VOL. 2 JANUARY, 1927 NO. 9

HILGARDIA

A Journal of Agricultural Science

PUBLISHED BY THE

California Agricultural Experiment Station

CONTENTS

UNIVERSITY OF CALIFORNIA PRINTING OFFICE
BERKELEY, CALIFORNIA

HILGARDIA

A JOURNAL OF AGRICULTURAL SCIENCE

PUBLISHED BY THE

CALIFORNIA AGRICULTURAL EXPERIMENT STATION

VOL. 2 JANUARY, 1927 No. 9

A PRELIMINARY STUDY OF PETROLEUM OIL AS AN INSECTICIDE FOR CITRUS TREES[1]

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INTRODUCTION

The general purpose of this investigation was a study of petroleum oils in relation to their availability as insecticides for use on citrus trees. This involved selection, first on the basis of tree tolerance, and secondly on the basis of insecticidal value. The data thus far obtained and the conclusions derived therefrom are believed to be of sufficient importance to justify this preliminary report. Investigations along the more promising lines opened up by the study are still in progress.

While the several phases of this investigation were conducted coöperatively and with free consultation between the authors, portions of the work were of necessity carried out semi-independently. Thus the selection of oils by foliage testing and the development of the chemical aspect of the paper have been largely the work of deOng at Berkeley and in southern California, while the insecticidal tests proper, together with their accompanying developments, were principally the joint work of Knight and Chamberlin at Riverside. The authors are indebted to H. J. Quayle for valuable suggestions and criticisms.

The study of petroleum-oil distillates in relation to their insecticidal effects was originally begun at the California Agricultural Experiment

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Station in 1914 but was later discontinued until 1924 because of lack of facilities. At that time a coöperative project was undertaken between the University of California Agricultural Experiment Station and the Standard Oil Company of California. Under this coöperative plan, the Standard Oil Company contributed the services of their oil chemists and the use of their laboratories in preparing oil samples for both laboratory and field tests. The Experiment Station was responsible for testing the various oils with reference to insect kill and plant tolerance.

A special advantage that has been realized from thus coöperating with a large commercial company lies in the fact that the distillates and oils were obtained from crude oils pooled from a large number of wells. Hence the samples tested may be safely considered representative of supplies which might be secured from any large oil company of California. This overcomes one of the principal difficulties in the study of petroleum oils, viz., that the oils used were not necessarily typical of supplies generally available.

HISTORY OF OIL SPRAYS IN RELATION TO CITRUS TREES

The use of petroleum-oil sprays as insecticides on citrus trees began about 1881 when kerosene emulsions first came into use. This type of oil has been found safe to use on citrus trees but does not control the more resistant scale insects and mealybugs. In an attempt to find a cheaper and more toxic oil, use was made of the so-called "stove distillates," these being unrefined distillates of 26° to 32° A.P.I.[5]

Severe injury to the fruit as well as to the foliage was frequently caused by these materials when emulsified with soap, as was ordinarily done, and when used in the form of a mechanical mixture of oil and water. Such mechanical mixtures of oil and water are, as their name implies, formed by violent agitation in the spray tank without the use of emulsifying agents. This type of "emulsion" separates almost instantaneously and it was found in practice that pure oil would occasionally be applied to parts of a tree with severe injury resulting. For some years, therefore, the spraying of citrus trees for the control of insects was of doubtful value. The perfection of fumigation with hydrocyanic acid gas also tended to discourage the use of other scalecides. The high cost of fumigation has, however, from its inception led to sporadic attempts to find an effective substitute.

[5] A.P.I.—American Petroleum Institute.

The factor which has probably done most to stimulate recent investigations of sprays has been the development of HCN-resistant strains of both the red and the black scale insects, as shown by Quayle.(1) These resistant strains show a distinct tolerance to dosages of hydrocyanic acid gas which in earlier fumigation practice were found to be fatal. Thus the scale kill by fumigation in the areas of resistance has dropped from over 99 per cent to as low as 85–95 per cent, so that the control of 85–96 per cent now commonly attained by spraying is hopeful, although below the standard of successful fumigation.

