such a mixture.

Perhaps the earliest use of a soap-lead arsenate spray mixture was made by Parker (1911). He mentioned that four bars of laundry soap when added to six pounds of lead arsenate paste per 100 gallons improved the spreading of the lead arsenate particles on the surface of cabbage leaves. Apparently, however, the principal object was to prevent rapid settling of the suspension in the particular type of spray tank which he used. He mentioned that amounts smaller than four bars caused the particles of lead arsenate "to appear to mass together and settle out more rapidly than in a non-soap mixture." This observation is interesting in the light of present developments in Washington. Publication of Parker's report soon had influence in Oregon, where Tartar and Bundy (1913) mentioned the occurrence of severe injury to apple foliage as a result of application of lead arsenate soap mixture. They discovered from laboratory experiments that the amount of soap used in practice, four pounds per 100 gallons, was sufficient to liberate large amounts of soluble arsenic from four pounds of acid lead arsenate when the mixture had been allowed to stand for six hours before filtering. The same year Edwardes-Ker (1913) in England reported that the addition of one per cent soft soap to a water suspension of lead arsenate did not lead to the formation of any lead soap,nor an increase in the production of soluble arsenic. However, he allowed the mixture to stand only one-half hour before filtering, and it is not known what type of lead arsenate he used. It has since been shown by Groves of the Washington Experiment Station (unpublished matter), that several days of constant shaking are necessary for a lead arsenate soap mixture to reach equilibrium, so the failure of Edwardes-Ker to detect an increase in soluble arsenic is not entirely surprising.

Little more was heard of the lead arsenate soap mixture until about

1926 when a few growers in the Wenatchee valley of Washington claimed an improvement in codling moth control by the addition of about 0.5 pound of pine tar soap to 100 gallons of water-lead arsenate mixture. Since 1933 the Washington Experiment Station has studied the use of soap as a spreader for this arsenical and has demonstrated that for soft water[2], in amount of not over 0.3 pound per 100 gallons of spray material, it undoubtedly improves codling moth control. The investigations have further shown the oleates of triethanolamine or ammonia to be the most logical soaps for this purpose.

2. Protein Spreaders

The first investigator to report on the addition of casein-lime to lead arsenate in order to improve its spreading qualities appears to have been Lovett of Oregon (1918). He adapted a formula previously used for spreading Bordeaux mixture in Australia and obtained encouraging results with four to eight ounces per 100 gallons of the casein-lime mixture. Later, Smith (1923) used a similar preparation and stated that "soaps, such as are commonly used with nicotine sprays, show a marked tendency to produce flocculation, precipitation, and insoluble soaps which deleteriously affect the physical and chemical composition of spray solutions and mixtures. . . . . The casein type of spreader has shown superior adhesiveness in comparison with soaps, oils, and gum arabic."

Still later, Smith (1926) claimed that in equal amounts a film coverage of lead arsenate, such as produced by calcium caseinate, was about three times as effective as a coarse spotted coverage. He concluded with the statement that "In all coverages, protectiveness varied directly with the

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[2] "Hardness" corresponding to about 20 parts per million calcium carbonate.

amount of arsenious oxide per square centimeter of apple surface." Reckendorfer (1933) expressed a similar idea when he wrote that under ordinary circumstances the effectiveness of an insecticide can be determined fairly well if its poison content and adhesiveness are known.

3. Fish Oils

Twelve years ago, investigators began to pay attention to another means of improving the effectiveness of arsenicals. Hood (1925) published an account of experiments dealing with adhesives for lead arsenate. He found the most satisfactory substances for the purpose were oils, and of these, menhaden (fish) oil appeared particularly suitable. Spuler (1927) in Washington, and Dozier (1929) in Delaware, followed Hood's suggestions, and reported that codling moth control was definitely improved when fish oil was used in combination with lead arsenate. However, it was determined later by Marshall, et al. (1934) that fish oil though increasing the quantity of arsenical deposited did not produce a uniform coverage in the field, as did soaps and protein spreaders. For this reason, codling moth control appeared to be less satisfactory than might have been expected from the increased deposit. They reported that the addition of a small amount of oleic acid to the fish oil improved the quality of the deposit, without sacrificing the quantity. They further suggested the saponification of the added oleic acid by triethanolamine, in order to insure a still more uniform coverage. Their experiments indicated that rapidly drying fish oil with an iodine number of about 180 when used as an adhesive for lead arsenate, resulted in less effective codling moth control than a slowly drying oil with an iodine number of about 135. It was concluded that an arsenical deposit that remained oily, was more effective than one which was not oily, or one in which the oil had dried to a varnish-like consistency, the quantities of arsenical being equal. Up to this point in their work, the most satisfactory control had resulted from an arsenical deposit which was uniformly distributed as an oily film on the fruit surface, and it seemed reasonably clear that in agreement with Smith (1926), the greater the amount of arsenical present per unit of area of fruit surface, the more effective the protection against codling moth attack.

4. Petroleum Oils

Closely paralleling the investigations with fish oil as an adhesive for lead arsenate were experiments with lead arsenate combined with petroleum oil emulsions.

To Lovett (1920) seems to belong priority for the observation that petroleum oil may improve the effectiveness of an arsenical deposit quite aside from its ovicidal effect. He used a miscible oil (composition and quantity not stated), and wrote that as a spreader for lead arsenate it showed considerable merit. This observation appears to have gone unnoticed. Shortly after its publication, attention was focused entirely on the ovicidal value of petroleum oils in codling moth control and even today this point of view persists.

Regan and Davenport (1928) were pioneers in the use of the combined petroleum oil-lead arsenate mixture. Their work at Yakima, Washington, begun in 1925, mentioned the unusual effectiveness of this mixture against the codling moth but had no reference to any increase in arsenical deposit. Webster and Marshall (1934), however, mentioned that an ammonium caseinate emulsion of petroleum oil, used in combination with lead arsenate, not only improved codling moth control but increased the arsenical deposit to some extent. This gave support to a new practice in spraying which had its incidence in the work of DeSellem (1932). Acting with C. D. Dolman, chemist of the Wenatchee Valley Traffic Association, he used petroleum oil emulsified with sodium oleate, in combination with lead arsenate, and reported an unusually heavy deposit of the arsenical. DeSellem's report has particular significance, and it is interesting to consider it more fully. The idea of emulsifying oil by the use of soap was not new. This practice had been advocated by Riley (1872), and a patent on the process of emulsifying petroleum with an alcohol-oleate was granted to Knopf (1911). Martin (1931) suggested a process of emulsification that was practically identical with that used by DeSellem. At least one commercial oil emulsion had depended on sodium oleate for emulsification for a number of years previous to DeSellem's report, but though having been used in great quantity in the Wenatchee district, it had not appeared to be noticeably superior to other emulsions for combination with lead arsenate in codling moth control.

Why had DeSellem obtained unusual results? Apparently it was a matter of higher soap content, and heavier application, than for previous somewhat similar mixtures. This became clear when Marshall, Eide, and Priest (1934) of the Washington Experiment Station published results of two seasons' investigations with soap-oil emulsions. They obtained much higher arsenical deposits, and better codling moth control, with triethanolamine oleate[3] and triethanolamine laurate as emulsifiers for petroleum summer oil and kerosene than with ammonium caseinate, and showed that it was possible to build up an arsenical deposit to almost any extent on the surface of an apple, by means of ordinary spray equipment.

Persing (1935) reported a series of laboratory experiments using oleic acid and oleates in combination with oils, and either lead arsenate or cryolite. He confirmed the findings of Marshall, Eide, and Priest, and advanced

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[3] Triethanolamine oleate was suggested as an emulsifier for oil sprays by Hockenyos (1929).

a hypothesis to account for the behaviour of these mixtures.

Following Persing, G. E. Marshall (1936) published an account of field experiments with oil-soap mixtures in Indiana. His results, apparently from somewhat similar mixtures, were as favorable as those in Washington. Though from the chemical point of view no unusual substance was involved, evidently a new principle of considerable promise had been demonstrated in the insecticide-fungicide field. By 1937, the inverted spray mixture had passed the strictly experimental stage.

IV. EXPERIMENTAL METHODS

A. Methods in Laboratory Investigations

1. Quantitative Deposit Determinations

Smith (1926) published an article which has been influential in stimulating the application of laboratory technique to codling moth investigations. Perhaps the most significant part of this paper mentions the principle of determining deposits quantitatively as a necessity to the accurate evaluation of arsenical preparations. This principle has played a major part in the work at Wenatchee during the past five years. It is pertinent to trace its development. Woods (1914) analyzed apples at harvest and attempted to calculate the deposits of lead and arsenic by washing the apples in water, collecting the washings, evaporating, then analyzing. He does not state what method of analysis was followed. O'Kane, Hadley, and Osgood (1917) reported arsenical deposits as milligrams of arsenic trioxide per apple but did not describe their procedure. Moore (1921) analyzed potato leaves for arsenic and reported deposits as milligrams of arsenic trioxide per leaf. His method was to digest the leaves in boiling nitric and sulphuric acids and determine arsenic by the Gutzeit method.

The next step was proposed by Smith (ibid.) who determined arsenical deposits in his laboratory experiments as micrograms of arsenic trioxide per square centimeter of fruit surface. Though he does not describe the analytical procedure, this was a distinct improvement on previous methods, in that it eliminated a potential source of error in variation in the size of the fruits. Smith's method of expressing deposits was used by Dolman working in conjunction with the Washington Experiment Station at Wenatchee.

Groves and Marshall (1935) reported that in the case of most spray materials, over a third of the entire deposit is to be found in the calyx and stem end of the apple. This is due to the accumulation of spray liquid at these points and settling out of the suspended arsenical. Obviously since few larvae attempt to penetrate very heavy deposits, particularly at the stem end, a deposit analysis for the entire surface of such fruit may be misleading. It indicates heavier coverage than actually is present on the most vulnerable part of the fruit, the equator. Accordingly, they removed discs of known size around the equator (cheek) of the fruit with a cork borer, and calculated the surface area of the discs from the formula $2\pi R(R-\sqrt{R^2 - r^2})$, where R is the radius of the apple and r the radius of the disc. A table of surface area computations for two sizes of discs will be found in the appendix, together with details of the analytical procedure.

The same authors determined that with care in sampling, duplicate samples of ten apples each, with five discs removed approximately equidistant from one another around the cheek of each apple, i.e., 50 discs per sample, gave reasonably reproducible results. They discarded the Gutzeit method in favor of the bromate method for determination of arsenic, pointing out that the Gutzeit is subject to an average error of about ten per cent with careful work, while the average error for bromate analysis is

Fig. 1. Equipment for preparation and storage of sample discs for deposit determinations. Left background, an apple with discs removed.

less than one per cent for spray coverage determinations. They further adopted the practice of complete digestion of the discs with boiling nitric and sulphuric acids.

This general procedure for determining arsenic deposits has been in use at the Washington Experiment Station since 1934. Some thousands of determinations have been made and results have been satisfactorily reproducible. So standardized is the method, that one can digest and titrate 25 samples per day after the apples have been measured, and the discs removed and stored in sample bottles. Since it requires approximately as long to collect the samples, measure the apples, and remove the discs, as it does to digest and titrate, about 12 samples from tree to titration represents a day's work.

2. Insectary Methods

Until 1933, the Wenatchee investigations had depended on what was rather inappropriately termed a "precision sprayer," for producing spray deposits on the individual fruits used in laboratory work. This apparatus atomized the spray liquid by means of an air jet operating at five to seven pounds pressure. Late in the season of 1932, it was observed that laboratory arsenic deposits did not correspond with field deposits of the same spray mixture, either qualitatively or quantitatively, and it was then determined that the atomizer type of equipment was quite unsuited for work of this kind. A spray liquid forced through the nozzle of a spray gun at pressure of about 300 pounds per square inch behaves quite differently on the fruit surface from one which is caught up in an air blast with practically no pressure, and so to speak, wafted on the fruit. The "precision" sprayer was abandoned in 1933 and gave way to high pressure equipment which after various modifications emerged in the form briefly described here.

A small, single cylinder pump, capable of delivering three gallons of liquid per minute at a pressure of 350 pounds per square inch, is operated by a three-quarter horse power electric motor. Pump and motor are mounted on a steel frame which carries a small tank with two five-liter and one ten-liter compartments. An agitator running through the lower part of the tanks is driven off the pump. Immediately behind the spray nozzle, which has a 3/64-inch aperture, is placed a quick-opening valve, the purpose of which is to enable a spray application to be accurately timed. The nozzle and valve, connected to the pump by eight feet of 3/8-inch steel pipe, are fastened to a spindle chamber containing three revolving spindles upon which are impaled the fruits to be sprayed. The spindles, turned through a gear box and driven by a small electric motor, are backed by baffles which prevent back-lash of liquid when a spray application is made. The spindle chamber is enclosed above, below, and at the sides and equipped with a drain pipe. A sliding door in one side facilitates the impaling and removing of fruits.

This equipment has been very satisfactory in reproducing coverages similar to those obtained in the field. Some such device appears to be essential in laboratory investigations where type of spray coverage is a matter of importance. Evidently some investigators still make use of the atomizer type of sprayer which as mentioned earlier may give misleading results, aside from being quite incapable of handling inverted mixtures.

Little need be said of the technique employed in obtaining first instar codling moth larvae for the laboratory investigations. Eventually there was evolved in 1933 by P. M. Eide and the writer, an oviposition cage which has been very satisfactory in this work. It is figured by Peterson (1934) and its operation later described by Eide (1936). By

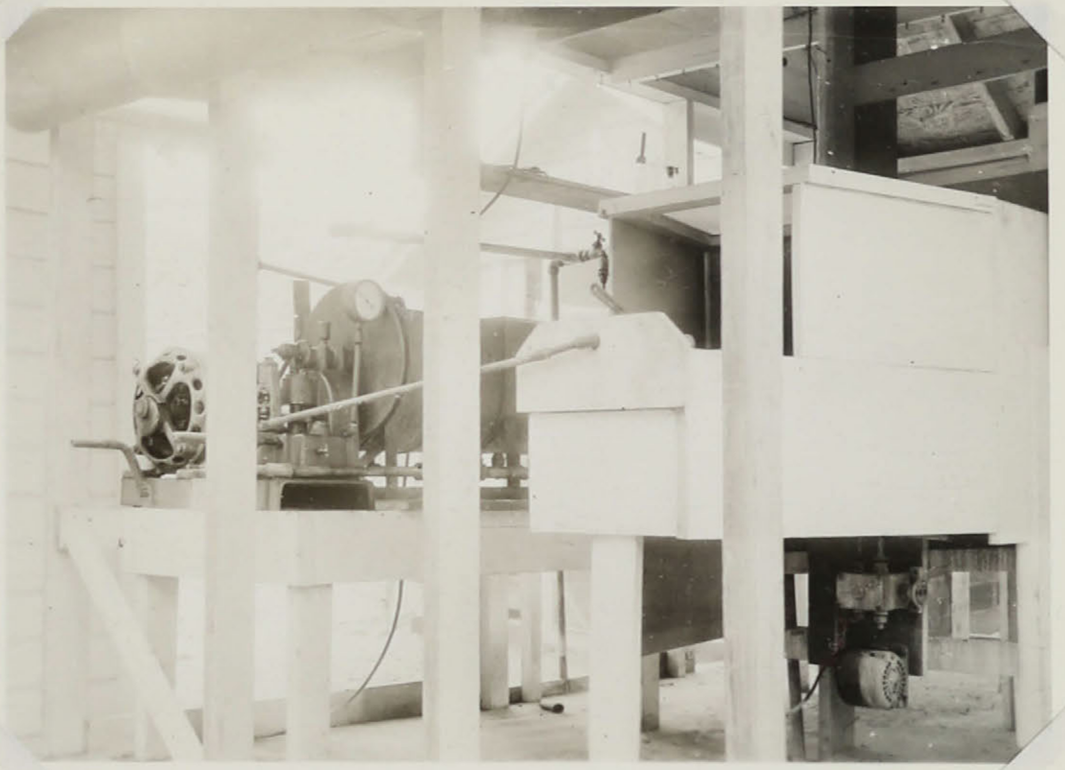

Fig. 2. Laboratory sprayer seen through screened wall of insectary. Left, motor, pump, and spray tank. Right, spindle chamber showing motor and gear box beneath. Tip of spray nozzle and lever operating quick-opening valve show directly behind plate attached to end of chamber.

means of this device it is a simple matter to obtain thousands of codling moth eggs on waxed paper, if larvicidal experiments are indicated, or on apples if ovicidal experiments are indicated.

In larvicidal work, apples are sprayed by the apparatus already described and allowed to dry. Then following Smith's method (1926) warm paraffin wax is applied to calyx and stem ends and the apples suspended from small wooden racks. Slips of waxed paper bearing a total of ten eggs in the "black-spot" stage are pinned to the stem of each apple, and the racks then placed in a constant temperature cabinet operated at about 80° F., and 70 to 80 per cent relative humidity. After 48 hours in this cabinet, the racks are removed to a screened insectary and held for two weeks before being examined for stings and entries.

In many cases, duplicate sets of apples are sprayed for arsenic determinations in connection with larvicidal work. The determinations are made in an adjoining field chemical laboratory which is equipped with the necessary apparatus for disc digestion, and the bromate method of analysis.

B. Methods in Field Investigations

In the matter of field experimental methods, here is a criticism by Fernald (1908). "At the present time there are too few data of experiments made under conditions known with exactness; with materials of fixed and known composition." Twenty-eight years have passed since that was written, but it applies as truly now as then. This warning has been heeded in the Wenatchee investigations, for the thought uppermost since 1932 has been to plan experiments so that they could be accurately repeated by others if desired, and so that the human equation would influence results and conclusions as little as possible. Only materials of known composition have been used. Proprietary materials which may vary in composition from year to year have been avoided. Plots have been so arranged that the approximate experimental error could be determined at least roughly, and this has necessitated frequent repetition of control plots. Only wide differences in results have been regarded as of probable significance, and in the case of distinctly new spray mixtures it has been necessary for such differences to be reproduced for at least a second, and preferably a third year, before being allowed to influence recommendations to growers. Finally, careful records have been made as to both the qualitative and quantitative characteristics of arsenical deposits. A more detailed discussion of these methods has been given by Marshall and Groves (1936a).

The field equipment at Wenatchee consists of two stationary electric sprayers, one a two-gun machine with a capacity of 16 gallons per minute, the other a four-gun machine of 32-gallon capacity.

The main plots have comprised three to six trees depending on the number of replicates, and supplementary plots have contained but single trees replicated from once to four times.

At harvest all trees have been checked for codling moth infestation; from 300 to 500 apples have been sampled per tree. Checking of all thinned fruits, once the rule at Wenatchee, has been discontinued because it was found that this practice, while adding much to the expense of the work, added little information.

Various orchards have been used for the experiments, but all have been located within ten miles of the city of Wenatchee, in a district in which it is perhaps more difficult to control the codling moth than any other in the United States. By way of example, growers in the lower Wenatchee valley commonly apply as many as eight or ten cover sprays in a single season, at the rate of 40 gallons of spray per tree, per application.

Yet in spite of such frequent and heavy applications, and the liberal use of stickers, spreaders, and frequently petroleum oils, they have difficulty in raising fruit that is less than ten per cent infested.

V. EXPERIMENTAL RESULTS

A. Laboratory Investigations

In the appendix, Table 4, will be found a list of experimental materials with analyses or constants. Detailed analyses of all samples of these materials can not be provided but routine determinations are given wherever there might be uncertainty as to gross composition.

1. Inverted Lead Arsenate Mixtures

a. Effect of Type of Emulsifier. One of the first points to be made in the early use of inverted mixtures, was that ammonium caseinate emulsions (the conventional paste or mayonnaise type) of either kerosene, or medium summer oil, had little value as deposit builders or adhesives for lead arsenate. As a matter of fact, for a single application they appeared to have no value whatever, though repeated applications made in the field had shown somewhat higher deposits than where lead arsenate alone was used.

On the other hand, when lead arsenate was used with a triethanolamine oleate emulsion of summer oil, or kerosene, the mixture showed entirely different characteristics when sprayed upon the surface of an apple. Instead of a spotted deposit of lead arsenate there appeared a uniform film, but more important, the film continued to increase steadily in thickness as spraying was continued. This point is brought out in Table 1, where apples were sprayed for 15 seconds while revolving on the spindles of the experimental machine. In the first experiment, triplicate samples of six apples each were analyzed, while in the second experiment, duplicate samples were used.

Fig. 3. Effect of inversion upon arsenical deposit. Left, apple sprayed with inverted mixture. Right, apple sprayed with non-inverted mixture containing same amount of oil.

Table 1. Effect of Emulsifier on Arsenical Deposit from Oil - Lead Arsenate and Kerosene - Lead Arsenate Mixtures.

Sample	Amounts per 100 gals.	Deposit as mmg As_2O_3 per cm^2 Exp. 1	Exp. 2	Average of Exps. 1 & 2	Type of coverage
1 a	Lead arsenate, 2 lbs.	7.1	9.5	8.1	Spot
b		7.4	9.7		
c		8.4			
2 a	Lead arsenate, 3 lbs.	12.8	10.1	11.3**	Spot
b		11.8	9.5		
c		13.8			
3 a	Lead arsenate, 2 lbs.		8.9	5.5	Spot
b	Kerosene, 2 qts.		2.2		
c	(Ammonium caseinate emulsion)*				
4 a	Lead arsenate, 3 lbs.	94.4	151.6	122.2	Film
b	Kerosene, 2 qts.	122.5	112.1		
c	Triethanolamine oleate, 0.25 lb.	121.2			
5 a	Lead arsenate, 3 lbs.	9.9	10.1	9.1	Spot
b	Medium summer petroleum oil, 2 qts.	9.9	8.6		
c	(Ammonium caseinate emulsion)	7.0			
6 a	Same as 5, but Trieth. oleate emulsion	147.3	131.2	119.4	Film
b	(0.25 lb. Trieth. oleate)	110.0	88.2		
c		130.2			

*Ammonium caseinate emulsion stock - oil or kerosene 100 gals., water 33 gals., lactic casein 3 lbs., 28 per cent ammonia 1 qt.