Gray(2) in 1915 noted the important relation existing between the refining of petroleum oil by the use of sulfuric acid and plant tolerance as discussed further on in this paper.[5a] The cost of highly refined white oils, however, prevented their effective utilization in the stable emulsions of high oil content. The development of a successful quick-breaking emulsion, as shown later, affords an effective means of overcoming this objection by reducing the necessary concentration of oil, and by permitting its more complete utilization.

COMPOSITION OF PETROLEUM OILS AND THEIR INJURY TO PLANTS

Nature of Injury to Trees by Petroleum Oils.—Volck(3) has shown that injury is most pronounced when the application of oil is made to the under side of the orange leaf where all the stomata of this plant are situated. This is owing to the fact that oil penetration into a leaf is much facilitated by any sort of opening, abrasion, or pore. According to the work of Magness and Burroughs(4) an oil film on the surface of stored apples may have a distinct effect on the gaseous exchange. The evolution of carbon dioxide from Winesap apples held at 65° F was reduced only 12 per cent by a coating of Oronite Crystal or other petroleum oil, but analyses of the air in the intercellular spaces showed a composition of 2.6 per cent oxygen and 25.3 per cent carbon dioxide, while check apples had 5.7 per cent oxygen and 18.3 per cent carbon dioxide. Burroughs(5) has noted a reduction in the amount of starch produced in apple leaves that seem to have been arrested in their growth by the application of an oil spray.

Gray and deOng(2) found a correlation between the specific gravity of the oil and resulting foliage injury. This correlation

[5a] A commercial emulsion of highly refined petroleum oil was being made by W. H. Volck when this later investigation by the California Experiment Station was begun in 1924.

applies only in a comparison of kerosenes with the heavier or lubricating oils. The former have a much lower boiling point and volatilize before penetration occurs; or even if penetration does take place, the oil may still volatilize before injury results. Injury may be possible, however, with certain fractions of a still lower boiling point than kerosene, especially if they contain a high percentage of unsaturated hydrocarbons. A study of lubricating oils having a much higher range of boiling points than kerosenes shows that their effect on plants and insects is more nearly related to viscosity than to specific gravity.

Injury to the foliage of citrus trees from petroleum oils is of two distinct types, acute and chronic. The former is caused by light (low-boiling-point) oils, the latter by heavy (high-boiling-point) oils. In the acute type of injury two distinct phases are noticeable. First, the leaf tissue may be killed within 48 hours after the application; and secondly, this may be followed by the leaves dropping after three or four days, although such leaves do not lose their color to any marked degree. Injury to the fruit or wood seldom occurs except with oils having a high percentage of unsaturated hydrocarbons, such as is commonly found in untreated oils, or those slightly refined. Contact of these oils with the roots may cause the death of the tree within a relatively short time.

Chronic injury is associated in varying degrees with oils of a high boiling point, which leave an oil film on the leaf and twig surface for a period of days or weeks. The foliage becomes yellow and defoliation begins within a few days and may last for weeks. The twigs and even the larger limbs are stunted or killed as shown in figure 1. The orange tree in the figure was photographed one year after a portion of it had been sprayed with lubricating distillate, untreated with sulfuric acid.

The damage occurred only on the sprayed portion. The normal growth in the background, which shows no sign of injury, was unsprayed. Stunted twigs often put out a few small, weak leaves, and frequently the tree sprouts freely just below the injured parts.

Fully mature leaves, especially if senile, are more susceptible to injury from neutral oils than younger ones which are still in the growing stage. On the other hand, very young leaves are much more susceptible to injury from unrefined oils than the mature, but not senile, leaves, although this varies a great deal according to the degree of refinement of the oil used.

Commercial Refining of Oils as a Means of Reducing Injury to Plants.—Petroleum distillates are not usually in a marketable condition without chemical treatment to remove such ingredients as sulfur, resinous matter and the unsaturated and aromatic hydrocarbons. The common refinery practice is to treat the raw distillates, resulting from the heating of crude oil, with sulfuric acid. The quantity of acid

Fig. 1. Orange tree showing dead wood where the tree was sprayed with unrefined oil distillate.

required and the length of time during which treatment is continued depend on the grade of product desired and on the purity of the distillate used.

After treatment with acid, the oils are washed with a solution of caustic soda in order to remove the unchanged petroleum acids and phenols and to neutralize and remove the sulfo-acids and the sulfuric acid remaining in the oil. The expense of refining operations is high, especially for the highly refined white oils, since the acid sludge resulting from the treatment is largely a waste product. In addition to the cost of the acid there is the loss of distillate which may amount to more than 50 per cent of the original volume treated.