**See Appendix, Table 2, for variation in deposit analyses for lead arsenate used alone at 3 pounds per 100 gallons water.

b. Effect of the Various Constituents of an Inverted Mixture When Used Individually with Lead Arsenate. Experiments with the individual components of an inverted mixture in combination with lead arsenate are summarized in Table 2. Triethanolamine oleate, oleic acid, and medium summer petroleum oil were used separately with lead arsenate. For comparison there are included analyses of deposits from an inverted mixture containing all the components in suitable proportions. The petroleum oil which was first emulsified by the lead arsenate, before being introduced into the spray tank, produced an arsenical deposit no greater than when emulsified with ammonium caseinate. It alone obviously is not responsible for the adhesiveness of inverted mixtures.

Table 2. Effect of the Individual Constituents of an Inverted Mixture.

	Amounts per 100 gals. water*	Micrograms As_2O_3 per cm^2					Type of deposit
		(a)	(b)	(c)	(d)	Ave.	
1	Lead arsenate, 2 lbs.	8.4	8.4	7.1	7.4	7.8	Spot
2	Lead arsenate, 2 lbs. Triethanolamine oleate, 0.36 lb.**	7.5	7.3	8.5	8.1	7.8	Film
3	Lead arsenate, 2 lbs. Oleic acid, 0.25 lb.	4.5	4.9	4.9	5.9	5.0	Oily film
4	Lead arsenate, 3 lbs. Medium summer petroleum oil, 2 qts.	6.1	--	--	--	6.1	Oily spot
5	Lead arsenate, 3 lbs. Medium summer petroleum oil, 2 qts. Triethanolamine oleate, 0.25 lb.	147.0	110.0	130.0	131.0	129.0	Oily film

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*Water contained approximately 20 parts "hardness" per million, expressed as calcium carbonate.

**Oleic acid 5% in excess of equivalent.

Other experiments showed that the arsenical deposit following the addition of 0.5 pound of triethanolamine oleate, was somewhat less than from 0.36 pound. However, 0.12 pound of this soap resulted in a deposit slightly greater than 0.36 pound, though it was not as uniformly filmed. For water containing less than 50 parts "hardness" per million, from two to four ounces of triethanolamine oleate per 100 gallons seems an optimum for use as a spreader for lead arsenate, but under no circumstances has soap alone shown any indication of being an adhesive agent, or deposit builder.

The use of 0.25 pound of oleic acid per 100 gallons of spray mixture gave no evidence of "build-up"[4] of arsenical, though causing it to spread in a uniform, thin, oily film over the fruit surface. However, later experiments revealed that a lead arsenate - oleic acid combination underwent inversion to some extent, if subjected to prolonged pumping through the release valve of the sprayer. Somewhat increased arsenical deposit then appeared.

c. Effect of Variation of Soap Content on Deposit and on the Formation of Soluble Arsenic. It was observed in 1933, that the behaviour of an inverted mixture was greatly influenced by the soap content. Subsequently it has been determined that for three pounds of lead arsenate and two quarts of oil per 100 gallons of water, approximately 0.25 pound of triethanolamine or ammonium oleate has given arsenical deposits as high as reasonably can be expected without excessive adhesion of the mixture to the sides of the spray tank.

In Table 3 are collected some laboratory analyses typical of the data in this connection. Unfortunately, they are scattered and can indicate only

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[4] The term "build-up" is expressive and will be used to indicate continuous increase of deposit with prolonged application of spray.

very roughly the important bearing that the soap content of these mixtures has upon the arsenical deposit. The fruits were sprayed for 15 seconds while revolving.

Table 3. Effect of Amount of Soap on Arsenical Deposit.

	Material added to 3 lbs. lead arsenate and 100 gals. water*	mmg As_2O_3 per cm^2		
		(a)	(b)	Ave.
1	Herring oil, 1 pt. Triethanolamine oleate, 0.06 lb.	27.8	16.1	21.9
2	Same, but Trieth. oleate, 0.12 lb.	16.3	18.7	17.5
3	Herring oil, 1 qt. Triethanolamine oleate, 0.12 lb.	33.3	26.3	29.8
4	Same, but Trieth. oleate, 0.25 lb.	45.7	61.7	53.7
5	Kerosene, 2 qts. Triethanolamine oleate, 0.12 lb.	62.5	69.5	66.0
6	Same, but Trieth. oleate, 0.25 lb.	204.9	195.5	200.2

*See Appendix, Table 2, for typical analyses of deposits from lead arsenate alone at 3 pounds.

In general, it has appeared that for amounts of oil of one pint or less, the soap content of a mixture has relatively little bearing on the arsenical deposit which with such an amount of oil has always been low. When the oil is increased to one quart, the soap plays a more important part, and at least with herring oil, under certain circumstances, the arsenical deposit increases as the soap content is raised to 0.25 pound.

With 0.12 pound of soap, in combination with two quarts of oil or kerosene, arsenic deposits have been low owing to excessive stability in the mixture. This apparently holds for most brands of lead arsenate available at present. When the soap content has been increased to 0.5 pound the opposite effect has occurred with unsatisfactory and irregular deposits resulting from excessive instability, unless the arsenical ~~has~~ contained some form of protective colloid. Aside from this, it is expected that the use of more than 0.25 pound of soap would be inadvisable because of the likelihood of increased production of soluble arsenic. The unpublished work of Brunstad of the Wenatchee Valley Traffic Association laboratories, agrees with that of Pinckney (1923) in indicating that when commercial acid lead arsenate at three pounds per 100 gallons of water is mixed with soap at two pounds, there is greater production of soluble arsenic than when 0.25 pound of soap is used (Table 4)

Table 4. Effect of Amount of Soap on the Production of Soluble Arsenic from Lead Arsenate.

Type of soap	Amount per 100 gallons	pH*	After 48 hrs. 65-75° F. soluble arsenic mg As_2O_3 per liter
Pine tar soap (largely sodium laurate and containing 13% moisture)	2 lbs.	9.41 9.35	119.0 115.0 124.0
	0.25 lb.	8.39 8.15	19.0 18.0 18.0
Triethanolamine oleate (10% excess oleic acid)	2 lbs.	8.37 8.34	88.0 75.0 79.0
	0.25 lb.	8.05 8.13	15.0 14.0 13.0
Control - Distilled water only		-- --	3.5 3.2 3.0

*Determined by a saturated calomel-antimony electrode with phosphate buffer.

It will be observed that the pH of the solutions, as determined shortly after they were made by Brunstad, is higher for the larger amounts of soap than the smaller. Groves of the Washington Experiment Station in later unpublished work, however, pointed out that even after several days of constant shaking, soap-lead arsenate mixtures may not reach equilibrium. He found that after continued shaking there was a tendency for the pH of certain soap-lead arsenate mixtures to become constant between 6.6 and 7.7.

Some of Groves' results, given in Table 5, indicate that there is considerable variation in the effects of different types of soap solutions upon lead arsenate. He used a mixture consisting of three pounds of commercial acid lead arsenate and 0.5 pound of soap per 100 gallons of water.

Table 5. Effect of Type of Soap on the Production of Soluble Arsenic from Lead Arsenate.

	Type of soap	pH of mixture*	Soluble arsenic mg. As_2O_3 per liter
1	Pine tar soap (2.5% moisture and largely sodium laurate)	7.12 7.21	58 58
2	Sodium oleate (NaOH:oleic acid = 9:10, i.e., "acid" soap)	7.40 7.33	44 42
3	Same as (2) but ratio = 1:1 ("neutral" soap)	7.55 7.65	55 62
4	Same as (2) but ratio = 11:10 ("basic" soap)	7.52 7.66	58 67
5	Ammonium oleate "neutral"	6.69 6.82	30 34
6	Triethanolamine oleate "neutral"	6.83 6.70	26 23
7	Lead arsenate and water - no soap	5.80 6.30 5.87	6.8 7.4 6.9

*Determined by a glass electrode with an estimated error of .05 pH. The two values for both pH and soluble arsenic are not merely analytical duplicates but represent two separate mixtures.

From Groves' work it appears that soaps containing an excess of oleic acid are likely to be less reactive with commercial acid lead arsenate than so-called neutral or basic soaps. The oleates of ammonia and triethanolamine were less reactive than that of sodium.

Since Pinckney (loc. cit.) has determined that sodium stearate attacks this form of lead arsenate more strongly than sodium oleate, presumably the oleates of either triethanolamine or ammonia are indicated for inverted lead arsenate spray mixtures. It seems preferable that these contain an excess of fatty acid - perhaps five or ten per cent.

It should be mentioned that in the Wenatchee investigations, sodium laurate was satisfactory for promoting inversion. But as found by both Groves and Brunstad, pine tar soaps, which according to the manufacturers largely consisted of sodium laurate, liberated considerably more soluble arsenic from lead arsenate, than did triethanolamine oleate.

d. Effect of Variation in Amount of Oil. Like the data dealing with differences in soap content of inverted mixtures, those concerning the effect of variations in amount of oil with a constant amount of soap are so scattered that they can not be readily collected into tabular form. However, the following examples indicate that the quantity of oil used is quite as important as the quantity of soap. Revolving fruits were sprayed for 15 seconds unless otherwise noted.

Table 6. The Influence of Oil upon Arsenical Deposit.

	Material with 3 lbs. lead arsenate	mmg As_2O_3 per cm^2		
		(a)	(b)	Ave.
1	Kerosene, 1 qt. Triethanolamine oleate, 0.12 lb.	27.0	27.1	27.0
2	Same as (1) but Kerosene, 2 qts.	62.5	69.5	66.0
3	Kerosene, 1 qt. Triethanolamine oleate, 0.25 lb.	19.4	18.9	19.1
4	Same as (3) but Kerosene, 2 qts.	204.9	195.5	200.2

In most cases, both in the laboratory and in the field, the less the amount of oil below two quarts per 100 gallons of water, the less has been the deposit resulting from three pounds of lead arsenate. On the other hand, though information concerning the use of larger amounts of oil is rather indefinite, it has not appeared that an increased deposit will ensue from an increase in oil above two quarts. Indeed, when excessively large quantities of oil have been present, it has been observed that the arsenical deposit tends to be continually flushed away by the impact of fresh spray material. This apparently results from a more or less fluid condition of the deposit, a point discussed later. Aside from this, however, the aim has been to hold the oil at a minimum because of its deleterious effects on apple fruits and foliage, if used to excess. Two quarts of medium summer oil per 100 gallons of spray have seemed sufficient when thoroughly applied, to prevent hatching of about 85 to 90 per cent of codling moth eggs, and since this amount is indicated for suitable inversion, with resultant heavy build-up of arsenical, it is believed that it represents an approximate optimum.

e. Type of Oil. Inverted mixtures have been made with herring oil, kerosene, medium petroleum summer oil, light petroleum summer oil, light petroleum oil of low sulphonation value, light medium petroleum oil of low sulphonation value, and herring oil - kerosene mixtures. The specifications of these oils are given in the Appendix.

It appears that the choice of oil will be limited only by plant tolerance and cost, aside, of course, from the possible necessity of an ovicidal or contact effect.

f. Quantity of Lead Arsenate. Though no field experiments have been conducted with quantities of lead arsenate above three pounds in 100 gallons of water, a laboratory experiment indicates that satisfactory results might follow from larger amounts, particularly if the spraying equipment is not of sufficient capacity to enable the operator to make the very heavy applications that are necessary for best results from the ordinary inverted mixtures. In other words, where codling moth control necessitates very heavy deposits, but the grower does not possess adequate spraying equipment to obtain them from a three pound dosage of lead arsenate, he might do so by doubling this amount, with perhaps no necessity of increasing the amount of either the soap or the oil.

Table 7 represents the results of a laboratory experiment that rather unexpectedly showed arsenical deposits nearly twice as heavy from six pounds of lead arsenate as from three pounds, though the oil content and the soap content were the same in each instance. It is possible that repetition of the experiment might have a different outcome, for in laboratory work it has been difficult to obtain strictly reproducible results with inverted mixtures. Nevertheless, the superior stability of the six pound mixture and the more consistent deposits are to be expected. It is the extent of these deposits that is puzzling.

Table 7. Variation in the Amount of Lead Arsenate.

	Mixture	When sampled*	Deposit**as mmg As_2O_3			Condition of mixture
			(a)	(b)	Ave.	
1	Lead arsenate, 1 lb. Medium summer oil, 2 qts. Triethanolamine oleate, 0.25 lb.	at once	19.5	20.1	19.7	Mostly broken at 4 mins.
		after 3 mins. overflow	13.0	12.4	12.7	
2	Same as (1) but lead arsenate, 3 lbs.	at once	74.7	88.4	81.5	Same as (1).
		after 3 mins.	48.2	24.4	36.3	
3	Same as (1) but lead arsenate, 6 lbs.	at once	121.3	127.9	124.0	Very slightly broken after 4 mins.
		after 3 mins.	128.5	138.5	133.0	

*The second set of samples was taken in each case after three minutes of pumping when the amount of overflow had about equaled the amount of material remaining in the spray tank.
**Samples sprayed for six seconds while rotating.

g. Variation in Fatty Acid: Base Ratio of Soap. Apart from the effect of excess base, or excess fatty acid of a soap, upon the breakdown of acid lead arsenate, it was found desirable to have information on the effect of the acid:base ratio on build-up of deposit and/or stability of an oil-soap-lead arsenate mixture in the spray tank. Soaps were made up containing approximately five per cent excess, 55 per cent excess, and 105 per cent excess oleic acid, as well as 45 per cent and 95 per cent excess base. They were used with a constant amount of lead arsenate (three pounds) and a constant amount of medium summer oil (two quarts). Observations were made of the stability of the mixtures upon being subjected for several minutes to a heavy overflow through the release valve of the sprayer at a pressure of 350 pounds per square inch. The amount of soap in each case was 0.25 pound, the excess of either acid or base being in addition to this.

Table 8. Effect of Excess Base and Excess Fatty Acid on Inverted Spray Mixtures.

	Type of soap	When sampled	Deposit as mmg As_2O_3 per cm^2 (a)	(b)*	Ave.	Condition of mixture
1	Triethanolamine oleate with 5% excess oleic acid. (Type of soap customarily used)	at once	103.0	100.5	101.0	Fair at 3 mins.; largely broken at 4 mins.
		after 3 mins.	78.7	38.5	58.6	
2	With 55% excess oleic acid	at once	96.3	72.8	84.6	Poor at 3 mins.; completely broken at 4 mins.
		after 3 mins.	26.3	16.2	21.2	
3	With 105% excess oleic acid	at once	92.1	81.2	86.6	Very poor at 2 mins.; completely broken at 3 mins.
		after 3 mins.	21.7	17.3	19.5	
4	With 45% excess base	at once	75.6	75.7	75.6	Breaking at 2 mins.; broken at 4 mins.
		after 3 mins.	13.5	9.9	11.7	
5	With 95% excess base	at once	50.5	46.4	48.4	Same as (4).
		after 3 mins.	21.3	16.6	18.9	

*Taken immediately after (a) but because of the instability of these mixtures not a true duplicate.

Once again, because of the nature of the problem a repetition of the experiment might have produced somewhat different results. However, even with this in mind, it seems reasonable to conclude from Table 7 that if 0.25 pound of "neutral" triethanolamine oleate be used, a considerable additional quantity of oleic acid tends to promote extreme instability in the mixture. The result is that it sticks to the sides of the spray tank and unsatisfactory deposits supervene. The use of a considerable excess of triethanolamine likewise appears to promote instability.

It should be kept in mind in any event that even a slightly "acid" soap, such as used in the first instance, and which has always been employed in field work, produces a condition of instability which quickly becomes troublesome if a heavy overflow is permitted to return to the spray tank. This is shown by the steadily decreasing arsenical deposits from beginning to end of the tank, a point which is further illustrated in a later experiment with an inverted calcium arsenate mixture.

h. Addition of Colloids and Electrolytes. In 1936, some trouble was encountered by Wenatchee growers who were attempting to use a particular brand of lead arsenate for making inverted mixtures. They complained that they could not obtain a heavy build-up of arsenical on their fruit. Examination of the product revealed that though presumed to contain no deflocculating substance, and though known to consist of at least 98 per cent acid lead arsenate, it contained a sufficient quantity of acid insoluble colloidal material to interfere with inversion. With the thought of forming calcium soap to de-stabilize the mixture, it was suggested that they add from 0.25 ounce to one ounce of calcium oxide or calcium hydrate per 100 gallons of spray mixture. In some instances, this had the desired effect, but in others the difficulty persisted and arsenical deposits continued to be low.

This led to an examination of the effect of colloidal substances upon inverted lead arsenate mixtures. A brand of lead arsenate was selected which had given consistently high deposits in the field. It was used with medium summer petroleum oil and triethanolamine oleate. Admixtures of ammonium caseinate were made in small amounts, and the arsenical deposits determined. The fruits were sprayed for six seconds while rotating. Four samples were taken for analysis from each tank, the first pair before the mixture had been subjected to any overflow and the second pair after the mixture had been pumped through the release valve, back into the spray tank, for three minutes. Table 9 gives the results of this experiment.

Table 9. The Effect of a Colloidal Substance upon Lead Arsenate Deposit from an Inverted Mixture.

	Material per 100 gals.	When sampled	mmg As_2O_3 per cm^2			Condition of mixture
			(a)	(b)	Ave.	
1	Lead arsenate, 3 lbs. Medium summer oil, 2 qts. Triethanolamine oleate, 0.25 lb.	at once	67.1	62.7	64.9	Started to break 2.5 mins.; broken 5 mins.; stuck to tank.
		after 3 mins.	33.1	15.1	24.1	
2	Same as (1) but with casein as ammonium caseinate, 0.25 oz.	at once	26.9	27.5	27.2	Not broken 6 mins.; not stuck to tank.
		after 3 mins.	27.9	28.5	28.2	
3	Same as (1) but with casein, 0.125 oz.	at once	22.3	21.9	22.1	Same as (2)
		after 3 mins.	25.4	23.8	24.6	
4	Same as (1) but with casein, 0.067 oz.	at once	26.9	22.3	24.6	Same as (2)
		after 3 mins.	26.6	31.6	29.1	
5	Same as (1) but with casein, 0.033 oz.	at once	58.0	55.2	57.5	Slight breaking 3 mins.; partly broken 6 mins.; not badly stuck to tank.
		after 3 mins.	57.6	42.6	50.1	
6	Repeat (1).	at once	71.6	64.5	68.0	Same as (1).
		after 3 mins.	36.9	23.3	30.1	

It is apparent that casein in the form of ammonium caseinate strongly stabilizes the inverted type of mixture. Without casein (1 and 6), breaking began to occur after 2.5 minutes of pumping and was complete at five minutes. When 0.067 ounce of casein was present in 100 gallons of spray liquid the mixture remained stable, and unbroken, even after six minutes of continued heavy overflow. However, in this case the deposit of arsenical though uniform was low, and a fairly heavy "run-off"[5] occurred. Low

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[5] The term "run-off" is used to denote the loss of either liquids or solids of a spray mixture by dripping from the fruit.

deposits in the case of the unstabilized mixtures,occurred not as a result of run-off, but from sticking of the broken mixture to the sides of the tank. So far the heaviest deposits have been obtained with mixtures which are sufficiently stable to withstand a moderate degree of agitation without breaking and sticking to the tank, yet sufficiently unstable to break or invert when ejected at high pressure through the spray gun. These investigations have not yet revealed a method of preparing a mixture which will invert satisfactorily on passage through the gun, yet remain unbroken in the spray tank after any considerable amount of it has gone through the release valve. Satisfactory inversion implies a condition in which virtually all of the arsenical adheres to the fruits on impact. The run-off should be practically clear water.

The pronounced effect of ammonium caseinate in stabilizing these mixtures is interesting. Apparently as little as 0.033 ounce of casein in this form was sufficient to have a measurable influence on the stability of 100 gallons of mixture, at the same time affecting the arsenical deposit. In another experiment, "hard" water having a "hardness" of 72 parts per million as calcium carbonate was used to make an inverted mixture. Without the addition of any colloidal material and without pumping through the release valve, breaking began at once, and was complete in one minute. The mixture was too unstable to be used. When casein, as ammonium caseinate, was introduced into the tank before the lead arsenate, oil, and soap, at the rate of 0.033 ounce per 100 gallons, the mixture was stabilized to the extent that it withstood a moderate amount of pumping through the release valve, and was sprayed out without difficulty. It gave fair build-up.

Evidently one part casein in approximately 425,000 parts of water may exert a noticeable effect on the stability of soap-oil-arsenical mixtures.

In terms of the arsenical, this means that 0.06 per cent casein or some equally effective colloid may affect its deposition; so from a theoretical standpoint, a lead arsenate sample might be 99.94 per cent pure, yet contain an excessive amount of colloidal material for satisfactory use in an inverted mixture.

It was felt that the addition of an electrolyte such as the sulphate of zinc or aluminum might be helpful in lessening the stability of mixtures which were resulting in heavy arsenical run-off under field conditions. In practice, when the introduction of calcium hydroxide at 0.25 to 0.5 ounce per 100 gallons had failed to increase the deposit from a lead arsenate-kerosene-ammonium oleate mixture, zinc sulphate at 1.5 ounces per 100 gallons gave an improvement. However, in a laboratory experiment in which low deposits were obtained even though the mixtures were comparatively unstable in the spray tank, the introduction of zinc sulphate in amounts of one ounce and three ounces had no effect. Apparently, the use of an electrolyte for the purpose of increasing the deposit of solid from soap-oil-lead arsenate mixtures may be beneficial only under certain circumstances, as for instance, where low deposit is due to excessive stability.

Another means of overcoming excessive stability is by increasing the quantity of soap. This practice, however, may not be as desirable as the former because of the potential danger of liberating soluble arsenic to the extent of causing fruit or foliage injury.

i. Effect of Continued Spraying upon Arsenical Deposit. It has been mentioned that the outstanding feature of an inverted spray mixture is its characteristic of forming a deposit which increases steadily in amount, as spraying is continued upon one point. This characteristic has been more pronounced on oily or waxy surfaces than on hairy surfaces. Accordingly, these mixtures have been less likely to produce heavy deposits per unit of area when apples are small and hairy than when they are larger and have a waxy surface. Maximum deposition of arsenical from inverted mixtures apparently has not been attained until the third or fourth cover sprays. Perhaps this is related to the condition of the surface of the fruit, as well as to an accumulation of material which may occur if early applications follow one another at close intervals.