In order to avoid the losses resulting from the chemical treatment, it is advisable to substitute a method of extraction more nearly of a physical type. This has been accomplished by Edeleanu(6) who found that if petroleum oil was treated with liquid sulfur dioxide the olefins are dissolved but the saturated hydrocarbons remain unaffected. Experimental work is now in progress with oils refined by this method in the hope that a satisfactory degree of refinement may be obtained at a lower cost than is possible from the sulfuric acid treatment.

Tests of Petroleum Oils in Relation to Plant Injury.—Differences in the insecticidal effects of, and plant tolerance for, various petroleum distillates have long been recognized, but until recently the only specifications commonly used for distinguishing between them were specific gravity and, perhaps, the flash point. We now know that these are inadequate criteria. The boiling point of different kerosenes, for example, has been shown by Moore(7) to be important in distinguishing between the toxicity of petroleum fractions as it relates both to insects and to plants.

Since some progress has been made in determining the relation between the unsaturated hydrocarbon content of oils and their toxicity to plants, our first attempt at selection was based on the degree of refinement, the assumption being that the oil fractions containing the least amount of sulfonatable oil would be the safest.

A series of lubricating and kerosene oils was obtained from the Standard Oil Company. These ranged from the raw untreated distillate resulting from the distillation of crude oil, up through the different degrees of refinement effected by the use of acid and filtration. Their physical and chemical specifications are shown in table 1.

These oils, with the exception of the one finally selected for study, are referred to by number throughout this paper, instead of by their trade names. Oils 1 to 6, inclusive (tables 1 and 2), are lubricating oils, oil 1 being the raw distillate, and oil 5 the end of the refined series as based on the sulfonation test. Oil 5 (Oronite Crystal) is a very bland and "neutral" oil; it is colorless, odorless and tasteless. Oils 1a to 4a are kerosenes arranged in the same way, oil 1a being the raw distillate and 4a the highly refined end product. The sulfonation test (table 2) shows the amount of unsaturated hydrocarbons present in the various samples. These oils were emulsified with

TABLE 1

PROPERTIES[a] OF OILS TESTED

No.	Gravity[b] (degrees A. P. I.)	Flash point[c] ° F	Fire point ° F	Viscosity[d] in seconds at 100° F	Color	Sulfur (per cent)	Unsulfonated residue of oil	Acidity in mg. of KOH per gm. of oil
1	19.2	305	....	105	....	.7	51	1.5
2	21.3	310	350	99	....	.65	52	1.0
3	22.5	310	350	96	6[e]	.6	56	.6
4	22.7	320	360	107	2.5−	.6	60	.4
4x	22.7	320	360	100–110	1.5	.6	62	.03
5[h]	29.8	320	360	106	+25[f]	.006	98	.0
5x[h]	28–31	280+	....	70–80	+25[f]	.015	98	.0
6	....	360+	....	330–340	3.	.6	58	.2
				KEROSENES				
1a	35.9	124CT[g]	....	375	....	....	81	....
2a	41	83CT	125	320	+25[f]	.016	82	....
3a	41.3	113CT	135	345	+25[f]	.010	93	....
4a	43.3	143CT	175	400	+25[f]	.006	98	....

[a] The pour point on all oils used was below zero Fahrenheit.

[b] The A.P.I. gravity table is so similar to the Baumé gravity table that for all practical purposes they may be considered identical for lubricating oils.

[c] Cleveland open cup.

[d] Viscosity of lubricating oils determined by the Saybolt Universal viscosimeter. Viscosity of kerosene fractions measured by the Saybolt "Thermoviscosimeter," which bears no relation to the lubricating-oil viscosimeter.

[e] A.S.T.M. standards.

[f] A.S.T.M. standard for kerosene by Saybolt colorimeter; the color number + 25 is an arbitrary value given to the most highly refined kerosenes.

[g] Closed Tagliabue Tester.

[h] No. 5 is Oronite Crystal oil, No. 5x, Oronite Cosmetic oil, trade names used by the Standard Oil Company of California to designate oils of the above specifications. Other numbers used in the table also refer to commercial brands of oil as sold by the Standard Oil Company. Note the gravity of Oronite Crystal oil (No. 5). This increase (from about 22.5° A.P.I. to 29.8°) is the result of the excessive treatment with acid. It follows that gravity alone is no criterion since this property of finished white oil is practically identical with that of some raw distillates such as gas oil, though obviously viscosity and flash (and molecular weight) are much higher. As a general rule the saturated hydrocarbons are much lighter in gravity than either olefins or aromatics, e.g., heptane (N), gravity 75° and toluene, gravity 32° A.P.I.

sodium oleate and applied to the trees with a hand sprayer at an oil concentration of 6 per cent. Field tests on orange and lemon trees were made during the season of 1924 at Riverside, California, where the typical high temperatures and low humidities of southern interior California occur; at Lindsay as typical of the upper San Joaquin Valley; and also at Santa Paula, which has the lower temperature characteristic of coastal conditions. The maximum temperature at the last point usually ranges 10° to 15° F lower than at Riverside. The latter experiments were made possible by the coöperation of Mr. C. T. Dodds of the Santa Paula Citrus Fruit Association. The results are clearly brought out in table 2.

TABLE 2

EFFECT OF PETROLEUM OILS OF DIFFERENT VISCOSITIES AND SULFONATION VALUES ON ORANGE TREES AT VARYING TEMPERATURES.* OIL CONCENTRATION IN FISH-OIL SOAP EMULSION SIX PER CENT†

Oil No.	Viscosity in seconds at 100° F	Sulfonation value,‡ per cent	Riverside				Santa Paula Series I	
			Series I		Series II			
			Max. temp. range 85–100° F Applied 6/29		Max. temp. range 87–104° F Applied 8/21	Max. temp. range 61–96° F Applied 10/31	Max. temp. range 80–90° F Applied 6/16	
			Observations made 7/9	Observations made 8/2	Observations made 8/30	Observations made 11/9	Observations made 6/23	Observations made 7/21
1	105	51	Severe defoliation and burn.	70% twigs dead, 20% defoliated but sprouting.	....	....	12% defoliation, 40% fruit scarred.	10% fruit scarred, 25% leaf burn.
2	99	52	Severe defoliation and burn on twigs and fruit.	60% twigs dead, 20% defoliated but sprouting.	....	....	8% defoliation........	40% fruit scarred, 20% leaf burn.
3	96	56	Slight defoliation, no burn.	5% twigs dead, 10% defoliation.	....	....	2% defoliation........	20% fruit scarred, 15% leaf burn.
4	107	60	Heavy defoliation, no burn.	10% twigs and fruit dead, sprouting next injured area.	15% defoliation, no twig or fruit injury.	....	12% defoliation, 30% fruit scarred.	No fruit scarred, 8% leaf burn.
4x	105	62	Same as No. 4........	Same as No. 4........	12% defoliation, no twig or fruit injury.	....	15% defoliation, 40% fruit scarred.	15% leaf burn, 20% fruit scarred.
5	106	98	Slight defoliation, but showing growth.	Normal........	2% defoliation........	....	1% defoliation........	Normal.
5x	75	98	Slight defoliation and twig burn, no fruit injury, new growth normal.	....	5% defoliation........	....	3% defoliation........	Almost normal.
6	330	58	Severe defoliation and burn, no new growth.	35% twigs dead, defoliated area sprouting.	12% defoliation........	Normal........	5% defoliation, 10% fruit scarred.	10% fruit scarred, 12% leaf burn.
1a	375	81	Normal........	3% defoliation........	....	....	Normal........	Normal.
2a	320	82	Normal........	Normal........	....	....	Normal........	Normal.
3a	400	93	Normal........	Normal........	....	....	Normal........	Normal.
4a	400	98	Normal........	Normal........	....	....	Normal........	Normal.

*Defoliation values are estimates only and are given in percentages for convenience in recording. † This is a stable emulsion. ‡ Amount of oil soluble in 37N H_2SO_4.