The nature of the sprayed surface plays a more evident part with the foliage of the apple than with the fruit. For example, a spray such as lead arsenate-protein spreader, or lead arsenate-Bordeaux, though not adhering strongly, may adhere somewhat similarly on both the waxy upper surface and the hairy lower surface of the leaf. On the other hand, inverted mixtures adhere much more firmly to the upper surface. Indeed with heavy application, so evident does the oily arsenical deposit become, that a question arises concerning the likelihood of interference with the vital functions of the leaf. So far no visibly deleterious effects have been noted. Perhaps the disposition of the stomates of the apple leaf may bear upon the matter. According to Miller (1931), there are no stomates on the heavily cutinized upper surface, but, varying with variety, from 186,000 to 266,000 per square inch on the lower surface. There seems no reason to expect, therefore, that the gas exchange of the leaf would be influenced beyond that which might occur with the ordinary combination spray, consisting of lead arsenate and petroleum oil emulsified by ammonium caseinate. Nothing is known concerning the possible effect of a very heavy oil-arsenical-soap deposit upon the absorption or reflection of light, as apart from stomatal behaviour.

Work dealing with the influence of inverted mixtures upon the photosynthetic activity of apple leaves is being done at the present time by the department of horticulture of the Washington Experiment Station, and it is hoped that it will help to explain the relationship between these spray deposits and the physiological processes of the apple tree.

Laboratory experiments, summarized graphically in Figure 4, emphasize the striking difference in capacity to build an arsenical deposit, between an inverted lead arsenate mixture and a non-inverted mixture. In these experiments two emulsions of kerosene were used with lead arsenate. The first emulsion was formed by the hydrophilic colloid, ammonium caseinate; the second by the water and oil soluble soap, triethanolamine oleate. Twenty-seven samples of apples, consisting of six fruits each, were divided into three series of nine samples. The first series was sprayed once, allowed to dry, then analyzed for arsenical deposit. The second series was sprayed once, allowed to dry, then sprayed a second time and analyzed. The third series was sprayed three times in this manner, then analyzed. Each mixture was sprayed upon one sample for two seconds, a second sample for five seconds, and a third for 15 seconds. The analytical determinations were made in duplicate, and the entire experiment repeated a second time with fresh mixtures. The figures in the graph, being averaged from the results of the two experiments, each represents four arsenical determinations. Lead arsenate applied alone was used as a check.

The following points are suggested by the experiments: 1. Lead arsenate used alone in water gives deposits of similar amounts, whether applied for two seconds or 15 seconds. (See Appendix, Table 2, for variations in such deposits).

2. When sprayed for a short time, lead arsenate alone gives heavier deposits after several applications, than when heavily applied. Apparently,

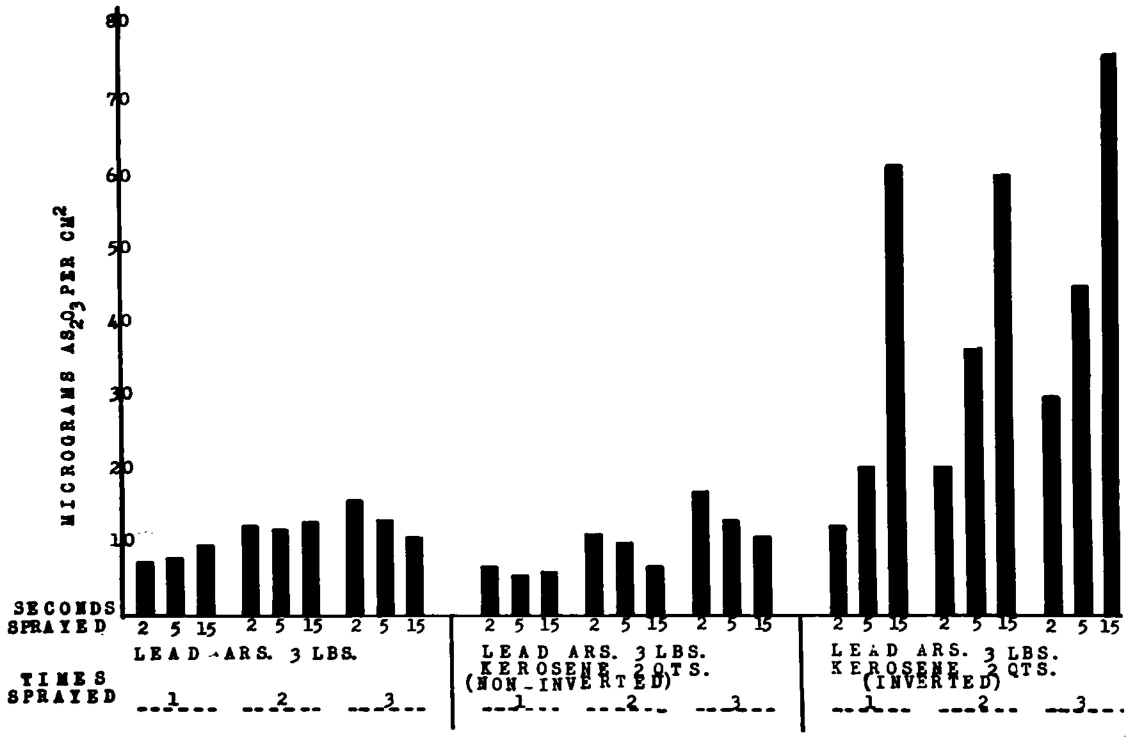

Fig. 4. Effect of continued application upon spray deposit. Lead arsenate used alone in water; lead arsenate with kerosene, non-inverted; lead arsenate with kerosene, inverted.

as indicated later, this is because heavy applications tend to remove the deposit previously present on the fruit surface, and re-deposition is insufficient to exceed the original load. In practice, light applications of lead arsenate alone are not likely to be as effective for codling moth control as heavy applications. Prolonged spraying generally results in more thorough, though not necessarily heavier, deposition, and the blotched deposits which supervene are more effective than the finely spotted deposits following light or mist-like applications. This has been demonstrated by Smith (1926).

3. When lead arsenate is used in combination with kerosene emulsified by ammonium caseinate, the resulting arsenical deposits are somewhat similar to those from lead arsenate used alone. No build-up occurs either from a single heavy application or from a series of heavy applications. Judging from field results, this generalization would not apply if a heavier fraction of petroleum oil is used. Medium grade summer petroleum oil emulsified with ammonium caseinate, and used with lead arsenate, at the end of the season has given somewhat heavier arsenical loads than lead arsenate used alone. Apparently, the oily nature of the fruit surface following the application of such a mixture affects the eventual deposit of the solid. Probably this is owing to the action of the oil in lessening the loss of arsenical from weathering, and possibly also, to the slightly increased tendency for the successive applications to adhere to the oily surface of the fruit. Kerosene, since it disappears soon after spraying, would have little, if any, value in this way.

4. When commercial acid lead arsenate is used in combination with kerosene emulsified by a suitable soap, and all constituents are in proper amount, a heavy application results in a much heavier arsenical deposit

than a light application, and the deposit is in the form of a film instead of being blotched or spotted as in the case of lead arsenate alone, or lead arsenate combined with an ammonium caseinate emulsion of kerosene.

It will be noticed that the average of the second of the heavy applications of the inverted mixture did not show an increased deposit over the first, though it was nevertheless very heavy. This was because in the first of the experiments the mixture was much more stable than in the second, and gave quite mediocre and inconsistent deposits. Until this time (1934), the strong stabilizing effect of colloids upon inverted mixtures had not been realized. But at this point it was suspected that even slight contamination of the spray pump might influence results, so when the experiment was repeated, particular precautions were taken to wash and flush the equipment thoroughly, to be sure that there remained in it none of the ammonium caseinate emulsion from the previous tankful of spray. The extremely heavy deposits characteristic of inverted spray mixtures then appeared. As demonstrated during the past season, in an experiment already mentioned, a minute amount of ammonium caseinate may completely change the behaviour of the inverted type of spray mixture, so the earlier suspicion seems to have been correct.

j. Influence of Pressure and Spray Gun Aperture upon Deposit. Experience in the field application of inverted mixtures suggested that the type of spray blast might influence the arsenical deposit. Laboratory experiments were planned with the object of obtaining definite information upon this point. Two sprays were selected for comparison; lead arsenate used alone in water, and lead arsenate in combination with two quarts of medium summer petroleum oil emulsified by 0.25 pound of triethanolamine oleate. The latter forms a typical inverted mixture. These sprays were applied by a

16-gallon "Bean" spray pump under pump pressures of 300, 425, and 500 pounds per square inch, with gun disc apertures 4/64-inch, 8/64-inch, and 10/64-inch in diameter. The spray gun was a 1934 "Hardie" Model E, connected to the pump by ten feet of 0.5-inch hose. Nozzle pressures were not determined, but with the larger disc openings they were probably in the neighborhood of 25 per cent less than the pump pressures. Duplicate samples of five apples were sprayed from a distance of three feet. Spraying was continued for ten seconds while the apples were rotating.

Table 10 gives the arsenical deposits where a finely fogged spray blast was employed with pressures of 300 pounds and 500 pounds at the pump.

Table 10. The Effect of Variation of Pressure and Disc Aperture upon Arsenical Deposit.

Pounds pump pressure	Disc aperture	Delivery gals. per min.	Spray Mixture	Deposit as mmg As_2O_3 per cm^2		
				(a)	(b)	Ave.
300	4/64"	1.7	Inverted mixture	27.9	23.5	25.6
			Lead arsenate alone	11.1	9.1	10.1
	8/64"	3.0	Inv. mixture	27.1	31.5	28.2
			L. A. alone	10.5	13.2	11.8
	10/64"	4.2	Inv. mixture	27.2	22.9	25.0
			L. A. alone	10.5	10.8	10.6
500	4/64"	2.2	Inv. mixture	37.6	35.2	36.6
			L. A. alone	9.0	8.7	8.8
	8/64"	4.0	Inv. mixture	61.1	77.9	69.5
			L. A. alone	10.0	10.5	10.2
	10/64"	7.2	Inv. mixture	36.7	43.3	40.0
			L. A. alone	12.8	11.9	12.3

In every comparison is illustrated the failure of lead arsenate alone to form deposits greater than about 12 micrograms As_2O_3 per square centimeter of fruit surface. Approximately the same deposit was obtained regardless of the pressure or rate of output of spray material. The reason for this condition is that without an adhesive, little if any more lead arsenate can remain on the fruit than that amount which is suspended in the water adhering to it when spraying ceases. In other words, the amount of lead arsenate deposited from such a mixture depends almost entirely upon the amount of lead arsenate introduced into the spray tank. Once the apple has been thoroughly wetted no more water will adhere. Since no more water adheres, no more lead arsenate is deposited with very heavy application than with light application.

Theorizing becomes more difficult with the inverted mixture for reasons which are stated elsewhere. Apparently somewhat higher deposits resulted with a pressure of 500 pounds per square inch, than with 300 pounds per square inch. Probably this depended mainly on the greater output of material at the higher pressure. It was observed that in neither case did the spray mixture strike the fruit so forcibly that any of the deposit was removed by washing off. Deposits were somewhat similar for the different gun apertures. Evidently this was due to the greater area covered by the spray blast with the larger apertures. No explanation can be offered for the particularly high deposit obtained with the 8/64-inch aperture at 500 pounds pressure, for unfortunately, repetition of the experiment was out of the question.

A common query from the grower who uses an inverted mixture concerns the effect of a driving type of spray blast upon the arsenical deposit. An experiment was planned with this in mind and the results are given in Table 11. The two mixtures of the previous experiment were used again with a constant pressure of 425 pounds at the pump, and the type of spray blast was varied from a wide fog to a driving spray. The disc aperture was constant at 8/64 inch, and the fruits were sprayed for 10 seconds.

Table 11. The Effect of Type of Spray Blast upon Arsenical Deposit.

Type of spray blast	Spray mixture	Deposit as mmg As_2O_3 per cm^2 (a)	(b)	Ave.
Wide fog	Inverted mixture	39.5	52.5	46.0
	Lead arsenate alone	10.7	11.9	11.3
Medium fog	Inverted mixture	51.0	40.7	45.7
	Lead arsenate alone	10.0	10.3	10.1
Driving spray	Inverted mixture	24.3	27.6	25.9
	Lead arsenate alone	10.6	10.6	10.6

It will be observed that with an overspray, i.e., ten seconds application upon revolving fruits, the extent of the deposit from lead arsenate-water mixtures was not related to the type of the spray blast. The output of spray was not determined for each of the types, but as the blast was varied from a fine fog to a driving spray, it increased by possibly 50 per cent. This is simply a further indication that the arsenical deposit from lead arsenate used alone in water at three pounds per 100 gallons can not be made to exceed a very small maximum under any circumstances.

It might be assumed that maximum deposit from an inverted mixture will occur when the blast of the spray gun is fogged. As a matter of fact, this may be observed under field conditions, but only when the fruit is rather close to the nozzle of the gun. It is questionable if a driving spray would show to such disadvantage when the fruit is, let us say, 15 feet from the gun.

Apparently disc apertures as large as 10/64 inch are satisfactory for the application of inverted mixtures, providing pressure is adequate, and the spray blast at least moderately fogged.

k. Inversion of Lead Arsenate-Oil Mixtures by the Addition of Substances Other Than Univalent Soaps. In attempting to find a workable explanation for the behaviour of inverted spray mixtures, some incidental experimental work has been done by the addition to lead arsenate-oil mixture of compounds apart from the univalent soaps. In view of the speculations which follow, these experiments are briefly summarized here.

1. The addition of two per cent by volume of diglycol oleate to medium summer oil resulted in rather weak inversion. Four per cent diglycol oleate gave more definite inversion, and eight per cent resulted in inversion and arsenical build-up rather comparable to that from a similar amount of triethanolamine oleate. When the temperature of the water was raised from 16° C to 40° C, inversion with four per cent diglycol oleate was more rapid.

2. Diglycol laurate, solidifying at about 14° C did not cause satisfactory inversion when the temperature of the water was 16° C. It was not as effective as diglycol oleate for this purpose, at 40° C.

3. The addition of 2.5 per cent by weight of lead oleate to medium summer oil caused more rapid inversion than either ammonium oleate, or triethanolamine oleate, at approximately seven per cent. Arsenical build-up was decidedly heavy.

4. Addition to medium summer oil (temperature 100° C) of 2.5 per cent aluminum naphthenate caused slight but unmistakable inversion. The exact composition of the sample of aluminum naphthenate is not known, but it is suspected that it may have contained a variety of other compounds.

5. Neither sodium oleyl sulphate nor sodium lauryl sulphate effected inversion when used in the amount of 0.25 per cent or 1.0 per cent of the weight of the oil.

6. Medium summer oil alone at 0.5 per cent of the water was added to lead arsenate so as to wet it thoroughly, and the mixture added to the water in the spray tank. No inversion occurred, and no build up even with prolonged pumping. However, flocculation of the lead arsenate particles

was pronounced. When the oil was mixed with lead arsenate at the rate of 100 gallons to three pounds, and the mixture sprayed upon apples without the introduction of any water, there was no build-up of the arsenical whatever. The addition of lead oleate to the oil at 0.2 per cent had no effect.

When the lead arsenate was used at the rate of 200 pounds in 100 gallons of oil, a thin paste was formed which was passed through the pump with difficulty in the absence of water. It gave a very heavy deposit upon sprayed apples. Heavy build-up thus occurred with only summer oil and lead arsenate, providing the mixture was suitably viscous.

1. Speculations Concerning the Nature of Inverted Lead Arsenate Mixtures.

The fundamental difference between an inverted spray mixture and the conventional type of mixture containing water, oil, and a suspended solid, is that the solid is wetted by oil instead of water; the phenomena concerned in wetting processes are then of prime importance.

Reinders (1913) examined the arrangement of a number of finely divided solids when intimately in contact with two immiscible liquids and observed that some remained at the liquid-liquid interface, some were apparently completely wetted by one of the liquids and some by the other liquid. Hofmann (1913) working on the same problem postulated that when a finely divided solid is wetted by water more than chloroform for example, the water will displace the chloroform and there will be formed an aqueous film around the solid particles. Water will eventually wet the particles regardless of which of the immiscible liquids first wetted them.

Davis and Curtis (1932) applied this idea of preferential wetting to the emulsification of liquids by finely divided solids, and suggested a simple procedure for its determination. This is as follows: About 20 grams of the solid, and either of the two immiscible liquids, are worked into a soft putty. The second liquid is then added, a few drops at a time, and worked into it. If the solid is preferentially wetted by the first liquid, very little of the second liquid can be worked into the putty. In case of preferential wetting by the second liquid, the mass becomes more or less the consistency of cottage cheese, with liberation of the first liquid.

The method of Davis and Curtis was used to determine the wetting characteristics of two types of acid lead arsenate. One of them was prepared by Doctor Kermit Groves in the chemical laboratory of the Washington Experiment Station; the other was a commercial product, by customary methods of analysis, over 98 per cent $PbHAsO_4$, and containing no stabilizing or deflocculating agent. These were the results with the laboratory prepared sample.

(1) It was preferentially wetted by water in the presence of medium summer petroleum oil, oleic acid, petroleum oil containing five per cent oleic acid, and herring oil. (2) When from two to four per cent (estimated) gum dammar was dissolved in medium summer petroleum oil, and this solution used to wet lead arsenate, it was possible to work water into the paste. Apparently water-in-oil emulsion was formed. However, when the lead arsenate was first wetted by water, the oil-gum dammar could not be worked into it. The simultaneous introduction of water and oil-gum dammar solution resulted in the formation of an oil-in-water emulsion. (3) When an aqueous sodium oleate solution was first used to wet the lead arsenate, what appeared to be a water-in-oil emulsion was eventually formed with the continued addition of petroleum oil. (4) A five per cent petroleum oil solution of lead oleate preferentially wetted lead arsenate in the presence of water, likewise forming what appeared to be a water-in-oil emulsion.

Although gum dammar promotes water-in-oil emulsions, its capacity to do so was evidently less than that of a large amount of lead arsenate to stabilize an oil-in-water system. On the other hand, lead oleate, also promoting water-in-oil emulsions, was able to stabilize such an emulsion, even in the presence of lead arsenate and even if the lead arsenate had been initially wetted by water. It is not known whether the oil-lead oleate solution actually displaced the water from the surfaces of the solid particles, or whether it merely served to disperse particles of solid still coated by an aqueous film. Since apparently similar results followed the introduction of sodium oleate, as compared to lead oleate, perhaps they had a similar genesis. In this connection, if when an aqueous solution of sodium oleate comes in contact with a lead arsenate particle, lead oleate should be formed by metathesis, it may exist as a coating on the particle. The question of preferential wetting would then concern not lead arsenate, but lead oleate, and lead oleate is fairly soluble in summer petroleum oil. In any event, there is to be considered the fact that by the presence of the additional oil soluble emulsifier, these systems are complicated beyond those examined by Davis and Curtis.

When a certain brand of commercial acid lead arsenate was used instead of the specially prepared laboratory sample, the preferential wetting test gave different results. Thus the commercial product was preferentially wetted by oleic acid in the presence of water. The gummy material adhered to glass, suggesting the formation of lead oleate. When the lead arsenate was first made into a putty with herring oil, and water added, an oil-in-water emulsion was eventually formed, instead of the herring oil being liberated from a curdy mass, as in the case of the laboratory sample of lead arsenate.

It seems logical to attribute these differences to variation in the physical or chemical nature of the lead arsenates, a point which is considered later.

Persing (1935) applied the Davis and Curtis method of determining preferential wetting to finely divided fluorine insecticides. He found that in some cases definitely preferential wetting occurred, and in others the effect was only partial. His opinion was that some of the oils had sufficient wetting power to hold the particles in the oil phase if they were initially oil-wetted, but not enough to cause the particles to pass from the water phase into the oil phase. However, Persing was working with a number of proprietary oils containing oil soluble emulsifiers, as well as with animal and vegetable oils which perhaps contained considerable proportions of free fatty acids. His evidence of oil or water preferences, therefore, might have depended at least partially upon the formation of trivalent soap, for both natural and artificial cryolite contain measurable amounts of water soluble aluminum. If such a soap were formed, there would be a system somewhat analogous to that already mentioned, i.e., mineral oil-lead oleate-lead arsenate-water.

Findings at Wenatchee have agreed with those of Persing in that inversion of cryolite mixtures is not as readily accomplished in diluted spray combinations as is inversion of arsenical mixtures. However, it has been quite marked, when a small amount of water was mixed with the oil-solid-wetting compound, before the whole was added to the spray tank. In every case where inversion ensued, there had been introduced either free fatty acid (oleic), univalent soap, or divalent soap.

The agglutinated material which forms in an inverted mixture after it has passed through the release valve of the sprayer might be termed a quasi-emulsion. The samples examined microscopically were composed of a greasy matrix of oil and lead arsenate, occluding water globules, and air bubbles. It appears probable that the water globules were prevented from coalescing, or being liberated, more by reason of the viscous nature of the matrix than by the presence about them of an adsorbed film of some emulsifying substance. In these spray combinations emulsion inversion in the strict sense does not occur, yet this does not preclude the formation of substances capable of producing this phenomenon, for the oil:water ratio is such as to rule out the existence of a water-in-oil system in any case, at least insofar as the entire volume of water is concerned.

Pickering (1907) first showed that finely divided solids which are more readily wetted by water than oil, may form oil-in-water emulsions by collecting at the liquid-liquid interface, and Scarlett, et al. (1927) added that both liquids must wet the solid before it will collect at the interface. Schlaepfer (1918) discovered that water-in-oil emulsions may likewise be formed with a finely divided solid as emulsifier. Using powdered carbon (soot) as the solid, he was able to disperse 70 per cent by volume of water in 30 per cent by volume of kerosene.

If inverted arsenical mixtures depend solely on the wetting properties of oil for their characteristic as deposit builders, it should be possible to simulate this effect by utilizing a finely divided solid preferentially wetted by oil in the first place; that is, without the necessity of introducing fatty acids which, as already mentioned, appear to promote oil-wetting for certain substances that nominally are hydrophilic. With Schlaepfer's experiments in mind, powdered carbon ("Norit") was introduced into a carefully cleaned spray tank which contained a mixture of medium summer petroleum oil, commercial acid lead arsenate, and water. For five minutes the whole was vigorously agitated and pumped back upon itself through the release valve at a pressure of 300 pounds per square inch; then it was sprayed out upon mature apples. At once the carbon commenced to form the uniform, steadily increasing deposit typical of inverted arsenical mixtures, while the lead arsenate particles collected in droplets of water which coalesced and dripped from the fruits. The accompanying photograph shows one of these apples after the water had evaporated and left a spotted white deposit of lead arsenate on a uniform black background composed of petroleum oil and carbon particles. Only one side of the apple was sprayed.

It has been found that when lead arsenate was wetted by a petroleum oil solution of lead oleate, a particular ratio had to be maintained between the solid and the oil before the arsenical would accumulate in a heavy film upon a sprayed surface. Excessive amounts of oil lowered the viscosity of the oil-solid mixture so that it dripped from the surface; insufficient oil caused only a portion of the solid particles to be wetted, with the result that only that portion was in a condition which favored adherence. The same applied to oil-carbon mixture, so because in the latter case there were concerned only two substances, both chemically inert in a water suspension, it is evident that the heavy and uniform deposit was conditioned principally by two factors; the wetting of solid by oil, and the ratio of solid to oil. The possible presence of gummy, oil soluble soaps should represent an accessory factor when arsenicals are in question, and used in combination with fatty acids or fatty acid compounds.

For the past ten years, attention has been focused upon the phenomenon of spreading in arsenical spray mixtures. It has been for many the first

Fig 5. Simultaneous formation of heavy, uniform deposit of oil-wetted carbon particles and light spotted deposit of water-wetted lead arsenate particles. Apple sprayed from right side only

desideratum, since without effective spreading, uniform deposits could not be obtained, and without uniform deposits codling moth control is adversely affected. Nevertheless, with the inverted mixture, resulting in as uniform deposits as the best spreaders, it has been manifest that spreading in the strict sense plays no part. Here uniformity evidently depends on the fact that the oil-wetted solid particles or agglomerates adhere immediately upon impact either to the fruit surface, or to previously deposited particles or agglomerates. A fine dispersion of the oil-wetted solid in the spray blast takes care of the rest.

In the present method of preparing inverted lead arsenate mixtures, the phenomenon of wetting comes into play three times; first, when the solid is wetted by water; second, when it is wetted by oil; and finally, when the oil film surrounding the solid particles wets the surface of the fruit and causes them to adhere to it.

There remains to be considered that important matter, the process by which lead arsenate, preferentially wetted by water, is transferred to the oil phase of an emulsion; in other words, the process by which the mixture is inverted. Woodman and Taylor (1930) reported that certain clays gave dual types of emulsions with fatty acids, or with fixed oils containing free fatty acids. They believed that this was due to chemical interaction of the fatty acids with the sodium and calcium hydroxides, etc., obtained by hydrolysis of the clay when in aqueous suspension, or with breakdown products of the clay itself. That is to say, the dual emulsions resulted from the simultaneous presence of univalent and divalent or trivalent soaps. If heavy metals should be liberated in sensible amounts from insecticide mixtures containing oil emulsified by a univalent soap or free fatty acid, then compounds could be formed which would radically affect the physical nature of the mixtures.

Persing's interesting paper (loc. cit.) while stressing the fact that the introduction of polar radicals into petroleum oil, results in oil-wetting of lead arsenate or cryolite, apparently adduces that such radicals are, per se, responsible for it. However, the Wenatchee investigations have shown that the oleates of lead and zinc when added to oil cause oil-wetting of lead arsenate which is decidedly more pronounced than that from oleic acid. Also when commercial acid lead arsenate is first wetted by mineral oil containing five per cent oleic acid, then added to a spray tank containing water, satisfactory build-up of deposit only occurs when the mixture has been subjected to prolonged agitation and pumping back upon itself. It is as though some reaction were in progress, and if this is the case, it seems logical that a reaction product might be lead oleate. This view is supported by the fact that in the presence of oleic acid or univalent soap in water solution, oil wetting of one brand of lead arsenate may be more rapid than that of another. Groves (unpublished matter) of this experiment station has found that this may be partly owing to the presence of variable amounts of basic lead arsenate in the commercial acid form. He determined that one widely used product, marketed as acid lead arsenate, actually contained about 15 per cent of the less toxic basic lead arsenate, while another equally well known brand contained very little basic lead arsenate. He presumed that since basic lead arsenate reacts with a weak acid such as acetic, it might also do so with oleic, though because oleic acid is water insoluble, the reaction would not proceed as rapidly. Another point brough out in his investigations was that particle size of lead arsenate seems to be an important point in wetting and inversion; in these heterogeneous systems chemical action takes place on the surface of the particles, so the smaller the particles the greater the surface area and the more pronounced the effect. As for the reactions with univalent soap, the situation may be somewhat different for the soap hydrolyzes lead acid arsenate and may combine directly with it. Groves has detected the presence of oil soluble lead by ether extraction of certain inverted lead arsenate mixtures, suggesting that commercial lead acid arsenate may indeed react with oleic acid, or univalent soap to form lead oleate.

The difficulty of attributing inversion to any particular cause is further complicated by impurities in the oleic acid. Tartar, et al. (1929), in studying emulsion inversion have attempted to prepare pure oleic acid. In their method lead acetate solution was added to oleic acid. The lead oleate thus formed was treated with hydrochloric acid and the oleic acid recovered from ether by distilling under reduced pressure in an atmosphere of carbon dioxide. In spite of these precautions they concluded, "The oleic acid thus obtained was probably somewhat impure; apparently very pure oleic acid has never been prepared." Groves has found that the so-called red oil (oleic acid) of commerce may contain appreciable amounts of iron, presumably as a result of having been stored in iron or steel containers. Iron oleate, like lead oleate, promotes oil-wetting of lead arsenate.

Present evidence concerning the nature of inverted lead arsenate mixtures is most definite in pointing to their complexity. In commercial practice, the lead arsenate, oil, oleic acid, and water may all contain impurities which are capable of affecting results to a marked degree. The following points summarize the situation:

1. Inverted lead arsenate mixtures are formed when some substance is present which causes the arsenical particles to be wetted by oil. The oil may be petroleum oil, animal oil, or vegetable oil.

2. Inversion occurs when divalent soaps are introduced into a mixture of lead arsenate, oil, and water in suitable proportions, and the whole is ejected through a small orifice at high pressure.

3. Inversion likewise occurs when univalent soaps are introduced into such a mixture. If oleic acid is substituted for univalent soap, partial inversion generally results if the mixture is subjected to prolonged pumping through the overflow valve.

4. In mixtures containing univalent soap, or free fatty acid, there is some evidence that lead soap is formed by metathesis from the monovalent soap, or directly from the free fatty acid.

5. Wetting of solid by oil appears to depend at least in part upon the formation of divalent or trivalent soaps. Probably lead oleate is principally concerned, but with certain grades of oleic acid, iron oleate may be a factor.

m. Ovicidal and Larvicidal Effectiveness of the Inverted Petroleum Oil Mixture. Porter and Sazama (1930) have mentioned that when a minimum concentration of oil is used with Bordeaux misture, it is less effective as a scalecide than when used alone. Referring to the work of De Ong, Knight, and Chamberlin (1927), they concluded that the particles of the Bordeaux mixture acted in a mechanical way, absorbing a certain volume of the oil and preventing penetration into the insect. In an inverted mixture, the oil is more intimately associated with the solid than in a comparable mixture containing oil emulsified by a hydrophilic colloid. The question then arises concerning the relative ovicidal values of the two types of spray combinations. It might be suspected that the latter mixture with more free oil would be the more effective. Laboratory experiments were undertaken to determine the point.

By suspending apples in the incubator cage mentioned previously, codling moth eggs were obtained in considerable numbers on the surface of the fruits. After the eggs had been counted and widely circled with India ink to facilitate recovery, the apples were sprayed for four seconds with the mixtures in question. Since they were rotating this meant that any given point was sprayed for two seconds, i.e., equivalent to a heavy application under field conditions. The experiment was repeated nine times with the results in Table 12.

Table 12. The Influence of Emulsifier on Ovicidal Effect of Oil-Lead Arsenate Mixture.

Materials per 100 gals. water		No. of eggs		No. of eggs unhatched		Average per cent unhatched
1 Lead arsenate, 3 lbs.	(1)	110		65		
Medium summer oil,	(2)	116		87		
2 qts.	(3)	13		13		
Triethanolamine oleate,	(4)	205		199		
0.25 lb.	(5)	124		115		84.1
(Inverted Mixture)	(6)	43		36		
	(7)	49		45		
	(8)	45		40		
	(9)	87		74		
	Total	792		674		
	Ave.		88.0		74.9	
2 Same, but Ammonium	(1)	102		89		
caseinate 0.015 lb.	(2)	85		67		
instead of triethano-	(3)	63		55		
lamine oleate.	(4)	205		197		
(Non-inverted Mixture)	(5)	61		57		90.6
	(6)	43		38		
	(7)	51		44		
	(8)	54		49		
	(9)	102		100		
	Total	766		696		
	Ave.		85.1		77.3	
3 Lead arsenate alone,	(1)	106		9		
3 lbs.	(2)	114		8		
	(3)	125		13		
	(4)	204		16		
	(5)	--		--		8.5
	(6)	43		5		
	(7)	42		4		
	(8)	50		7		
	(9)	91		5		
	Total	775		67		
	Ave.		96.9		8.3	

It might seem that the oil in the inverted mixture was somewhat less effective as an ovicide than in the non-inverted mixture. The point can not be made clearer by statistical treatment of the data for the human equation is too variable a factor in this work. It is more difficult to detect eggs after fruits have been sprayed with the former mixture. But in any event, it is improbable that from the ovicidal standpoint, the inverted mixture is superior to the ordinary type of non-inverted oil-lead arsenate combination. The greater effectiveness of the former in the field evidently depends on its superiority as a larvicide.

The comparative larvicidal values of the two mixtures have been briefly examined in the laboratory and though the experimental work is quite inadequate, it is suggestive of the close connection between the extent of an arsenical deposit and the degree of codling moth control, a relationship which has been obvious repeatedly, both in the laboratory and the field.

The laboratory procedure in larvicide experiments has been briefly described earlier. As for the experiment reported in Table 13, four spray mixtures were used. Each was applied for five seconds and 15 seconds respectively to two groups of ten Winesap apples. Each apple was then infested with ten eggs attached to waxed paper, so that a total of 600 eggs was used for the four mixtures. There were no arsenic determinations for this particular experiment, but Table 1 gives a general idea of the extent of the deposits.

Table 13. The Influence of Emulsifier on Larvicidal Effect of Oil-Lead Arsenate Mixtures.

Materials per 100 gallons of water	Time sprayed	No. eggs hatched	No. Entries	Per cent mortality
1 Lead arsenate, 3 lbs. Medium summer oil, 2 qts. Triethanolamine oleate, 0.25 lb. (Inverted Mixture)	5 secs.	80	15	81
	15 secs.	82	3	96
2 Same, but Ammonium caseinate, 0.015 lb., instead of triethanolamine oleate. (Non-inverted Mixture)	5 secs.	87	32	63
	15 secs.	88	31	65
3 Lead arsenate alone, 3 lbs.	5 secs.	92	58	37
	15 secs.	84	37	56

There undoubtedly would be considerable variation from these mortality figures if the experiment were repeated, but the superiority of the inverted mixture as a larvicide appears to be as decided as might be predicted on the basis of its much heavier and more uniform arsenical deposit. It is interesting to note that lead arsenate with the ammonium caseinate emulsion, though not giving a higher arsenical deposit for a single application than lead arsenate alone (Table 1), was apparently more effective as a larvicide. This is in accord with frequent field and laboratory observations, indicating that, the amounts being equal, an oily arsenical deposit is more effective as a larvicide than a non-oily deposit. In each case a similar type of deposit is assumed, e.g., spotted, filmed, etc. Haseman (1934) suggests that an oily coverage may deter establishment by making it difficult for the codling moth larva to attach its silken thread. This life-line, metaphorically speaking, is fastened to the fruit surface with each movement of the newly hatched insect, and in the form of a silken mat provides a fulcrum for the leverage necessary to enable the minute insect to pierce the skin of the fruit with its mandibles.

The reason for the great superiority of petroleum oil-arsenical mixtures over arsenical mixtures without the oil becomes evident when Tables 12 and 13 are considered together - when the effects of ovicide and larvicide are combined. Let us suppose that a number of apples in the insectary bear 1000 codling moth eggs and are sprayed for five seconds with lead arsenate alone. About 95 per cent of the eggs will hatch, liberating some 950 larvae. Frequent experiments have shown that under laboratory conditions and depending on variety of apple and time of year, about 60 to 80 per cent of the larvae will establish themselves in fruit sprayed once with lead arsenate alone. Seventy per cent establishment would result in 665 entries from the 1000 eggs. On the other hand, let us suppose the eggs had been sprayed for 5 seconds with an inverted mixture containing 0.5 per cent oil (two quarts). Mortality in the egg stage will amount to perhaps 85 or 90 per cent, so that eclosion will take place from about 125 eggs. The 125 larvae will then be subject to some 80 per cent mortality, and establishment will only be effected in about 25 cases. Thus the inverted mixture, for a single heavy application before eclosion, would be some twenty-five times as effective in preventing entries as lead arsenate alone. It should be kept in mind, however, that under field conditions oftentimes the oil has no opportunity to act as an ovicide, because not applied with sufficient frequency.

Atmospheric temperatures during May and June, at which time the overwintered moths are in flight in central Washington, are not as high as during later flights. For this reason, the egg stage generally lasts considerably longer, and the unusual effectiveness of the inverted mixture has therefore a much better opportunity to come into full play. Furthermore, spray applications are made more frequently then than later, so providing several "first brood"[6] applications are made, most of the eggs will be exposed to the ovicidal effect of the oil mixture before eclosion can take place.

It should be mentioned that mortality of first generation larvae at least, appears to be distinctly greater in the field than in the laboratory where light is subdued, and temperature and humidity maintained at the most favorable levels. There is little question that in the presence of a deposit of lead arsenate, amounting to 10-12 micrograms As_2O_3 per square centimeter of fruit surface, considerably less than 70 per cent establishment of

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[6] The term "first brood" is used to indicate the larvae hatching up to mid-July. It should be kept in mind, however, that certain of the overwintered individuals may lay eggs subsequent to this time.

first generation larvae will occur in the orchard. Although field mortality of larvae of the second generation, as a general rule is manifestly lower than that of larvae of the first generation in the face of a similar arsenical deposit, it is doubtful if even then it is as low as in the laboratory.

2. Inverted Calcium Arsenate Mixtures

Previous published work of this experiment station by Marshall and Groves (1936b) has provided considerable evidence that for the arid climate of central Washington, at least one type of commercial calcium arsenate may be a reasonably satisfactory substitute for acid lead arsenate. It must be used in combination with some substance which renders it innocuous to apple foliage and fruits, without lowering its effectiveness as an insecticide, and a deposit must be maintained equivalent to lead arsenate on a total arsenical basis. Like lead arsenate, when used with an oil emulsified by a hydrophilic colloid, it produces a spotted deposit which shows practically no capacity to increase with prolonged spraying. Laboratory experiments were undertaken to remedy this defect, and though from force of circumstance lacking repetition, they illustrate the development of the work.

When a univalent soap is added to a mixture of that complex of substances known as commercial tricalcium arsenate, and water, a dry granular mass is formed. Evidently this is largely a result of formation of calcium oleate from free calcium hydrate by metathesis. The calcium soap coats the suspended particles and the whole settles out as a waxy mass. If a sufficient quantity of free petroleum oil be introduced previous to the addition of the soap, a rapid breaking or inversion takes place. The mixture, if sprayed out before it has an opportunity to separate entirely, produces the typical arsenical build-up of an inverted mixture. Apparently, the petroleum oil wets the calcium oleate coated arsenical particles, and lacking a water-borne emulsifier in sufficient amount, or sufficient effectiveness, the mixture largely separates, with the arsenical remaining in the oil. This is a different condition than occurs with lead arsenate in a similar mixture, and it calls for the introduction of some additional substance which will act as a stabilizer. A satisfactory substance for the purpose has been zinc sulphate. In practice a small quantity of zinc sulphate is dissolved in water in the spray tank, next the calcium arsenate is introduced, and finally the soap-petroleum oil emulsion is added when the tank is practically full. One effect of the zinc sulphate is to react with at least part of the calcium hydrate present in the calcium arsenate as an impurity. The resulting precipitate, consisting for the most part of zinc hydroxide, probably serves to delay or impede the intimate contact of oil and calcium arsenate until this is accomplished by passage through the spray gun or release valve. With intimate contact, the arsenical becomes wetted by the oil and inversion takes place.

It is not known what substance brings about the wetting of calcium arsenate particles by oil in this mixture. But as mentioned by Bhatnagar (1921), divalent soaps promote water-in-oil emulsions, and salts of divalent metals tend to cause emulsion inversion if added to oil-in-water emulsions stabilized by univalent soaps. Since as just pointed out, inversion of the mixture occurs when a univalent soap is introduced into an oil-water-calcium arsenate system, it seems reasonable to assume that it results at least in part from the formation of calcium oleate. It has been determined by experiment that if oleic acid is dissolved in the oil and used in the place of a univalent soap, inversion will likewise occur.

Here again, calcium oleate could, and probably would be formed. As a further illustration, either zinc oleate or lead oleate dissolved in oil and added to a water suspension of commercial calcium arsenate caused inversion and heavy arsenical build-up.

In a mixture stabilized by the addition of zinc sulphate, it may be that either calcium oleate, zinc oleate, or both, are present. As shown in Table 14, even when zinc sulphate is added in excess of the amount necessary to react with all the calcium hydroxide, inversion still occurs. Stoichiometrically, the calcium arsenate, containing 2.5 per cent calcium as calcium hydroxide, required about 0.38 pound of zinc sulphate for its removal.

In the experiment summarized in this table, the spray mixtures were made up in 100 gallon quantities and pumped through a machine with a capacity of ten gallons per minute at a pressure of 425 pounds per square inch. The fruits were sprayed for six seconds. Two samples were taken when pumping had just commenced, two when 40 gallons had been pumped out, and two when 70 gallons had been pumped out.

Table 14. The Effect of Zinc Sulphate upon Inversion of a Calcium Arsenate Mixture.

	Materials per 100 gallons water	Gallons pumped out when sampled	Estimated gallons returned to tank via overflow	Deposit as micrograms As_2O_3 per cm^2		
				(a)	(b)	Ave.
1	Zinc sulphate ($ZnSO_4\ 7H_2O$) 0.18 lb. Calcium arsenate, 4 lbs. Medium summer oil, 2 qts. Triethanolamine oleate, 0.25 lb.	(10	12	270	291	280
		(40	28	143	294	218
		(70	68	113	70	91
2	Same, but Zinc sulphate, 0.25 lb.	(10	18	318	268	293
		(40	28	277	159	218
		(70	65	37	27	32
3	Same, but Zinc sulphate, 0.43 lb.	(10	10	417	387	402
		(40	22	422	367	394
		(70	55	194	56	125
4	Same, but Zinc sulphate, 0.62 lb.	(10	10	312	246	279
		(40	24	287	262	274
		(70	60	380	393	386

One might assume from the table that increased stability with no loss in deposit is obtained as the zinc sulphate is increased from 0.18 pound to 0.62 pound. Yet as is often the case with inverted mixtures, it is difficult to generalize. In actual practice, it has not been desirable to use more than 0.25 pound of zinc sulphate for the particular type of calcium arsenate in question. Other brands of calcium arsenate, or indeed other batches of the same brand, might require different amounts of the sulphate, depending at least in part on that extremely variable factor, the amount of calcium hydrate present in the arsenical.

The conclusion that can be drawn from Table 14 is that inversion may occur though all the calcium hydroxide has, theoretically at least, entered into chemical combination with the zinc sulphate. A further point, apparently borne out in practice, is that greater stability follows the use of the larger amounts of zinc sulphate, but on the other hand under these conditions the arsenical deposits have inclined to be too light, no doubt because of excessive stability.

The optimum amount of soap for inversion of calcium arsenate mixtures has not yet been determined. The results from orchard and laboratory work have varied somewhat. For example, it appears from the deposits in Tables 15 and 16 that 0.12 pound of triethanolamine is more satisfactory than 0.25 pound. These deposits were determined on fruits sprayed in the laboratory. In practice, with one type of stationary spray equipment, 0.25 pound appeared to give better results, with another, 0.12 pound was quite enough.

Table 15 represents an experiment with the small laboratory sprayer in which ten liters of water were used and pressure was about 300 pounds per square inch at the pump.

Table 15. Quantity of Soap and Inversion of Calcium Arsenate Mixture with Three Gallon Laboratory Pump.

	Materials per 100 gallons	Condition of mixture in tank when spraying was finished	Seconds sprayed	Deposit as micrograms As_2O_3 per cm^2 (a)	(b)	Ave.
1	Zinc sulphate, 0.25 lb. Calcium arsenate, 4 lbs. Medium summer oil, 2 qts. Triethanolamine oleate, 1 lb.	Some settling, very little sticking to tank	4	lost	4.2	4.2
			12	3.2	7.3	5.2
2	Same, but Triethanolamine oleate, 0.75 lb.	Same	4	7.2	6.8	7.0
			12	3.6	6.0	4.8
3	Same, but Triethanolamine oleate, 0.50 lb.	Heavy floating curd, come sticking to tank	4	43.7	11.8	27.7
			12	66.1	39.5	52.8
4	Same, but Triethanolamine oleate, 0.25 lb.	No floating curd. Sticking to tank	4	16.2	30.6	23.4
			12	15.2	22.4	18.8
5	Same, but Triethanolamine oleate, 0.12 lb.	No curd. Less sticking than (4)	4	57.5	57.8	57.6
			12	153.0	194.2	173.6
6	Same, but Triethanolamine oleate, 0.06 lb.	No curd. No sticking to tank	4	46.2	53.2	49.7
			12	126.8	125.5	126.1

It will be seen that the use of one pound of the soap did not cause excessive curdling of the mixture; on the contrary it seemingly rendered the emulsion so stable and so lowered the surface tension of the water that there occurred no arsenical build-up whatever. Similar effects were obtained when 0.75 pound of soap was used. However, apparently 0.50 pound was enough to complete the inversion without offsetting the effect by stabilizing the mixture; as a result there was considerable adhesion to the spray tank, to the accompaniment of erratic and unsatisfactory deposits on the fruit.

In practice, generally the deposits from mixtures containing 0.25 pound of soap have been very heavy, so the low deposit from such a mixture in the small laboratory machine is unexpected. Possibly this was occasioned by contamination from the pump. The fact that the deposits were consistently high with the mixture containing 0.12 pound of soap indicates that such an amount used in conjunction with 0.25 pound of zinc sulphate promoted inversion without adversely affecting the condition of the system. This is confirmed in Table 16. Here the mixtures were used in 100-gallon quantities and pumped at 16 gallons per minute with a pressure of 425 pounds per square inch.

Table 16. Quantity of Soap and Inversion of Calcium Arsenate Mixture with 16 Gallon Pump.