On the basis of these experiments it was possible to eliminate all those lubricating oils which did not show a high degree of refinement. The data in table 2 show that the first four oils used were dangerous to fruit and foliage and even to the tree itself. As expected, the degree of injury corresponded very closely to the amount of sulfonatable oil present. Filtration through Fuller's earth seemed to have no effect whatever in reducing injury. For example, oil 4x is a filtered oil of the type of oil 4 and, although variation in the degree of injury resulting from the use of these two oils is sometimes seen, a comparison of the effects produced in all field work thus far shows that no distinction can be drawn between them. Oils 5 and 5x are very similar from the sulfonation standpoint, but the latter is less viscous and has a lower boiling point. It "evaporates" or rather disappears from the foliage more quickly than the former and for that reason is possibly the safer. This disappearance of an oil film from foliage is not a simple phenomenon. It seems probable that it is due primarily to absorption followed by oxidation rather than to simple volatility. This point requires much further investigation before any safe generalization can be drawn. Oil 6 has a high viscosity and boiling point and is not very highly refined, and thus caused serious injury, especially at high temperatures.

These data show that only the most highly refined lubricating oils (such as 5 and 5x) are safe enough to justify experimentation on citrus trees at summer temperatures.

Under summer conditions at Riverside, the leaf drop may begin from a week to ten days after spraying. Under coastal conditions (i.e., at Santa Paula) it may be delayed six weeks or more. Under winter temperatures with maxima of 50° to 70° F, oils of lower refinement and higher boiling point are safe to use. As a result of these tests our succeeding work involved primarily a close study of oil 5, known commercially as Oronite Crystal oil.

The kerosene type of oil shows a reaction similar to the lubricating oil, in that the raw distillate 1a was more injurious than any of the three oils 2a to 4a, having various degrees of refinement. It will be noticed that 2a is less injurious than 3a, probably owing to its greater volatility. These kerosenes are all very much safer to use than the lubricating oils, but on account of their low boiling point they evaporate relatively quickly and hence are not satisfactory scalecides except possibly for the very youngest stages of scale insects.

In general, these tests indicate that a petroleum lubricating oil, to be safely used on citrus foliage in summer, must be of a very high degree of refinement and neutrality. The "white" lubricating oils such as Oronite Crystal and Oronite Cosmetic most nearly meet this requirement. It is also evident that most kerosenes are safe under ordinary conditions but these oils must be eliminated because their volatility limits their insecticidal value. Their lack of injury to foliage is also in large part to be ascribed to their volatility.

PHYSIOLOGICAL EFFECT OF NEUTRAL WHITE OILS ON CITRUS TREES

While the neutral white oils such as Oronite Crystal have been spoken of as non-toxic, nevertheless, their presence upon a citrus tree sometimes induces certain characteristic effects which are more or less deleterious. These effects have not been studied enough to be at all adequately understood, and hence the following statement is mainly descriptive.

The most characteristic effect is a more or less heavy leaf drop, principally of senile or semi-senile leaves. For the most part this seems to be an acceleration of a normal process. It occurs on both oranges and lemons.

The next most characteristic effect consists of fruit "injury," particularly to lemons. The most common effect is the dropping of tree-ripe fruits, which is analogous to the dropping of senile leaves. A second and more important kind of fruit injury is a more or less marked delay in the coloring of green lemons subjected to the ethylene gas treatment. In some instances this delay is almost or quite permanent. This has not yet been satisfactorily explained, but it is apparently correlated with a morphological change in the oil cells in the rind of the fruit. The effect seems to consist in a withdrawal of the essential oil contained in the oil cells and may be due to its extraction by the spray oil. As shown by Fawcett(8) in 1916 the application of its own essential oil to the rind of a growing lemon inhibits or entirely prevents normal coloration.

In certain coastal areas, notably in Orange County, it is now well known that a drop of green Valencia oranges may follow application of the Oronite Crystal oil, particularly during humid weather conditions. Furthermore, ripening may be considerably retarded.

Various other pathological phenomena are continually being ascribed to the use of this oil on citrus trees, in addition to the well established ones given above. These include claims of such effects as reduction in set of fruit, actual twig, leaf, and fruit burn, dropping of newly set fruit (analogous to ordinary heat-induced "June drop") and so on, but the data available at present are too contradictory to be evaluated without further study.

THEORY OF OIL EMULSIONS

Petroleum oil is an insecticide of great value, but on account of its inherent danger to the plant, when used in effective amounts, it has been found necessary to dilute it with a material which acts as a carrier. Water lends itself readily to this purpose, but since these two liquids are immiscible it is necessary to employ some chemical or mechanical means of dispersing the oil in droplets uniformly throughout the water.