	Materials per 100 gallons water	Gallons pumped out when sampled	Estimated gallons returned to tank via overflow	Deposit as micrograms As_2O_3 per cm^2		
				(a)	(b)	Ave.
1	Zinc sulphate, 0.25 lb.	(10	18	318	268	293
	Calcium arsenate, 4 lbs.	(40	28	277	159	218
	Medium summer oil, 2 qts.	(70	65	37	27	32
	Triethanolamine oleate, 0.25 lb.					
2	Same, except Triethanolamine oleate, 0.12 lb.	(10	13	192	232	212
		(40	25	310	329	319
		(70	60	384	375	379
		(85	80	353	(lost)	353

While the mixture with 0.25 pound of triethanolamine oleate immediately gave high deposits, it was evidently too unstable to withstand the heavy overflow which passed back into it. This is indicated in the steadily decreasing deposits of the successive samples, as also by the loss of a considerable amount of the arsenical from sticking to the sides of the spray tank. The superior stability of the mixture with 0.12 pound of triethanolamine oleate is evinced by the high deposit obtained after about 80 gallons or 80 per cent of the volume of material originally in the tank had been pumped back through the overflow. Nevertheless, the initial deposits from this mixture were lower than from the previous one, pointing to the likelihood of unsatisfactory results in equipment with light, or moderate agitation, and very light overflow. For this type of sprayer, the use of the larger amount of soap seems in order.

It was recognized early that extent of overflow and vigor of agitation are factors which exert great influence on the behaviour of inverted mixtures. Experiments with calcium arsenate mixture consisting of zinc sulphate, 0.25 pound; calcium arsenate, 4 pounds; medium summer oil, 2 quarts; and triethanolamine oleate, 0.25 pound; showed that both heavy overflow and vigorous agitation are deleterious. For example, in one experiment a tank of the mixture was agitated without overflow for 4.5 minutes and a deposit sample showed 178.5 micrograms As_2O_3 per square centimeter. A second mixture was both agitated and pumped through the overflow for 3.5 minutes, and the deposit amounted to only 74.4 micrograms.

In another experiment, deposit samples were taken immediately upon spraying and in one case after three minutes of heavy agitation only, and in a second, after three minutes of both pumping through the overflow and heavy agitation. With heavy agitation only, there was a decrease of about

40 per cent in the deposit, while with both agitation and pumping there was a decrease of about 80 per cent.

3. Comparative Larvicidal Values of Partially Inverted Calcium Arsenate and Lead Arsenate Mixtures

An experiment was undertaken in the laboratory to gain some idea of the larvicidal value of a comparatively heavy calcium arsenate deposit as compared to a comparatively heavy lead arsenate deposit. This was accomplished by spraying fruits with partially inverted mixtures of each, i.e., containing approximately half as much summer oil as appears to be required for complete inversion. The experiment was repeated six times using varying numbers of codling moth larvae, and arsenical deposit determinations were made in three instances. The results are given in Table 17.

Table 17. Larvicidal Value of Calcium Arsenate and Lead Arsenate Mixtures.

Materials per 100 gallons	Ave. deposit As_2O_3	Exp. No.	Larvae	Entries	Ave. per cent entries
1 Lead arsenate, 3 lbs. Medium summer oil, 1 qt. Triethanolamine oleate, 0.12 lb.	21.2 mmg/cm^2	1	99	57	59.8
		2	90	55	
		3	47	32	
		4	92	48	
		5	89	57	
		6	89	54	
		Ave:	84.4	50.5	
2 Calcium arsenate, 3 lbs. Zinc sulphate, 0.18 lb. Medium summer oil, 1 qt. Triethanolamine oleate, 0.12 lb.	31.4 mmg/cm^2	1	99	56	59.6
		2	99	67	
		3	46	23	
		4	93	63	
		5	102	62	
		6	92	46	
		Ave.	88.5	52.7	
3 Not sprayed	-	1	—	—	90.4
		2	48	47	
		3	48	46	
		4	44	38	
		5	87	80	
		6	96	81	
		Ave:	64.6	58.4	

The type of commercial calcium arsenate used, contained somewhat over 40 per cent arsenic pentoxide, and the commercial acid lead arsenate (diplumbic ortho) contained about 30 per cent. On the basis of a similar degree of adherence, a calcium arsenate deposit would contain approximately one-third more arsenic than a lead arsenate deposit. Microscopic examination of the two arsenicals indicated that their particles were of a rather similar size, varying from about one to four microns in diameter, though the observations were not strictly accurate because it was difficult to distinguish individual particles from aggregates. But in any case, it is presumed that in order to contain as many particles, a deposit of calcium arsenate would have to yield about one-third more arsenic trioxide than a lead arsenate deposit. Table 17 records an average deposit for calcium arsenate of 31.4 micrograms arsenic trioxide per square centimeter, and 21.2 micrograms for lead arsenate. Allowing for a fairly large expected variation in the determinations, it appears that the two deposits contained roughly corresponding numbers of arsenical particles.

A total of approximately 500 larvae was used with each type of arsenical deposit, and the average mortality was almost identical. Deposits of the calcium arsenate mixture and the lead arsenate mixture containing equal numbers of particles were approximately equally toxic to codling moth larvae under the conditions of the experiment. However, field work discussed later indicates that factors may come into play which appeared to be inoperative in the laboratory, so in practice, for deposits of the inverted type, a modification of that view is indicated.

4. Some Physical Characteristics of Oil-Arsenical Spray Mixtures and Deposits

a. Flocculation. Spuler, et al. (1931) had this to say concerning flocculation of lead arsenate: "What is referred to here as flocculation occurs when certain brands of lead arsenate, and certain types of oil emulsion are placed together in a combination spray . . . . . Each flake is a mass of these larger (oil) droplets coated with lead arsenate particles. Because of the size of these flakes and their irregular distribution through the water, an even distribution of both the oil and the lead arsenate is not to be expected in a spraying mixture in this condition. . . . . . in several instances where such flocculation has been overcome by the use of spreaders, a better control of the codling moth has ensued."

Partly as a result of these conclusions, and partly because of the occasional occurrence of arsenical foliage injury, it was recommended that a spreader be used with such flocculated mixtures. It has since been determined that unless agitation is so weak as to allow settling, in which case it is unsatisfactory for any type of spray mixture, the irregular distribution of flocs to which Spuler evidently referred, has no bearing on the type or uniformity of the spray deposit. The physical condition of an oil-arsenical spray mixture subsequent to impact on the fruit surface may be quite unrelated to that in the spray tank, not only because the flocs have been literally torn to pieces by passage through the spray gun, but because the oil:water ratio has changed by adherence of oil and run-off of water. The flocs which form in the tank after passage through the overflow are not identical with those which were formed in the tank previously.

Referring to the Wenatchee district, Marshall and Groves (1936) wrote as follows: "Whereas a few years ago, (the) ideal mixture contained lead arsenate as a uniform, slowly settling suspension, it is now flocculated and settles rapidly In fact, flocculation has become so much a household word that many men believe flocculation is synonymous with good deposit."

"At the present time, the most effective arsenical spray deposits have three characteristics in common. First, they are uniformly distributed or 'filmed' on the fruit surface. Second, they have the capacity of increasing steadily in quantity as spraying is continued on one point. Third, they are oily. It is incidental that these mixtures flocculate in the spray tank."

Some mixtures, though flocculated and bearing oil, do not produce a film deposit and show no capacity for steady increase or build-up, an example being lead arsenate with ammonium caseinate emulsion of mineral oil. Some flocculated mixtures produce a non-oily filmed deposit that does not increase with prolonged spraying; example, lead arsenate with soap. Others produce both a filmed coverage and heavy build-up, but the deposit is not oily, as the case with lead arsenate-soap, plus 0.5 per cent kerosene. Still others showing a lesser degree of flocculation give filmed deposits which though oily, build-up only slightly, an example being lead arsenate with herring oil-oleic acid mixture. In brief, flocculation is an effect not a cause, yet the fact that is a feature of the best arsenical spray mixtures suggests its connection with some important characteristic. It is always manifested in inverted mixtures.

When summer petroleum oil is intimately mixed with a thin paste made of water and lead arsenate, there forms an emulsion which upon dilution and passage through a small orifice at high pressure is resolved into pronounced flocs suspended in the water. By staining the oil with Sudan III and the water with methylene blue, it was determined by microscopic examination that the flocs consist of oil, lead arsenate and water. The oil exists in the flocs as globules surrounded by lead arsenate particles which are definitely at the oil-water interface. It is a case of a collection of more or less isolated little oil-in-water systems, stabilized by a finely divided solid.

When petroleum oil is emulsified by ammonium caseinate then added to a lead arsenate-water suspension, heavy flocculation occurs as soon as the mixture is pumped out at high pressure. Microscopic examination of the flocs revealed them to be rather similar to those just described, though the oil globules were smaller and showed less tendency to coalesce. Here the oil-in-water emulsion was stabilized by both a finely divided solid and a hydrophilic colloid. The lead arsenate particles were either at the oil-water interface or suspended in the water phase.

A similar method of staining was employed in order to examine the flocs of an inverted mixture, but it was found that heavy staining of the water by methylene blue prevented typical inversion. On the other hand, heavy staining of the oil with Sudan III, with the water unstained, resulted in accelerated inversion. When a degree of deposit build-up was being obtained, a small quantity of the agglutinated flocs was examined. Here was found a complex system of air bubbles, water droplets, and arsenical particles dispersed in oil. As previously mentioned, the rather greasy material might be characterized as a quasi-emulsion. Before being sprayed out, it was observed that much of the lead arsenate was still suspended in the water. Apparently, it becomes more completely wetted by the oil as a consequence of the intimate mixing which is effected at the aperture of the spray gun. Speculations have already been offered as to the cause of preferential wetting of arsenical particles by oil in this type of mixture.

b. Effects of Fruit Growth and Weathering on Deposits. There is no question that by far the most important factor in reduction of spray deposits, in the arid fruit growing areas of the Northwest, is fruit growth. Fahey and Rusk (1936) have conducted an investigation into the effects of fruit growth upon spray deposits, and concluded that under Indiana conditions "during May and the first part of June, the rate of increase in area may be as much as 24 per cent per day, thus reducing the spray residue per unit area one-fifth each day." They found that after the middle of June there is a gradual decline in the daily surface area increment which led to the statement, "Thus fruit growth directly opposes the efforts of the orchardist, for when he wishes to build up a heavy residue to protect the fruit, growth is most active in reducing the coverage, and when it is desired to decrease the residue load to assist in residue removal, growth is least active in reducing spray deposit." They record that from May 7 to June 30, Jonathan apples increased about 11 times in surface area. From June 30 to August 31, the increase in area was about twice.

Spuler, et al. (1930) have reported for the Wenatchee district a decrease in deposit early in the season of 3.6 per cent daily, though in view of the work of Fahey and Rusk this figure appears to be too low. However, the important point is that at the time when it is most essential to have protection from codling moth attack, and at the time when arsenical appear to be most effective in preventing entries, it is most difficult to maintain adequate coverage.

It has been noticed with certain types of spray deposits that the percentage decrease in amount from spray to spray, is greater than with others. For instance, following prolonged and very heavy rainfall in early June, the deposit from a soap-lead arsenate mixture decreased about 30 per cent while that from an inverted medium summer oil mixture showed no decrease. Indeed, the latter type of coverage is so resistant to weathering and fruit growth, that it has been possible by fruit measurements alone, to calculate the deposit any time after a given application, providing no additional arsenical spray was used. Such calculations were made for deposits from inverted mixtures containing 0.5 per cent medium summer oil, and as shown in Table 18, they agreed reasonably well with the actual amounts of arsenic as determined by chemical analysis. Theoretical deposits may be computed by comparing the diameter of the fruit when analyzed for deposit, with that at any time later. The decrease in deposit should be in inverse proportion to the square of the diameter of the fruit if only fruit growth is involved.

Table 18. Fruit Measurements and Arsenical Deposits, Theoretical and Found.

Spray Mixture	Immediately following 4th Cover			46 days later				106 days later			
	D*	D^2	mmg As_2O_3 cm^2	D	D^2	mmg As_2O_3 cm^2 Theoretical	Found	D	D^2	mmg As_2O_3 cm^2 Theoretical	Found
Inverted calcium arsenate	35	1225	98.9	64	4096	29.5	26.4	81	6561	18.4	20.8
Inverted lead arsenate	36	1296	61.0	63	3969	19.8	20.9	80	6400	12.3	14.5

*Average diameter of fruits in millimeters.

For the calcium arsenate mixture, the found deposit after 46 days was about 10 per cent less than the calculated, and after 106 days about 13 per cent greater. The corresponding variations for the lead arsenate were about 5 per cent greater at 46 days and 17 per cent greater at 106 days. Evidently in spite of about 0.5 inch precipitation during the lapse of 3.5 months, little if any of the arsenical deposits disappeared from the surface of the fruit. The variations might well have occurred between individual analytical samples, for deposits determinations from inverted mixtures are prone to be somewhat irregular because of the importance of the time factor in application.

c. Microscopic Examinations of Spray Coverage. By the use of a Leitz "Ultropak" illuminator and a Leitz "Makam" micro-camera, photographs were made of various types of spray deposits some time after sprays had been applied, in order to record the visual effects of fruit growth on coverage. When a Wratten "Red F" filter was used in conjunction with high speed panchromatic film, greater definition was obtained on the film than could be detected by direct observation. Some of the photographs are reproduced for comparison. In each case, with the exception of the unsprayed fruit, a newly hatched codling moth larva was placed in the microscope field in order to convey a better impression of the size of the fissures, and the agglomerates of arsenical particles in the coverage.

The photographs reveal distinct differences in the coverages. Lead arsenate applied without spreader or sticker formed a spotted deposit leaving considerable areas totally uncovered. These areas were frequently far larger than the newly hatched larva. The spots, after a short period of growth, underwent extensive fissuring which must evidently have left the deposit more susceptible to loss from weathering. Even with no spreader,

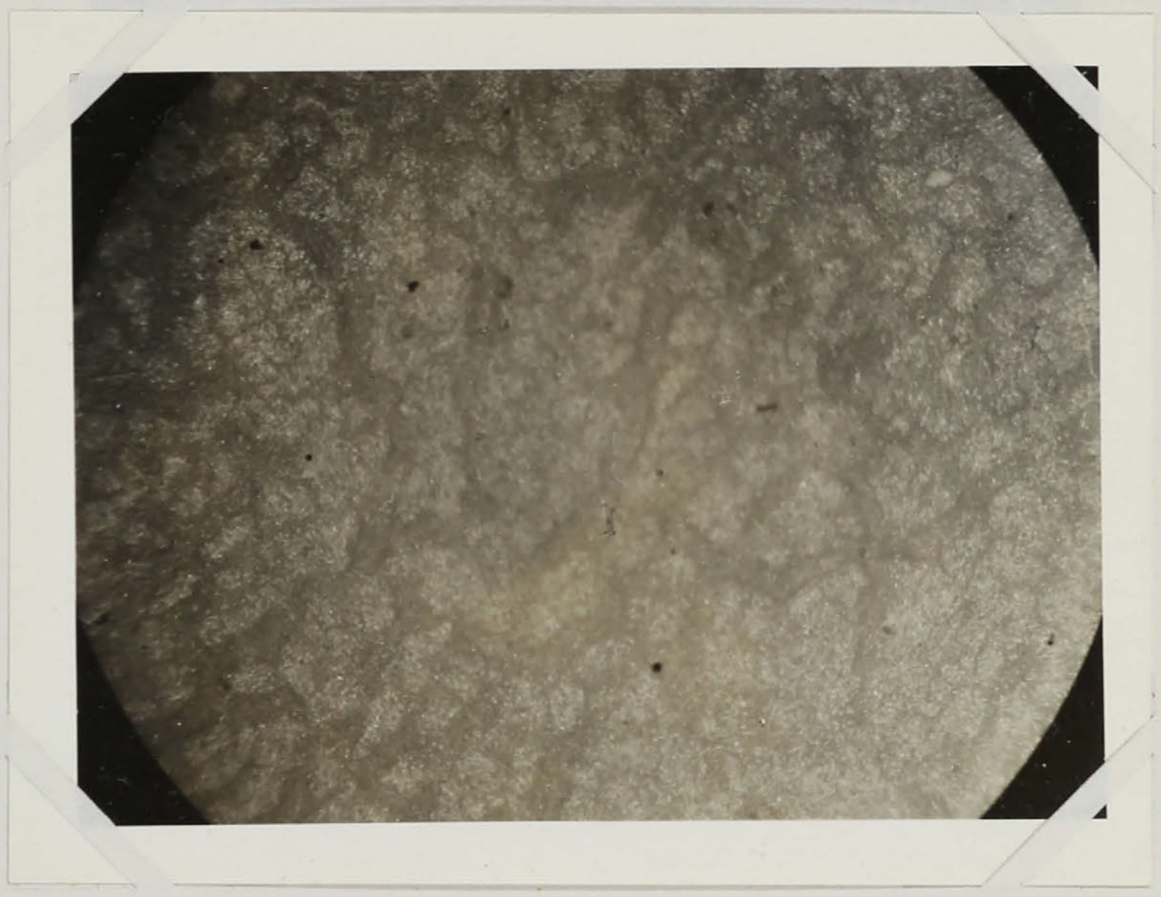

Fig. 6. Skin of unsprayed Winesap apple in mid-August. Note growth fissures in wax. X30.

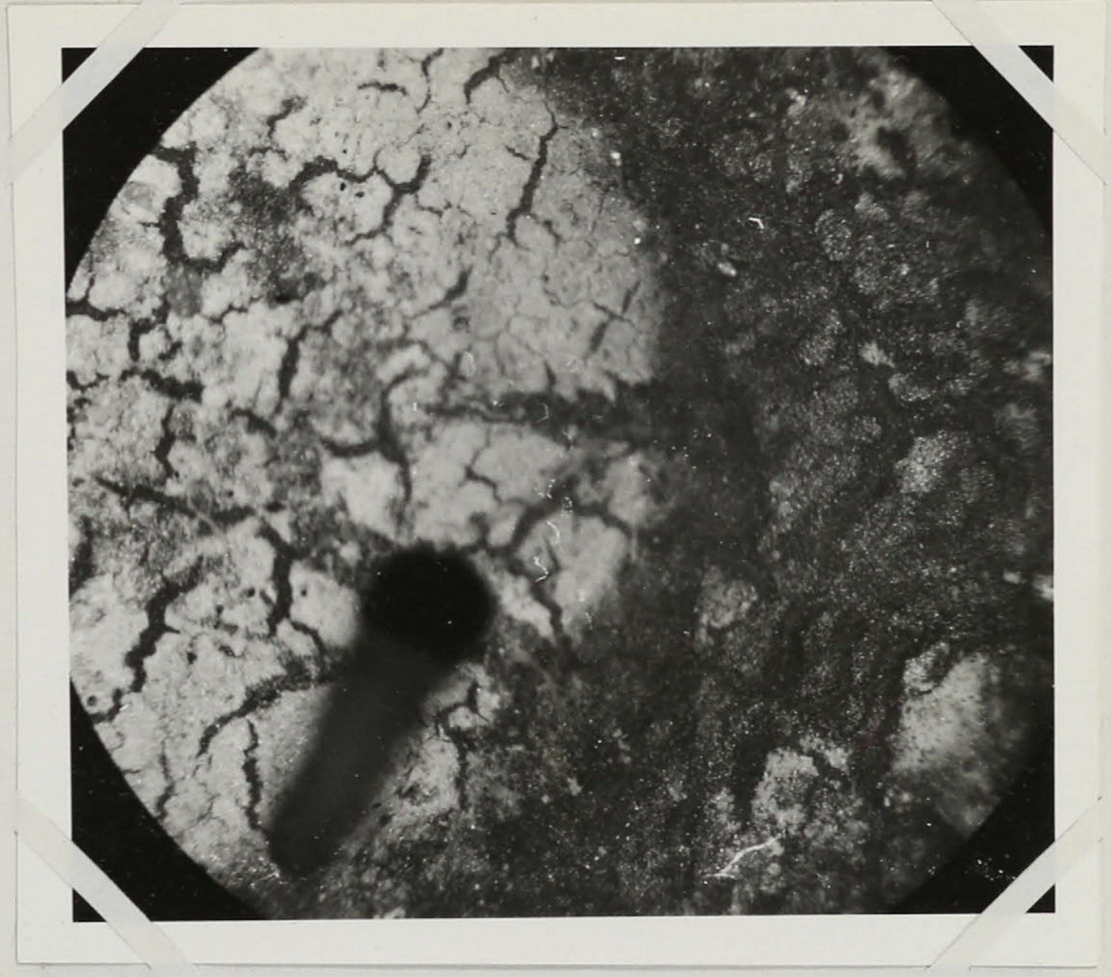

Fig. 7 Lead arsenate deposit, no spreader or adhesive, one week after sixth cover spray in mid-August. White area at left is portion of a spot of the arsenical. Note fissuring of deposit due to growth of fruit and large area, right, lacking spray coverage. X30.