There are two types of oil emulsions. In the first, the "oil-in-water" type, the oil is dispersed as small globules throughout the water. In the second, the "water-in-oil" type, the reverse system is found. The prevailing type of oil emulsion used in insecticidal work is of the first or "oil-in-water" type, the invert form having been studied only very recently.

The nature of the emulsion, whether of the ordinary or invert type, is determined by the kind of emulsifier as has been shown by Tinkle, Draper, and Hildebrand(9) and Bhatnagar(10). Soaps of monovalent cations form the typical oil-in-water emulsion, while soaps of divalent cations, such as calcium oleate, make the invert form of emulsion with oil as the external phase.

Parsons and Wilson(11) have shown the possibility of inversion of an emulsion by mixing solutions of sodium oleate in water with magnesium oleate in oil. The addition of di- and trivalent salts such as magnesium sulfate and ferric chloride inverted the oil-in-water emulsion, for instance. Our own experiments with calcium casein mixture[6] as the emulsifier have also shown the possibility of changing the type of emulsion by varying the proportions of oil to emulsifier.

Theoretically an emulsion with oil as the external phase would be more effective than one with water as the external phase, since then the active insecticide would come immediately into direct contact with the insect. Since, however, such emulsions cannot be diluted with water and are usually of such a tough, gummy nature that they cannot be broken up readily, they do not lend themselves to orchard practice.

Quick-Breaking Oil Emulsions.—The disadvantages of the oil-in-water emulsion have been overcome to a large extent by the

[6] The commercial mixture of powdered casein and hydrated lime used as an emulsifier is, in solution form, commonly spoken of as "calcium caseinate." This term will be used henceforth in this paper. The proportions of casein and lime are approximately 1 to 4.

development of a "quick-breaking" type of emulsion, which allows the water to separate out immediately on contact and run off, leaving a film of pure oil on the leaf surface. This brings the active insecticide, oil, instead of water or a hydrated colloidal solution, into direct contact with the insect. Neither water nor a hydrated colloidal solution has any practical insecticidal value. The "quick-breaking" emulsion thus increases the insecticidal action to such an extent that the almost prohibitive cost for an effective stable emulsion made from such highly refined lubricating oils as Oronite Crystal, is reduced to a point where these oils are economically practicable for orchard spraying.

The type of oil emulsion generally used in insecticidal work is that in which the oil is broken up into the smallest possible globules and distributed uniformly throughout the water. When this is accomplished, and the oil remains thus dispersed for an indefinite period of time without separation, the resulting mixture is known as a "stable" emulsion. If there is a tendency in the course of a short period of time for the oil to separate from the mixture, the emulsion is known as "unstable." Within certain limits this instability varies inversely as the percentage of the emulsifying agent.

In practice it appears that the strength of the interfacial membrane which separates the two phases of an emulsion varies a great deal, according to the emulsifier used. Some, such as are formed by "sodium-fatty-acid" soaps, are apparently very elastic and tough; others, such as are formed by typical colloids, as, for example, starch or colloidal copper, and also by calcium caseinate, are relatively very weak and easily disrupted.

In accordance with the general principle that the stronger the interfacial membrane the more stable the emulsion, it follows that the emulsifying agent which produces the weakest possible interfacial membrane is the best from the insecticidal standpoint. On this basis casein is better than soap and a metallic colloid is better than casein.

Some emulsifiers, such as lime or kaolin and other earths, are capable of absorbing considerable amounts of oil, as well as emulsifying them. This is particularly pronounced and important when the emulsifier or spreader is used in large quantities. All such absorbed oil is unavailable for liberation as a free liquid and constitutes, therefore, a permanent loss—assuming, of course, that free oil is the effective agent. Hence, from a theoretical standpoint, the use of the emulsifier which has the least possible oil-absorptive capacity is advisable (other things being equal). Colloidal copper is an almost ideal substance in all these respects, and much superior to typical soaps, calcium caseinate, and lime. While we regard colloidal copper as a theoretically better emulsifier than calcium caseinate, the former in a pure state requires such care in its preparation and is so difficult to buy that it is impracticable for any but laboratory work. Calcium caseinate, however, is a widely distributed commercial preparation, and hence was chosen as the emulsifier for our experimental work.