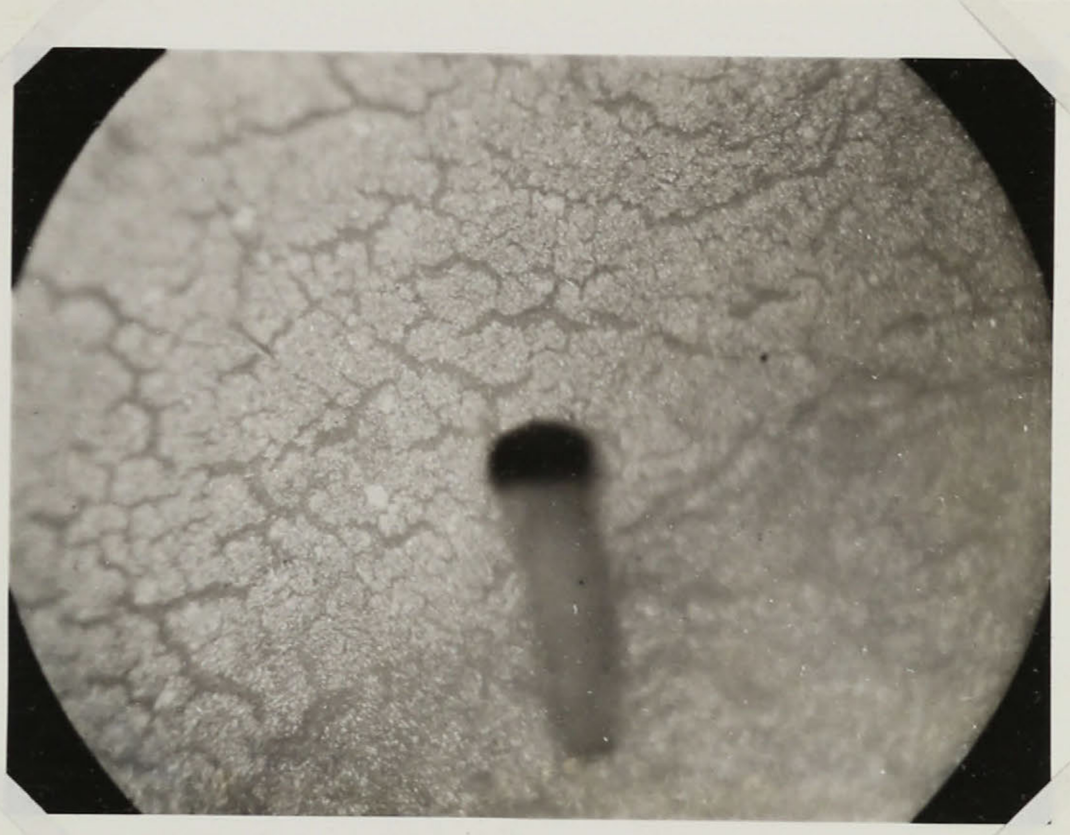

Fig. 8. Lead arsenate-soap spreader deposit in late July, 20 days after fourth cover spray. Edge of heavy blotch of arsenical showing growth fissures. X30.

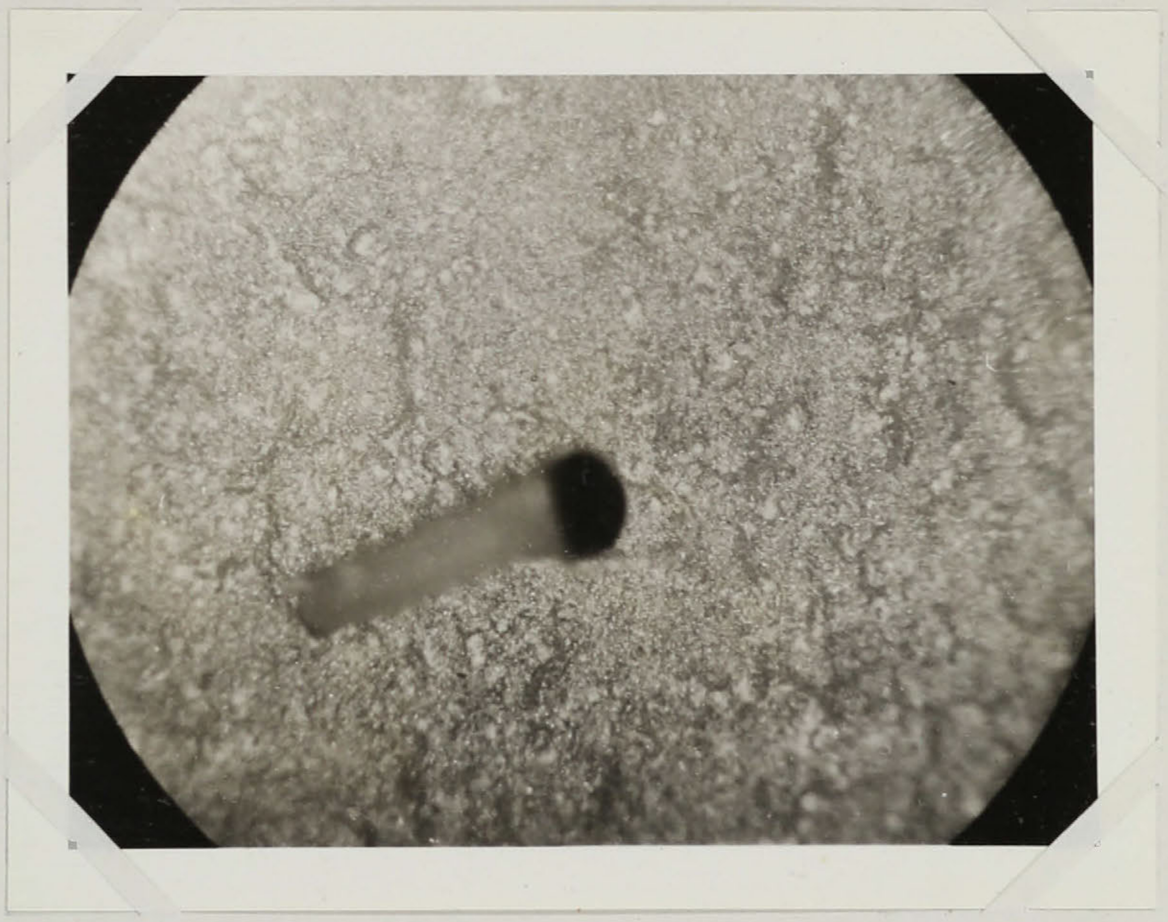

Fig. 9. Lead arsenate-summer oil-ammonium oleate deposit (inverted mixture) in late July, 20 days after previous cover spray. Note uniformity of deposit and relative absence of growth fissures. X30.

Fig. 10. Calcium arsenate-summer oil-zinc sulphate-triethanolamine oleate deposit (inverted mixture) in late July, 20 days after previous cover spray. Note large agglomerates. X30.

lead arsenate particles were found to form agglomerates on a sprayed apple varying up to perhaps 30 microns in diameter a week subsequent to the date of application.

Lead arsenate in combination with triethanolamine oleate (soap) and without oil formed a much more uniform coverage. Though fissuring resulting from fruit growth was less obvious, the size of the agglomerates was rather similar to that from lead arsenate alone. A lead arsenate-soap deposit has a characteristic granulated appearance at a magnification of about X30.

With the introduction of a suitable fish oil, the lead arsenate was deposited more uniformly than when used alone but less uniformly than when used with soap. On the other hand, petroleum oil with only the lead arsenate as an emulsifier resulted in an even more spotted deposit than lead arsenate alone. The free fatty acid of the fish oil seemingly plays an important part in the bringing about uniformity of coverage. Fruit growth when fish oil was present caused less fissuring of deposit than when soap was used. It is suspected that this effect results from a softening of the apple wax which might render it less susceptible to cracking.

Inverted lead arsenate mixture bearing 0.5 per cent medium summer petroleum oil, like the fish oil combination, appeared less susceptible to fissuring than when oil was not present. But when kerosene was substituted for the petroleum oil, fissuring was quite as noticeable as with soap alone. In order to produce a suitably adhesive lead arsenate deposit, kerosene seems to require an emendment. For this purpose, herring oil has had the desired effect. In practice, a mixture containing one pint herring oil, 3 pints kerosene, 0.25 pound ammonium oleate, or triethanolamine oleate, and 3 pounds of lead arsenate has with heavy application given deposits which were heavy, uniform, and resistant to weathering.

A difficulty with certain inverted mixtures has been, that considering the amount of the deposit and its uniform distribution, protection has not quite met expectations late in the season when the deposit had lost its definitely oily nature. This may be a result of less pronounced adhesion to the insect, as well as a result of the formation of large agglomerates which is particularly characteristic of mixtures containing summer oils of a viscosity of 55 seconds Saybolt, or over. A representative coverage of this type consisted of agglomerates which were of an average diameter of about 10 microns. Some measured 100 microns, obviously too large for ingestion in toto by a first instar codling moth larva.

Late in the season, certain inverted calcium arsenate mixtures have exhibited even more apparent inferiority as compared to freshly applied deposits. Several weeks following its application, an inverted calcium arsenate deposit, achieved by the use of medium summer petroleum oil, is somewhat hard to the touch. It generally consists of unusually large agglomerates with an average diameter of perhaps 15 microns. Sometimes with particularly unstable mixtures, agglomerates may exceed 500 microns. Chemical analysis of such a deposit may unduly accent its larvicidal potentialities, for on the assumption that ingestion is accidental and more likely to occur in the case of small particles, or groups of particles, than large ones, much of the arsenical will not be available for the minute, newly hatched insect. There is some evidence that this undesirable characteristic of the inverted calcium arsenate mixture can be overcome by further investigation.

The question of the availability of a deposit for ingestion has been given some little consideration at Wenatchee. As previously mentioned, experimental evidence as well as practical experience has indicated that the amounts of arsenical being equal, an oily arsenical deposit is a more effective larvicide than a non-oily deposit. In order to find an explanation for the superiority of the oily deposit, a number of observations were made.

It had been noticed that contact with chloroform, or ether, leads to rapid desiccation of a first instar codling moth larva. This suggests the presence of an oily or waxy substance on the integument, a point that is further suggested by microscopic examination with reflected light. It might then be assumed that if one type of arsenical deposit adheres more readily to an oily or waxy apple surface than another, it should also adhere more readily to an oily or waxy insect integument. Using powerful illumination at X30, with the microscopic apparatus previously mentioned, the point was investigated by examining first instar larvae after they had been allowed to crawl for two minutes over various types of spray deposits. More arsenical particles or agglomerates were found to have adhered to the ventral surface of the head when the larva had traversed an oily coverage than when it had traversed a non-oily coverage. Table 19 gives some results of these observations.

Table 19. Adherence of Arsenical Deposits to the Ventral Surface of the Head of First Instar Codling Moth Larvae.

	Materials per 100 gallons water	Estimated deposit mmg As_2O_3 per cm^2	Number of arsenical agglomerates adhering						
			1	2	3	4	5	6	Ave.
1	Lead arsenate, 3 lbs. Triethanolamine oleate, 0.12 lb. (non-oily deposit)	15	3	2	1	3	10	3	3.6
		Repeat	6	4	1	3	4	1	3.1
		Repeat	3	2	8	0	4	6	3.8
2	Lead arsenate, 3 lbs. Triethanolamine oleate, 0.25 lb. Medium summer oil, 2 qts. (oily deposit)	30	1	7	18	17	17	13	12.1
3	Calcium arsenate, 4 lbs. Zinc sulphate, 0.25 lb. Triethanolamine oleate, 0.25 lb. Medium summer oil, 2 qts. (oily deposit)	40	9	25	6	17	12	16	14.1
4	Same as (3) but Kerosene instead of summer oil (non-oily deposit)	30	14	3	2	7	16	5	7.8
	Unsprayed	0	0	0	0	0	0	0	0

Since the oily deposit was undoubtedly heavier with both types of arsenical than the non-oily deposit, its greater adhesiveness to the insect head can not be attributed entirely to the presence of the oil. Nevertheless, this does seem to be fair evidence that even for similar amounts of arsenical the former should adhere the more readily. Of course, even if this were conclusively demonstrated, it would prove nothing concerning the toxicity of the two deposits. Adherence of aggregates or particles, and ingestion of aggregates or particles may not be related, though there is a likelihood that they are. This point has been studied by Gilmer (1933), who wrote that juice is absorbed, although larvae may reject particles of pulp for 24 to 28 hours

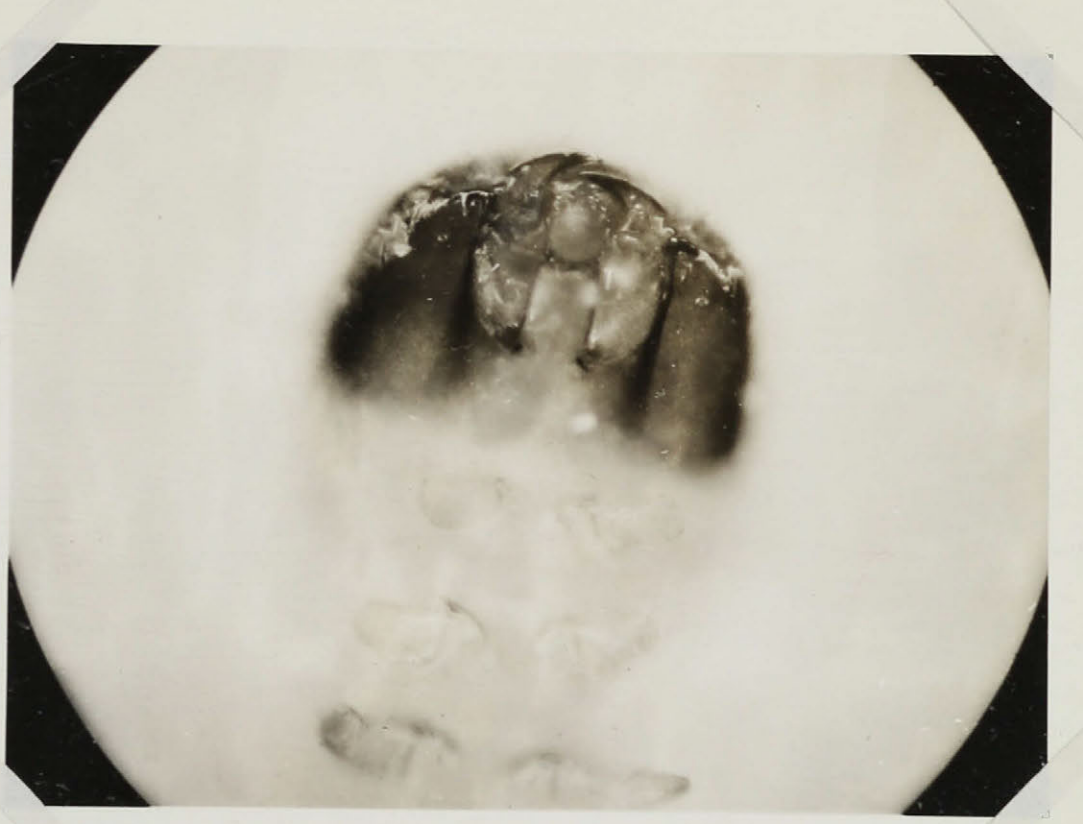

Fig. 11. Ventral surface of head of newly hatched codling moth larva after crawling for two minutes over a non-oily lead arsenate-soap deposit. The outlines of three arsenical agglomerates are dimly visible. X130.

Fig. 12. Ventral surface of head of codling moth larva after crawling for two minutes over an oily coverage of lead arsenate (inverted mixture). Note the number of agglomerates adhering to setae and compare with Fig. 11. X130.

after entering an apple. He dusted fruits with powdered carmine, and was able to demonstrate its presence in about 75 per cent of the larvae that entered the fruit after having crawled over it.

A second point which should be considered in this connection is that made by Haseman (loc. cit.) with reference to the difficulty experienced by newly hatched larvae in attaching their silken web to an oily surface. Perhaps an oily film is more effective as a larvicide than a non-oily film for both of these reasons.

B. Field Investigations

The field work with inverted mixtures for codling moth control has comprised both small experimental plots, and demonstrations for growers requiring several acres. Only a summary of some of the results can be included, but it should convey a general idea of the performance of these spray combinations outside the laboratory. The experimental methods have been briefly described already.

1. Lead Arsenate Mixtures

In each of the tables which follows, a value is included which serves to indicate in a rough way, the extent of the error unavoidably introduced into the experiment. This value, applying both to deposit analyses, and codling moth infestation, is the average deviation from the mean, for the particular number of replicated control plots involved in the data.

The Wenatchee investigations have stressed the necessity of numerous controls, and plot layouts have varied from year to year to meet changing conditions. Detailed statistical treatment of the data is considered both unnecessary and inadvisable.

Comparing the effectiveness of several lead arsenate mixtures, one experiment will illustrate the general trend of other related experiments as well as grower experience. These mixtures were applied at moderate dosage[7] four times during first brood attack, and twice during second brood attack, on Romes, and five times and twice respectively on Stayman Winesaps. The Rome plots consisted of three trees each, replicated four times in a modified restricted random arrangement. The Stayman Winesap plots consisted of single trees duplicated.

In these tables are certain comments, the purpose of which is to convey impressions derived from a study of infestation maps of the experimental orchards. It is not possible to include the maps, but it is nevertheless advisable they should accompany codling moth field data in order that one unfamiliar with the experiments may be aided in interpreting the results to his own satisfaction.

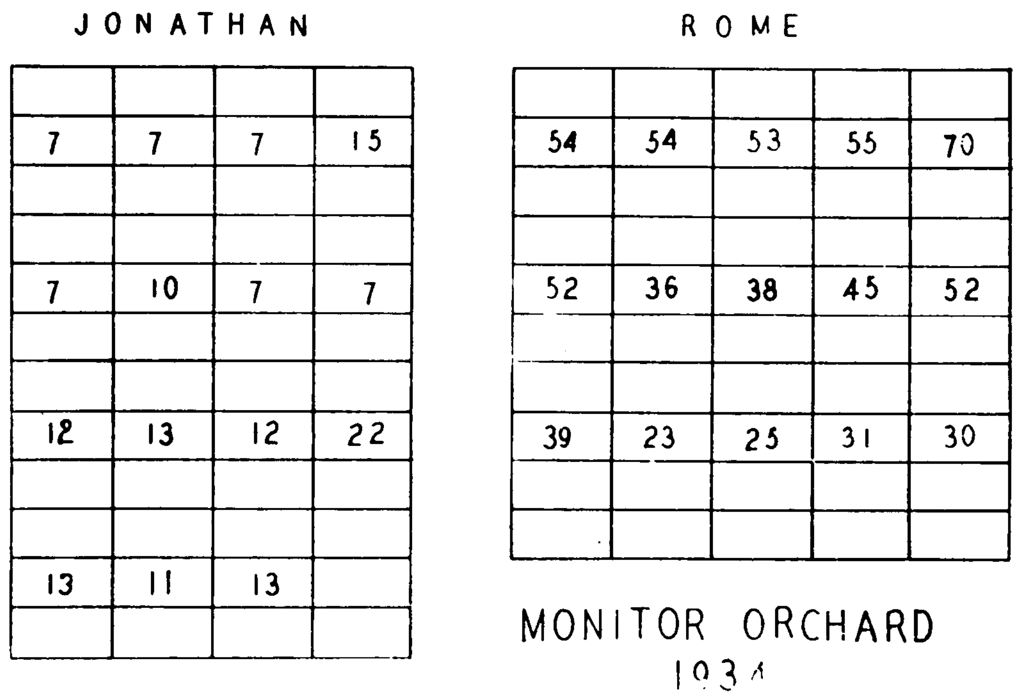

Fig. 13. Map of a twelve acre experimental orchard used at Wenatchee in 1934. Each rectangle represents a plot containing six trees. Numbers indicate larvae per one hundred fruits in the check plots.

Table 20. Arsenical Deposits and Codling Moth Infestation for Lead Arsenate-Oil Mixtures.

	Materials per 100 gallons	Variety	Type of coverage	Deposit as mmg As_2O_3 per cm^2	Larvae per 100 frts.	Comments on infestations	Spray injury
1	Lead arsenate, 3 lbs. Kerosene, 2 qts. Triethanolamine oleate 0.25 lb. (Inverted Mixture)	Rome	film	15.7	67.5		none
		Stayman	"	20.6	(crop failure)		very slight
2	Same as (1) but medium summer oil instead of kerosene (Inverted Mixture)	Rome	"	23.7	38.0		none
		Stayman	"	24.7	5.8		very slight
3	Same as (2) but ammonium oleate instead of triethanolamine oleate (Inverted Mixture)	Rome	"	24.0	50.4	-(probably (lighter	none
		Stayman	"	30.8	2.0		very slight
4	Same as (2) but light summer oil instead of medium summer oil (Inverted Mixture	Rome	"	22.4	28.3	-(probably (heavier	none
		Stayman	"	26.7	5.2		very slight
5	Same as (2) but oil emulsified by ammonium caseinate (Non-inverted Mixture)	Rome	spot	17.8	43.4		none
		Stayman	blotch	23.7	6.5		slight
6	Average of 7 controls. Lead arsenate, 3 lbs. Herring oil (containing 5% added oleic acid), 1 pt.	Rome	blotch	14.2	80.5		slight
		Stayman	blotch	18.2	12.2		slight to moderate
	Average deviation from mean for control plots	Rome		± 0.8	±22.2		
		Stayman		± 1.0	± 3.2		

In these comparisons it should be kept in mind the benefit of heavy build-up of deposit from inverted mixtures could not come into play, since application of spray material was discontinued when the trees commenced to drip. Nevertheless, the inverted summer oil mixtures showed both definitely heavier and more uniform deposits than the non-inverted mixture, and with one evidently irregular exception, apparently somewhat better codling moth control. Ammonium oleate mixture has, generally speaking, given slightly better deposit and control than triethanolamine oleate mixture.

Kerosene in an inverted mixture gave decidedly lower deposit, and apparently poorer codling moth control than the summer oils. As previously mentioned, the lower deposit may result from the non-oily coverage tending to impede rapid build-up from successive applications. In addition, satisfactory inversion takes place less readily with kerosene than with summer oils or fish oil. Poorer codling moth control is, of course, to be expected, since 0.5 per cent kerosene has no ovicidal effect. Indeed, laboratory investigations at Wenatchee have shown that even 2.0 per cent kerosene has practically no ovicidal value.

The control or check plots indicate the tremendous infestation faced in the Rome orchard. Although there was little variation in the amount of the arsenical deposit in the seven plots, the variation in infestation was high and shows very forcibly the need of estimating the experimental error. An average deviation from the mean of seven control plots amounting to 22 larvae per 100 fruits, greatly minimizes the significance of small differences in results of experimental treatments. The Stayman Winesaps were much less heavily infested than the Romes, but the percentage variation in the control plots was practically as great (26.2 per cent as compared to 27.5 per cent for Romes).

Of the six spray mixtures, only one caused foliage injury in sufficient amount to be considered objectionable. That was the lead arsenate-herring oil combination used as a control mixture because of its rather general adoption by growers of the Wenatchee-Okanogan district. The injury which occurred on Stayman Winesap after 7 cover sprays was typical of arsenical injury. During 1934, 1935, and 1936, no inverted lead arsenate mixture made with either ammonium oleate or triethanolamine oleate, has caused significant arsenical injury on any variety of apple in the lower Wenatchee valley. The original inverted "Dynamite" spray containing oil emulsified with sodium silicate and oleic acid, caused some damage to McIntosh foliage after six moderately heavy applications.

2. Calcium Arsenate Mixtures

The development of inverted calcium arsenate mixtures was not begun until the summer of 1935, so field experiments lack the necessary corroboration that comes when similar experiments have been repeated with essentially similar results for several years. Table 21 gives results of one field experiment with inverted and partially inverted calcium arsenate mixtures, containing petroleum oils. Preliminary work in 1933, resulting in very severe arsenical injury, eliminated animal or vegetable oils from consideration as adhesives for this arsenical.

Table 21. Arsenical Deposit and Codling Moth Infestation for Calcium Arsenate-Oil Mixtures.

	Materials per 100 gallons	Type of coverage	Deposit as mmg As_2O_3 per cm^2	Larvae per 100 frts.	Comments on infestation	Spray injury
1	Calcium arsenate, 4 lbs. Zinc sulphate, 0.25 lb. Medium summer oil, 1 qt. Triethanolamine oleate, 0.12 lb. (Partially Inverted)	film-blotch	35.2	22.4	Probably somewhat heavier	none
2	Same as (1) but trieth. oleate, 0.25 lb. (Partially Inverted)	film	29.8	40.0		none
3	Calcium arsenate, 4 lbs. Zinc sulphate, 0.25 lb. Medium summer oil, 2 qts. Trieth. oleate, 0.25 lb. (Inverted)	film (large aggregates)	54.1	19.8	Probably somewhat lighter	oil injury from first cover
4	Same as (3) but special light oil instead of medium oil. (Inverted)	film (fine aggregates)	47.0	7.2	Probably somewhat heavier	none
5	Same as (3) but kerosene instead of medium oil (Inverted)	film (fine aggregates)	35.9	32.1		none
6	Calcium arsenate, 4 lbs. Zinc sulphate, 0.36 lb. Calcium hydroxide, 1 lb. Medium summer oil, ammonium caseinate emulsion, 2 qts. (Non-inverted Mixture)	spot-blotch	30.2	30.8		oil injury from first cover
7	Average of 5 control plots. Lead arsenate, 3 lbs. Trieth. oleate (soap), 0.12 lb.	blotch-film	15.8	45.2		none
	Average deviation from mean for control plots		±0.8	±9.2		

In this experiment, the plots consisted of single trees replicated four times in restricted random arrangement. Five control, or check plots, were provided, each consisting of four single tree replicates. Stayman Winesap trees were used in every plot.

As in the previous table, it will be seen that the approximate experimental error for the deposit determinations is low, amounting to perhaps five per cent of the determination. The estimated error for the infestation amounts to perhaps 20 to 30 per cent, since the average deviation from the mean, i.e., 45.2 larvae per 100 fruits, was ± 9.2. Though small deposit variations are probably significant, small infestation variations are more probably due to chance.

The use of 0.25 pound of triethanolamine oleate with one quart of medium summer oil and four pounds of calcium arsenate was evidently too much in view of the amount of zinc sulphate employed. But the amount of zinc sulphate necessary in this type of mixture is conditioned, at least in part, by the amount of soluble calcium present in the calcium arsenate, and would therefore be a variable quantity. Though only partial inversion appeared to take place in the mixture and though it produced a filmed deposit, it was somewhat too unstable, and the arsenical deposit in addition to being low was irregular. When only 0.12 pound of soap was present, the amounts of the other constituents being the same, both arsenical deposit and codling moth control were more satisfactory. The improvement in each case was greater than the estimated experimental error.

In the third mixture, in which the use of two quarts of oil resulted in apparently complete inversion, the arsenical deposit was greatly increased over the previous mixtures containing only one quart of oil. The difference in codling moth infestation between the first and third mixtures, however, is undoubtedly less than should have been the case. Probably the experimental error operated in favor of the first mixture and against the third, which in addition to having a much higher deposit, had a distinctly greater ovicidal value.

As mentioned earlier, an apparent weakness of inverted calcium arsenate mixtures, has been the tendency to form very large agglomerates on the fruit surface when the usual summer oils have been used. In the fourth mixture when a special light oil with a viscosity of 52 seconds Saybolt was substituted for medium oil which had a viscosity of 73 seconds (See Appendix for additional specifications), the size of the agglomerates was greatly reduced. This effect, however, was not evident in another experiment where the ordinary type of light summer oil was employed. The difference in the behaviour of the two oils seems to relate to their distillation ranges. The special oil contained about 22 per cent of a very light fraction as against none for the ordinary type of light oil. When kerosene was used, inversion did not seem to occur to the same extent as with the same quantity of light or medium summer oils, and the arsenical deposit was lower. Codling moth control with the kerosene mixture was evidently inferior, as would be expected from the lower and non-oily deposit, and the lack of ovicidal effect.

The sixth mixture in Table 21 with a paste or mayonnaise type of medium oil emulsion gave results which agreed substantially with those from similar combinations used during the previous three years. Generally speaking, these non-inverted oil-calcium arsenate mixtures containing four pounds of arsenical have given codling moth control about 50 per cent better than three pounds of lead arsenate used with soap or herring oil.

The third mixture containing the same amount of oil, and the same type of oil, but being inverted, resulted in a far heavier deposit and evidently superior codling moth control than the non-inverted mixture. Even making allowance for its production of excessively large agglomerates, the inverted calcium arsenate mixture seems to excel in insecticidal value the corresponding non-inverted mixture, just as the inverted lead arsenate mixture excels the non-inverted mixture.

Late in the season of 1936, some arsenical foliage injury was observed on Winesap trees that had been sprayed with inverted summer oil-calcium arsenate mixture during May and June only. No injury was evident, where in addition, two later applications had been made in July and August. It has been reported previously by Marshall and Groves (1936b) that highly refined petroleum oil acts as a sozophyt[8] when in combination with calcium arsenate, and it is thought that injury may have supervened when the oil had been exposed to the atmosphere so long that it had largely volatilized or undergone decomposition. As mentioned in the same article, zinc hydroxide is also a sozophyt but in the small amount which is formed in an inverted mixture, probably its effect would not be great.

3. Zinc Arsenite Mixture

Although summer petroleum oil exerts a sozophytic action when used with commercial calcium arsenate, it would be undoubtedly insufficient to prevent arsenical injury when in combination with commercial zinc arsenite, because of the lesser stability of the zinc compound. A relatively large amount of

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[8] The term "sozophyt" was coined by Doctor M. W. Bundy of the Department of English, Washington State College, to express a thought for which there does not appear to be an apt expression in the English language. It is derived from the Greek words meaning "to safen" and "plant" and implies a substance which prevents injury to a plant. "Safener" another coined word is too inclusive, since it might apply equally to plant and insect.

freshly precipitated zinc hydroxide was found to prevent arsenical injury from zinc arsenite under arid conditions, but such an amount would interfere considerably with the formation of an inverted mixture. In order to achieve a sozophytic effect without interfering with inversion, use was made of the peculiar effectiveness of ferric oxide as an adsorbent for arsenic in water solution. As suggested by Doctor Kermit Groves, ferric chloride was dissolved in a small amount of boiling water and the solution added to a zinc arsenite suspension in the spray tank. The iron was at once precipitated on the zinc arsenite particles in exceedingly finely divided condition, presumably as hydrated ferric oxide which upon exposure to air probably went for the most part to the oxide. The small amount of iron exerted a decided effect upon the action of the arsenical. Where no oil was used, 0.75 ounce of ferric chloride was sufficient to prevent arsenical injury from three pounds of one batch of commercial zinc arsenite in 1934. But since this amount seemed to lower its insecticidal effectiveness considerably, 0.5 ounce was the quantity decided upon for investigation in an inverted mixture the following year.

This mixture was formed by adding ferric chloride solution to a zinc arsenite suspension consisting of three pounds of zinc arsenite per 100 gallons of water, then introducing medium summer petroleum oil emulsion at the rate of two quarts actual oil per 100 gallons of spray mixture. The emulsion, made up with triethanolamine oleate at the rate of 0.25 pound per two quarts of oil and containing about 50 per cent more water than oil, caused flocculation of the arsenical almost as soon as added to the spray tank. Exceedingly heavy build-up of deposit was then obtained upon sprayed fruits, a result of inversion carried to the point of somewhat excessive instability.

This mixture was applied in two orchards, and resulted in control of the codling moth rather comparable to inverted lead arsenate mixture made from the same oil. However, the amount of arsenic in the deposit was nearly twice as great as from lead arsenate, and allowing for about 50 per cent higher arsenic content in zinc arsenite than lead arsenate, this meant that actually considerably more of the zinc arsenite adhered to the fruits. The fact that the deposits appeared equally uniform, suggests that the iron "coated" zinc arsenite was not as effective as lead arsenate, pound for pound.

Although there was no evidence of arsenical injury from the inverted zinc arsenite mixture for the greater part of the season, definite foliage injury occurred just before harvest. It was attributed to soluble arsenic, since no injury was present where oil was similarly used with lead arsenate. Apparently, it was not feasible to use a greater amount of ferric chloride in order to eliminate late injury, because it was suspected that the insecticidal value of the arsenical had already been somewhat impaired by it. This led to the conclusion that in the search for a non-lead spray mixture for codling moth control, it would be more profitable to develop inverted calcium arsenate mixtures, than zinc arsenite mixtures, for in addition to being less prone to incite arsenical injury, they were evidently as effective in the matter of control and somewhat less expensive.

VI. DEMONSTRATIONS OF INVERTED MIXTURES FOR GROWERS

A. Season of 1935

In 1935, after two years' investigation of inverted lead arsenate mixtures, a very severely infested five-acre orchard was selected for demonstration of their effectiveness to fruit growers. This tract represented as difficult a problem in codling moth control as could be found in the Wenatchee district, for failure had not resulted from neglect. On the contrary, the owner had in the previous season applied a calyx spray and ten lead arsenate cover sprays, all of which cover sprays had contained either herring oil or mineral oil. For his pains, he had approximately 80 per cent wormy Romes and Pearmains, 50 per cent wormy Winesaps, 100 per cent wormy Delicious, and fruit that could not be cleaned below the domestic tolerance for lead and arsenic residue. There were at least five reasons why he failed to control the codling moth. First, the trees were old, offering ideal winter quarters for hibernating larvae. Second, the trees were large, heavily fertilized, and very leafy. They were in some cases over 25 feet high and many of them interlaced, making spray application difficult. Third, the shading effect of the trees throughout the tract evidently prolonged the emergence of moths from the overwintering generation, so that larval attack from this source was practically continuous from about the middle of May to the middle of July, and perhaps even later. Fourth, a tremendous moth population had developed in the orchard, and being in one of the most heavily infested areas in the district, surrounding tracts likewise contained heavy moth populations. Finally, the owner was under-equipped and applied only 30 gallons of spray mixture per tree per application, when about 40 gallons were necessary for complete wetting.

Beginning May 10, 1935, the Washington Experiment Station applied to a portion of this orchard, a calyx spray of lead arsenate, three pounds, and calcium caseinate spreader, 0.25 pound. This was followed in seven days by the first cover spray, an inverted mixture consisting of lead arsenate, three pounds, medium summer petroleum oil, two quarts, and triethanolamine oleate, 0.25 pound. The second, third, fourth, and fifth cover sprays were all of the same mixture and applied at intervals from the preceding application of nine days, nine days, 11 days, and 14 days respectively. No spray was applied to two-thirds of the orchard subsequent to July 2. On July 24, an inverted mixture composed of lead arsenate, three pounds, herring oil, two pints, and kerosene, one pint, and triethanolamine oleate, 0.25 pound, was applied to the remainder of the orchard. So two-thirds of the tract received no second brood sprays, so-called, and one-third received a single second brood spray.

The inverted mixtures were very heavily applied, sixty gallons being used per tree, per application, on trees capable of bearing a normal crop of 30 to 35 packed boxes. In order to determine the suitability of different types of lead arsenate for these mixtures, 11 brands were used on separate blocks of trees. One of these contained a deflocculator, probably calcium caseinate, one contained a very small amount of an acid insoluble gum-like substance, and the remainder appeared to contain only those impurities incidental to the manufacturing process.

During the growing season, 14 arsenical deposit analyses were made for each brand of lead arsenate and with the exception of the material containing the deflocculator, which was quite unsatisfactory, and that containing the gum-like substance, they gave somewhat similar coverage. Maximum deposits of about 50 micrograms As_2O_3 per square centimeter of fruit surface were obtained after the fifth cover spray which was applied July 2. By harvest time, this deposit had been reduced to about 15 micrograms per square centimeter, almost solely as a result of the increase in surface area of the fruits. This point has been discussed previously.

When lead arsenate has been used alone or with soap or protein spreader, the maximum deposit expected following the fifth cover spray would be about 20 micrograms As_2O_3 per square centimeter, but because of the necessity for late or second brood applications where such spray mixtures are employed in the lower Wenatchee valley, this deposit will be retained practically undiminished up to harvest. Thus, although the deposit from the inverted mixture was very much greater than customary, up to the middle of July, it was somewhat less than customary when the time arrived to remove the residue. In practice, it has been found that residue from an inverted lead arsenate mixture containing summer petroleum oil is more difficult to remove than an equal deposit from a mixture not containing petroleum oil. However, as in this demonstration, where such inverted mixtures have been used early in the season, residue removal has been accomplished without complications, in tandem washers with heated sodium silicate and hydrochloric acid solutions. According to F. L. Overley, as far as experience at this experiment station is concerned, their application in late July or August has caused extreme difficulty in residue removal, as indeed has every type of lead arsenate mixture which contained a similar amount of summer petroleum oil.

Table 22 gives the average infestation at harvest for all brands of lead arsenate according to varieties. Instead of recording the infestation as number of larvae per 100 apples, the percentage of wormy fruit was taken as more representative of grower viewpoint, and for direct comparison of the owner's results the previous season.

Table 22. Percentage Wormy Fruits for Inverted Lead Arsenate Mixtures - 1935 Demonstration.

Variety	Per cent wormy fruit	
	5 "first brood" applications (last application July 1)	5 "first brood" and 1 "second brood" application
Pearmain	7.7	6.0
Rome	5.9	3.6
Winesap	1.8	1.1

These comparisons are weak since there is no means of computing significant differences. Nevertheless, the figures are expressive of two points. In the first place, though infestation throughout the district was quite as severe in 1935 as in 1934, in round figures the amount of wormy fruit in this orchard dropped from 80 per cent to eight per cent for Pearmains, from 80 per cent to six per cent for Romes, and from 50 per cent to two per cent for Winesaps. In 1934, the owner applied ten cover sprays which left a residue too heavy and tenacious to be removed to the domestic tolerance, while in 1935 five cover sprays, much more effective than the ten of the preceding year, left a residue that was satisfactorily removed by good commercial washing practice. In the second place, though the application of a very heavy arsenical deposit late in July evidently improved codling moth control, the improvement was not sufficient to pay for the extra spray materials, aside from the fact that a difficult residue removal problem ensued.

Four factors appear to have been principally responsible for the improved codling moth control in 1935 compared to 1934. First, the trees were more carefully sprayed, and much more heavily sprayed. Second, greater use was made of an ovicide early in the season. Third, with heavy application, the new inverted mixture produced an arsenical deposit far in excess of anything ever achieved by the grower himself. Fourth, attention was concentrated upon protection from larval attack during flight of the overwintered generation, or as commonly phrased "first brood control."

The necessity of concentrating upon early spray applications was stressed by Forbes of Illinois as early as 1886, when he wrote, "Not only do these experimental facts point to the inefficiency of Paris green as against the later broods of the codling moth, but it is plain that the result is what we must have expected a priori." Nevertheless, the fact remains that in the intervening 50 years, the significance of this fundamental principle frequently has been overlooked and "second brood" sprays taken as a matter of course.

B. Season of 1936

The orchard used for demonstrations in 1935 was again selected for that purpose in 1936, the second year's work being undertaken with the following objects:

(1) To verify results of the 1935 demonstration.

(2) To determine if in a badly infested district, it is possible to obtain satisfactory codling moth control with only four first brood applications of a highly effective spray deposit.

(3) To compare an inverted lead arsenate mixture with an inverted calcium arsenate mixture.

Unlike the problem of the preceding year, the carry-over of larvae amounted to only some five per cent. However, the trees were in the same leafy condition as in 1935, and in addition the owner paid no attention whatever to the ordinary practices of sanitation. There was no scraping the banding of trees, and no removal and destruction of thinnings, though as a matter of fact, only one or two wormy apples were found up to the end of June. The crop was very light, a condition favoring heavy infestation.

The calyx spray for the entire demonstration block consisted of calcium arsenate four pounds, zinc sulphate one pound, and calcium hydrate two pounds per 100 gallons. For cover sprays one portion received inverted lead arsenate mixture, and a second portion, inverted calcium arsenate mixture costing approximately the same amount. Both mixtures contained 0.5 per cent medium summer petroleum oil.

A part of each of these subdivisions in addition to the calyx application was sprayed four times, the last application being made June 13 when the apples were the size of walnuts. A second part received a fifth application on June 30. Five days elapsed between the application of the calyx and first cover sprays, seven days between the first and second cover sprays, eight days between the second and third, 16 days between the third and fourth, and where applied, 17 days between the fourth and fifth.

Again the trees were sprayed very heavily; approximately 75 gallons per tree per application. Since each tree might bear a normal crop of 35 packed boxes, this amounts to two gallons of spray material per application, per packed box of fruit.

Samples were taken for arsenic determinations four times during the growing season, as well as at harvest. Table 23 gives averages of these analyses, as well as the percentages of wormy fruit when picked.

Table 23. Arsenical Deposits and Infestation at Harvest - Demonstration 1936

	Materials per 100 gallons	No. of cover sprays	Average deposit all varieties mmg As_2O_3 per cm^2	Per cent wormy fruit		
				Pearmain	Rome	Winesap
1	Lead arsenate, 3 lbs. Medium summer oil, 2 qts. Ammonium oleate, 0.25 lb.	4	33.7	8.1	---	10.7
2	Same	5	44.6	---	5.9	3.6
3	Calcium arsenate, 4 lbs. Zinc sulphate, 0.25 lb. Medium summer oil, 2 qts. Triethanolamine oleate, 0.25 lb.	4	47.3	8.0	---	15.5*
4	Same	5	68.6	---	8.3	15.8*

*Trees in a group and apparently in an unfavorable location.

Though in Table 23 the deposit figures are reliable, the infestation records give only vague indications of the effectiveness of the mixtures. Nevertheless, it seems evident that in the lower Wenatchee district, four first brood spray applications will not suffice for satisfactory codling moth control. This will apply, particularly where blocks of trees are only a few rows wide, and adjoining severaly infested trees, as was the case with this demonstration. Apparently in orchards where moths of the overwintered generation appear to emerge until well into July, it is necessary that a cover spray be applied late in June regardless of the number, or effectiveness of previous spray applications. By the end of June, the rate of increase of the surface area of the fuits is declining rather rapidly, with the result that a heavy deposit applied at that time should continue to be reasonably effective even in August when the later attacks of the codling moth are unusually hard to combat.

It has been mentioned that deposits from inverted mixtures applied in June seem less effective in August or September than their amount and degree of uniformity would suggest. This was apparent in the demonstration of 1936, and especially so with the inverted calcium arsenate mixture. The present theory is that lessened effectiveness late in the season may relate to volatilization or chemical change in the oil of the deposit, as well as to increased activity of the codling moth larva. The calcium arsenate deposit was particularly rough and quite devoid of the oiliness which has characterized the most effective arsenical coverages. Apparently, the inverted calcium arsenate mixture, though having given a considerably higher arsenic deposit than the lead arsenate mixture, was a trifle less effective in controlling the codling moth. It is suspected that if there is found a means of retaining the oiliness of the deposit, it will be at once more effective in control, and more likely to be innocuous to the tree, at least as far as arsenical injury is concerned. A reduction in the size of the arsenical agglomerates would evidently be a further improvement.

The degree of codling moth control obtained from early season applications of these inverted mixtures, under the adverse conditions which prevailed in this orchard, as well as the results reported by G. E. Marshall in Indiana (loc. cit.), leave open to question this statement made by Headlee (1935). "We know also that a population of codling moth of sufficient size can develop in an orchard to render its adequate control by understood methods of summer spray impractical." That may apply to eastern conditions, but at the present time at least, it certainly does not apply to those of central Washington.

C. Cost of Inverted Spray Mixtures

Inverted spray mixtures containing 0.5 per cent summer petroleum oil, cost approximately the same for a given amount of spray as non-inverted mixtures with a similar quantity of oil. At moderate dosages they have been measurably more effective in controlling the codling moth, but it is only when heavy applications are made that their superiority over non-inverted mixtures is striking.

When it becomes necessary to use summer oil for codling moth control, the situation will be serious enough that the best of mixtures, and methods of application, are advisable. Under these circumstances, heavy application of an inverted mixture is indicated during May or June. It would seem that heavier dosage would mean a larger spray budget, but that might be so only if no reduction could be effected in the number of applications required. Actually, one heavy application of such a mixture for the third, fourth, or fifth cover spray may reduce the amount of infested fruit at harvest to a greater extent than two applications of lead arsenate-spreader, or lead arsenate-soap combinations. Since the spray budget must be considered in the light of the value of the marketable fruit which it makes possible, the cost of any particular spray application is difficult to calculate. For example, let us take the case of the demonstration orchard just mentioned. In 1934, the owner using light dosages of non-inverted mixtures, applied ten cover sprays at an average cost per tree of about $1.50. He had practically no marketable crop. The following year, in the face of a tremendous carry-over of larvae and under seasonal conditions quite as favorable for codling moth development as in 1934, five very heavy inverted applications were made, at a total cost for materials of about $1.80 per tree. The cost for spray materials was about 30 cents per tree more than in 1934, but instead of practically no marketable fruit there were about 20 boxes per tree, normally worth perhaps $9.00 or $10.00 to the operator. The extra investment of 30 cents had returned dividends of about $9.00 per tree or $350 per acre, with normal apple prices. The "cost" of a particular spray mixture or method of spraying may refer quite as well to loss of fruit as to outlay for spray materials.

D. Preparation of Inverted Lead Arsenate Mixtures by the Grower

Marshall and Groves (1937) have given suggestions for the preparation of inverted lead arsenate mixtures by the orchard operator himself. In 1936, such suggestions were adopted with satisfactory results by operators controlling perhaps 300 acres of apple orchard in the lower Wenatchee valley. The present season (1937), one or more applications of inverted mixtures were made on about ten times this acreage.

VII. SUMMARY

1. During the past fifty years, numerous attempts have been made to increase the effectiveness of certain insecticides, such as lead arsenate, by the addition of spreaders and adhesives. A few of these have been definitely beneficial, but, for this purpose, their efficacy has been relatively insignificant in comparison to the improvement resulting from the application of a new principle recently developed at the Washington Experiment Station. This is the principle of the inverted mixture.

2. An inverted spray mixture is one in which a suspended solid initially wetted by water becomes wetted by oil prior to, or at the moment of impact upon a sprayed surface.

3. Inversion of arsenical spray mixtures requires the addition of some substance promoting oil-wetting of the arsenical which is nominally preferentially wetted by water. This substance may be a fatty acid, such as oleic acid, a univalent, divalent, or trivalent soap, or other fatty acid compounds, such as diglycol oleate.

4. When univalent soaps or free fatty acids produce inversion, it is believed that oil-wetting is due to the formation of oil soluble, or preferentially oil wettable, divalent or trivalent soap.

5. Inverted spray mixtures have the capacity to cause enormous increase in solid deposit as spraying is prolonged upon one point. This characteristic appears to depend on the solid particles being coated by a film of oil, yet not loosely dispersed in it.

6. Uniformly filmed deposits are typical of these spray combinations, but this effect is one of wetting and adhesion. Spreading does not appear to be a factor.

7. Inverted mixtures have been made for codling moth control, using lead acid arsenate, synthetic cryolite, natural cryolite, commercial "tricalcium" arsenate, or zinc arsenite as the solid. However, there is no a priori reason why the principle of inversion can not be utilized for any finely divided solid, whether it be an insecticide or a fungicide. The solid should be completely oil and water insoluble, or nearly so.

8. Inversion may be strongly influenced by impurities in the solid insecticide, oil, water or oleic acid. The introduction of fungicides would represent a problem for additional investigation.

9. Hydrophilic colloids, such as ammonium caseinate, exert a strong stabilizing effect upon inverted mixtures. Under ordinary conditions they interfere with heavy deposition, but with hard water their use in small amounts is indicated.

10. The salts of divalent or trivalent metals cause inversion of oil-in-water to water-in-oil emulsions, when the former are stabilized by univalent soap. They also promote oil-wetting of arsenical particles when these are present in such a system. Sometimes the inverted type of mixture is too stable. In such cases, electrolytes, such as zinc sulphate, are suggested for de-stabilization, i.e., promotion of oil-wetting of the lead arsenate. An increase in soap content, or the introduction of free fatty acid may serve the same purpose.

11. Inversion is influenced both by agitation in the spray tank, and passage of the mixture through the release valve of the pump. Optimum agitation is the minimum degree of agitation necessary to prevent the flocs from settling to the bottom of the tank. Overflow should likewise be at a minimum, for excessive overflow has caused breaking of mixture in the spray tank with consequent adhesion of oil and solid to its sides.

12. The ovicidal effect of inverted mixtures appears to be slightly less than that of non-inverted mixtures. This is evidently because the oil is adsorbed by the solid particles to a greater extent, and hence less is available to coat the codling moth eggs. The former type of spray combination is evidently superior because of its capacity to build heavier and more uniform deposits of the solid insecticide.

13. Aside from ovicidal effect, oily arsenical deposits have been found more effective in preventing the establishment of codling moth larvae than non-oily deposits of equal type and amount. In the main, this may result from the greater difficulty experienced by larvae in attaching their silken threads to an oily surface, as well as from the greater likelihood of their picking up oily arsenical particles, than non-oily particles.

14. Though moderate applications of inverted spray mixtures have given heavier deposits and better codling moth control than moderate applications of non-inverted mixtures containing the same amount of oil, their outstanding superiority only becomes evident with heavy application. With the non-inverted mixture, once the fruit has been wetted with water no more solid can be made to adhere, while with the inverted mix-

ture, the oil and solid remain upon the fruit while the water drips to the ground.

15. Inverted arsenical mixtures made with the ordinary type of highly refined, light to medium summer petroleum oil, tend to form relatively large agglomerates of the solid particles on the fruit surface. These agglomerates, particularly in the case of calcium arsenate, may be so large as to prohibit their ingestion by the newly hatched codling moth larva. The size of the agglomerates depends to a considerable extent upon the type of oil which is used.

16. Fissuring and weathering of arsenical deposits is less evident where oil is present than where not present. This applies especially to inverted mixtures, and seems to be caused by the oil softening the apple wax. Kerosene has apparently no influence upon fissuring of deposit.

17. Under arid conditions, practically no loss has occurred from weathering of inverted spray deposits containing petroleum oil. Decrease in deposit is attributable to fruit growth. There has been considerable loss from weathering of non-oily deposits.

18. Inverted spray mixtures have been made with various grades of summer petroleum oil, as well as with herring oil, kerosene, and herring oil-kerosene mixtures.

19. When it has been necessary to avoid the use of petroleum oil, a mixture consisting of 25 per cent herring oil and 75 per cent kerosene has produced satisfactory inversion, an oily deposit, and good codling moth control. However, such a mixture has practically no ovicidal effect.

20. Approximately 0.5 per cent of oil and 0.25 pound of univalent soap have been necessary for the inversion of three pounds of lead arsenate in 100 gallons of water. The amount of soap required for calcium arsenate has been variable.

21. The most satisfactory soaps for these spray combinations have been the oleates of triethanolamine or ammonia.

22. In a district where from two to four second brood applications are the rule, satisfactory control of even the heaviest of codling moth infestations has been accomplished solely by early season applications of inverted lead arsenate mixtures.

23. Four inverted lead arsenate applications containing 0.5 per cent summer petroleum oil, applied during May and June, have not caused any visibly deleterious effects to fruit or foliage of the apple under the arid conditions of the Wenatchee valley.

24. Residue removal is complicated by the presence of petroleum oil in inverted mixtures, and by the fact that they result in very high arsenical deposits if heavily applied. Such mixtures containing petroleum oil should not be used later than July 1. If applied heavily in May and June, however, they have not caused unusual difficulties in residue removal.

25. The cost of controlling very severe codling moth infestations with inverted mixtures, should be less than that of any other type of spray mixture at present commercially available. They have been both more effective, and more efficient, than non-inverted mixtures. Nevertheless,

because they are more difficult to handle than the ordinary type of mixture, their use is not indicated at present, unless codling moth control is a serious problem.

26. Commercial "tricalcium" arsenate has been used in the form of an inverted mixture by the addition of a small but variable amount of zinc sulphate, as well as univalent soap and summer petroleum oil. This combination appears promising as a means of eliminating lead from apple sprays, but there are points concerning it which require further investigation.

27. Nothing is known concerning the behaviour of these inverted arsenical mixtures in any district but the arid fruit growing area of central Washington.

VIII. ACKNOWLEDGMENTS

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X. APPENDIX

A. Table of Areas of Apple Discs for Deposit Analyses

Formula for calculation of area of discs from the surface of a sphere:

$$2\pi R\,(R - \sqrt{R^2 - r^2})$$

where R = radius of sphere and
r = radius of disc

Table 1

(A) Diameter of disc = 1.15 cm. (for small fruits)

Diameter of fruit in centimeters	Area in square centimeters		
	One disc	Five discs	Six discs
2.00	1.144	5.72	6.86
2.26	1.117	5.58	6.70
2.50	1.100	5.50	6.60
2.76	1.093	5.46	6.55
3.00	1.084	5.42	6.50
3.26	1.075	5.37	6.45
3.50	1.066	5.33	6.39
3.76	1.063	5.31	6.37
4.00	1.060	5.30	6.36
(B) Diameter of disc = 1.83 cm. (for large fruits)			
3.57	2.830	14.15	16.98
3.73	2.811	14.05	16.86
4.01	2.783	13.91	16.70
4.25	2.764	13.82	16.58
4.52	2.747	13.73	16.48
4.76	2.735	13.67	16.41
5.00	2.724	13.62	16.34
5.24	2.715	13.57	16.29
5.50	2.707	13.53	16.24
5.76	2.700	13.50	16.20
6.01	2.694	13.47	16.16
6.25	2.689	13.44	16.13
6.51	2.684	13.42	16.10
6.75	2.680	13.40	16.08
6.99	2.677	13.38	16.06
7.26	2.673	13.36	16.04
7.50	2.671	13.35	16.02
7.75	2.668	13.34	16.01
8.00	2.666	13.33	15.99
8.26	2.663	13.31	15.98
8.37	2.662	13.31	15.97

B. Procedure in Preparing Analytical Samples and Determination of Arsenic

1. Using care to touch only their stem and calyx ends, fruits are taken by random sampling in the outer and inner portions of the tree, about midway between the upper and lower branches.

2. The fruits are impaled upon nails driven through boards and removed to the laboratory. Ten fruits constitute a satisfactory sample.

3. Measurements are made of the diameter of each fruit in the sample and the average diameter is determined. This is very conveniently done with a steel Vernier caliper.

4. Using a well sharpened brass cork borer and touching the fruits only at the stem and calyx ends, a predetermined number of borings is made approximately equidistant from one another around the equator or cheek of each fruit. Generally five borings per fruit are sufficient. They should be about one centimeter in depth.

5. Discs are removed from the surface of the fruit by slicing with a thin bladed knife directly beneath the borings. If only a few samples are to be analyzed, the discs may be dropped at once into Kjeldahl flasks; if a considerable number, they are best handled by storing until required in large mouthed sample bottles (see Fig. 1). The discs need never be touched by hand, though some find it helpful to give them a slight tap on the edge as they are transferred from the blade of the knife to the flask or sample bottle. With a little practice this can be done rapidly and accurately.

6. In transferring discs from sample bottles to Kjeldahl flasks, the bottles are rinsed with about 25-50 ml. of dilute nitric acid (1:4)

7. Digestion is accomplished by boiling the discs in concentrated

nitric and sulphuric acids, and distillation of arsenic by introducing hydrazine sulphate, sodium bromide, hydrochloric acid, and sodium chloride.[1] Arsenic is determined by titrating with potassium bromate in the presence of methyl orange. (See A.O.A.C. Methods)

In practice, it has been found desirable to run about one blank or standard for every 10-15 determinations, though the method calls for only one blank for each fresh bottle of sulphuric acid.

8. After the amount of arsenic has been determined and the necessary blank correction applied, reference is made to the table of areas.

The average diameter for a given sample is noted in the first column and if five discs have been removed from each fruit, the combined surface area of these will be found in the third column. The total surface area of the discs in a ten apple sample is obtained at once by shifting the decimal point. The number of micrograms of arsenic trioxide per square centimeter of fruit surface is then computed by dividing the amount of arsenic by the surface area involved.

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[1] Ordinary dairy salt is suitable. It may be added directly to the cooled flask.

C. Variation in Deposit of Lead Arsenate Used Alone in Water

Table 2

	mmg As_2O_3 per cm^2
Lead arsenate, 3 lbs.)	9.9
Water, 100 gallons)	9.2
	12.7
Applied with an experimental machine of 5-gallon capacity at 400 pounds per square inch. Apples sprayed for 15 seconds while rotating. Analyses extending over a two-year period, 1935-1936, with a single brand of lead arsenate.	14.8
	12.8
	11.8
	13.8
	10.1
	9.5
	8.5
	16.0
	5.0
	10.0
	11.1
	9.1
	10.5
	13.2
	10.5
	10.8
	9.0
	8.7
	10.0
	10.5
	12.8
	11.9
	8.6
	6.5
	7.8
	10.0
	305.1
Average	10.5
Average deviation from the mean	1.78

Probable error = ± 0.3

Average determination 10.5 ± 0.3 micrograms As_2O_3 per square centimeter.

D. Analyses of Materials

The following analyses and constantswere supplied by Doctor Kermit Groves, division of chemistry, Washington Experiment Station:

Lead acid arsenate	Lead (Pb)	60.3% (Theor. 59.7%)
	Arsenic (As_2O_3)	26.5% (Theor. 28.5%)
	Water soluble arsenic	Less than 0.2%
Calcium arsenate - Commercial tricalcium	Total arsenic (As_2O_3)	39.0%
	Total calcium	46.1%
	Moisture	1.0%
	Water soluble calcium ($Ca(OH)_2$)	2.5% to 4.0%
	Water soluble arsenic (A.O.A.C. Method) less than	0.1%
Zinc arsenite	Arsenic (trivalent)	40.0%
	Arsenic (total) as As_2O_3	40.1%
	Zinc as ZnO	57.8%
	Zinc (Zn)	46.4%
Calcium hydroxide - Special reground product	Calcium as $Ca(OH_2)$	92.4%
	Magnesium as MgO	1.0%
Zinc sulphate - Crystals	$ZnSO_4 . 5 H_2O$, about	23.0% zinc
Medium summer petroleum oil -	Standard No. 6	
	Unsulphonatable residue	90.0%
	Viscosity Saybolt at 37.8° C.	70-75 seconds
Light summer petroleum oil -	Standard No. 4	
	Unsulphonatable residue	91.0%
	Viscosity Saybolt at 37.8° C.	56 seconds
	Percentage distilled at 271° C.	none
	" " " 335.5° C.	63.0%
	" " " 351.5° C.	81.0%
Special light-medium summer petroleum oil		
	Unsulphonatable residue	70.0%
	Viscosity Saybolt at 37.8° C.	64 seconds

Special light summer petroleum oil	Unsulphonatable residue	67.0%
	Viscosity Saybolt at 37.8° C.	52 seconds
	Percentage distilled at 271° C.	22.0%
	" " " 335.5° C.	67.0%
	" " " 351.5° C.	77.0%
Kerosene - Illuminating grade	Unsulphonatable residue	93.0% - 94.0%
	Viscosity Saybolt at 37.8° C.	32-34 seconds
Herring oil - Pacific Coast production	Free fatty acid	0.60% to 1.75%
	Iodine number (Hanus)	124 - 135
Oleic acid	Unsaponifiable matter	4.0%
	Equivalent weight	284
Triethanolamine	Equivalent weight	132
	Technical grade containing about 2% monoethanolamine and 11% diethanolamine	
Ammonium hydroxide	28% strength	
Casein	Grade, prime lactic	
Ferric chloride	U.S.P. lump, $FeCl_3.6 H_2O$	

Fig. 14. Entomological field laboratory, Washington Experiment Station, Wenatchee, Washington. Left, sprayer shed; center, insectary; right, chemical laboratory

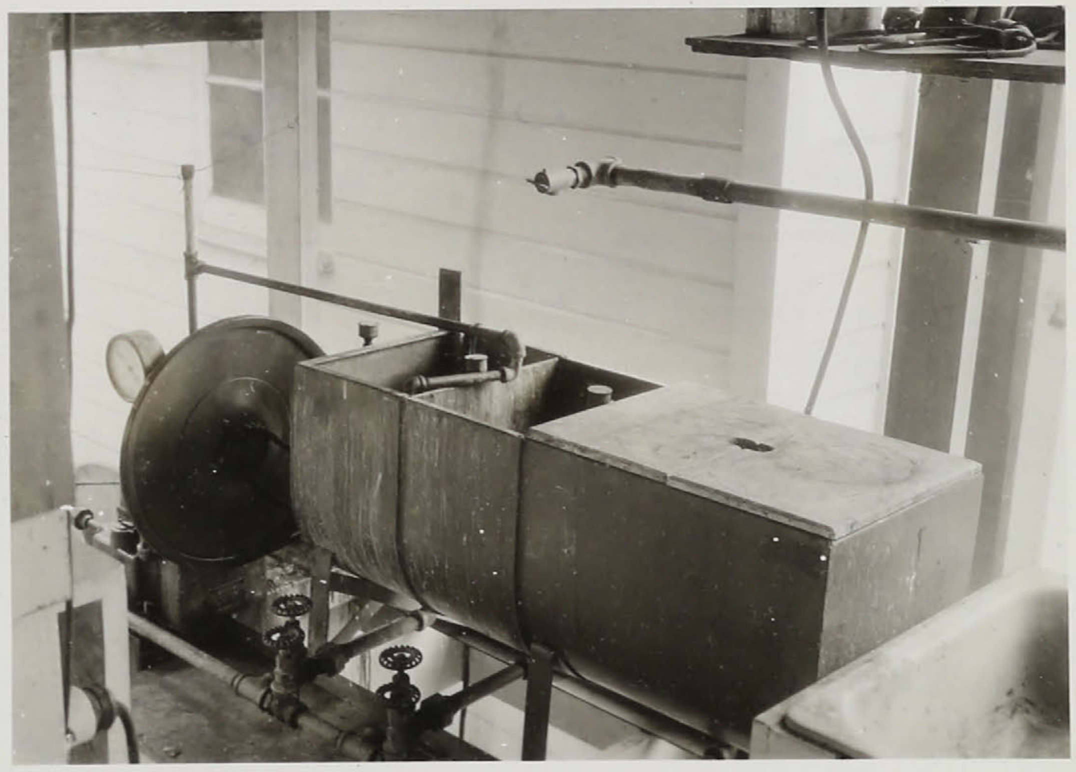

Fig. 14. Laboratory sprayer, showing divided spray tank and valves. Capacity 2-3 gallons per minute at 350 pounds pressure per square inch.

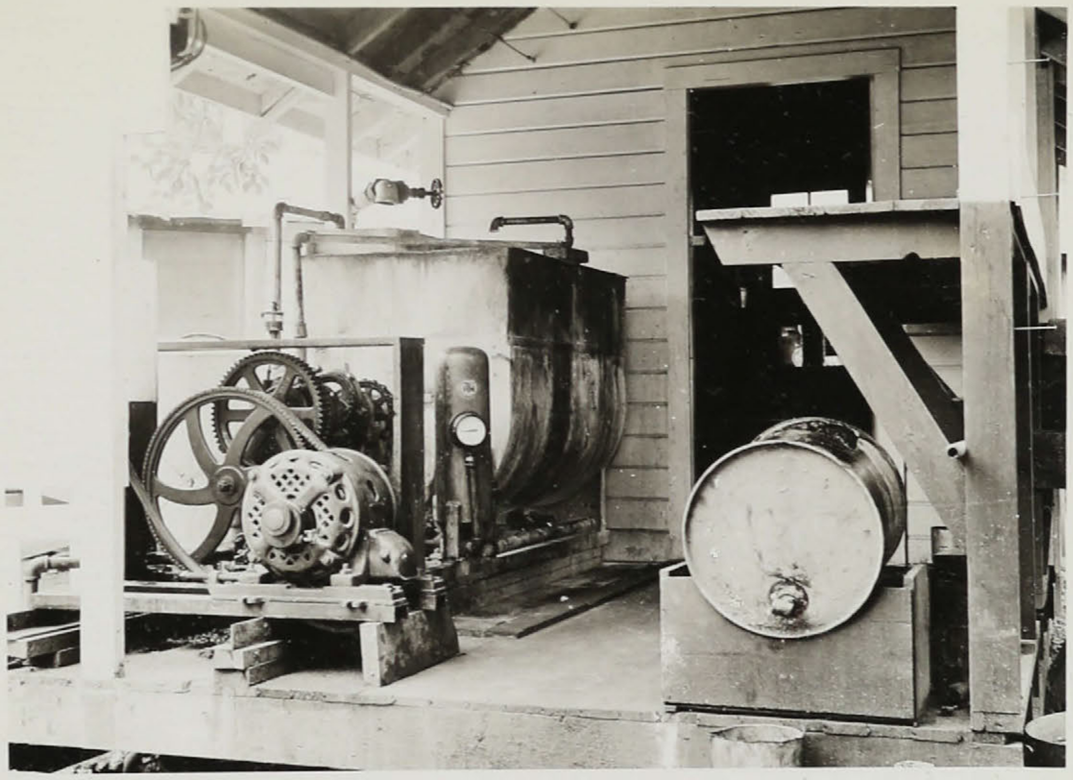

Fig. 15. Stationary electric sprayer for preliminary field experiments, capacity 16 gallons per minute at 450 pounds pressure per square inch. This machine operates two spray guns.

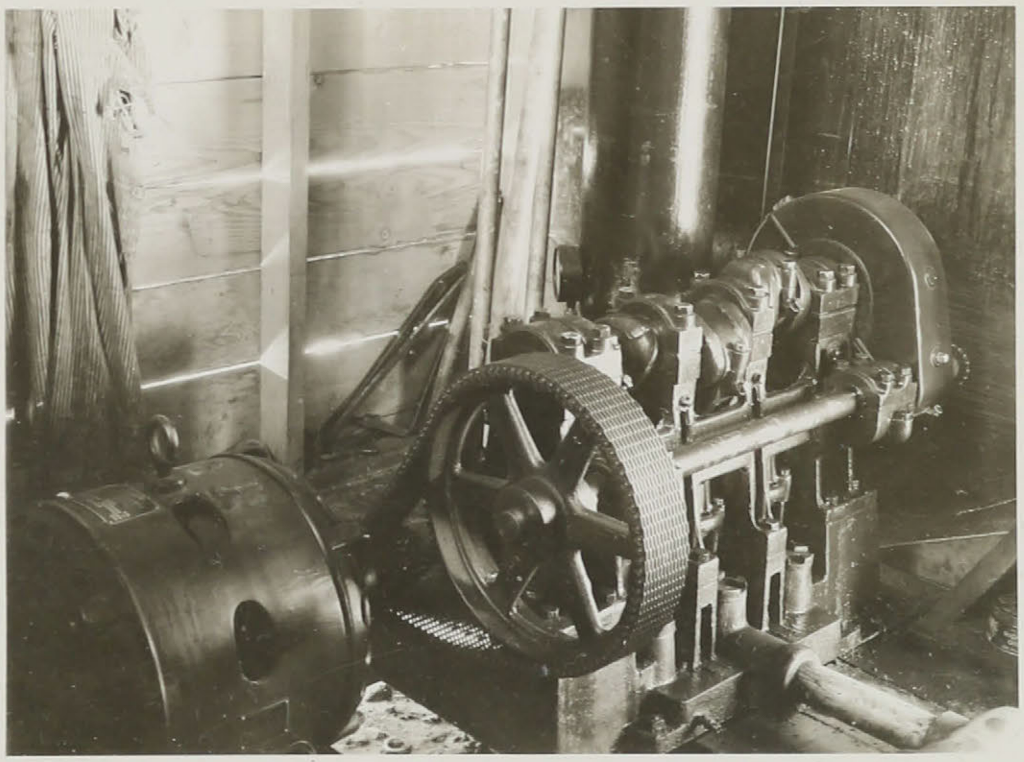

Fig. 16. Stationary electric sprayer for main field experiments, capacity 32 gallons per minute at 650 pounds pressure per square inch. This machine operates four spray guns.

Fig. 17 Field telephone, one of several used to facilitate communication between spray shed and spray gun operators.

Fig. 18. Equipment used in field checking of harvested fruits.

Fig. 19. Checking crew at work during harvest.

Fig. 20. A demonstration of the spray coverage obtained by heavy application of an inverted mixture. As seen where the spray deposit was removed, this apple was red.