In a stable emulsion of oil in water, the oil itself cannot come into contact with the object sprayed until separation of the two phases takes place, which in a highly stable emulsion may not occur except as the water disappears by evaporation. This obviously means a greater or lesser delay before the insecticidal (particularly wax-solvent) activities of the oil can begin. Secondly, it means a large loss of oil contained in the unavoidable "drip" or "run-off" from the sprayed surface. Thirdly, it appears reasonable to suppose that the interfacial film of emulsifier will be deposited as a more or less definite layer of inert substance between the oil and the leaf or fruit surface in such a way as to delay, even where it is not sufficient to prevent, the insecticidal action of the oil. This type of action would be especially important with typical "sodium-fatty-acid" soaps.

Lime, by its absorptive capacity, tends to prevent the oil from coming into direct contact with the object sprayed, and hence serves as an inhibiting factor. If we assume, therefore, that pure oil is the effective agent, it follows that the more "stable" the emulsion or the greater the absorptive capacity of the emulsifier the less value it possesses as an insecticide. This point was brought out early in 1925 by deOng and Knight(12) in a preliminary note based upon this project.

Most of the emulsions now on the market use various "sodium-fatty-acid" soaps as the emulsifying agent. While soap itself, owing to its fatty-acid content, is a weak insecticide, and may be fairly effective against soft-bodied insects like aphis and young scale insects, it is almost certain that when used as an emulsifier it is probably never in concentration sufficiently strong to be independently effective. This was demonstrated in our laboratory work when very strong solutions of many different soaps applied as sprays failed to affect a satisfactory kill of red scale, which is an armored species.

LABORATORY EXPERIMENTS WITH OIL EMULSIONS

For the purpose of routine insecticidal tests in the laboratory, the red scale, *Chrysomphalus aurantii* (Maskell), of the strain which has developed a resistance to HCN fumigation under orchard conditions, was chosen. So far as known, this is the most difficult of all citrus scales to kill by spraying, and it was assumed that if a spray could be developed which would kill this species, it would be effective against any of the others. A spray which apparently fulfills this requirement has been developed. From data thus far obtained it seems to be equally effective against the black and purple scales. This spray, however, has not yet had wide enough testing in the field to justify recommendation by this station for general use. Furthermore, as has been shown, certain peculiar effects are often produced upon the tree, which are not yet sufficiently well understood. For this spray a "neutral" white lubricating oil (Oronite Crystal oil, specific gravity 88, viscosity 106) was taken as the insecticidal agent, calcium caseinate (see p. 361) being selected as the emulsifier.

Lemons heavily infested with scale were used in the laboratory tests. Spraying was done by means of a small atomizer, and counts for determination of scale kill were made from ten days to two weeks after the application of the spray. The scale-infested lemons were hung in the laboratory during the interim.

The inhibiting effect, previously noted, of excess emulsifier was particularly well shown in an experiment wherein the amount of oil was maintained constant at 2 per cent, while the emulsifier was progressively reduced from 2 per cent to .0078 per cent (or from equal parts of oil and emulsifier to a ratio of 100 parts of oil to 0.39 parts of emulsifier). The killing efficiency was markedly accentuated as the amount of emulsifier was decreased. This is shown in table 3.

The natural mortality on checks kept under the same conditions was 49.7 per cent, or practically the same as lot 2 in table 3. The mortality was somewhat higher in lot 1 because one of the lemons had dried out. Desiccation has of itself a marked effect on the mortality of scale insects.

In the first three lots there were many live young present after treatment. Some were crawling about over the fruit while many others had just settled. Not until an oil film was formed over the surface of the fruit, was there any marked rise in the mortality. When this did occur the kill quickly rose to 100 per cent. It would seem, therefore, that the insecticidal agent is the free oil.

It is customary to use a spreader (generally calcium caseinate or glue) with many oil sprays for citrus trees. But a spreader is also an emulsifier, and tends further to inhibit the action of the oil through increased stabilization of the emulsion. Also, as in the case of certain emulsifiers such as lime or calcium caseinate, a spreader may accentuate the loss of oil through its additional oil-absorptive capacity.

TABLE 3

RELATION OF SCALE MORTALITY TO CONCENTRATION OF EMULSIFIER IN A TWO-PER-CENT EMULSION OF ORONITE CRYSTAL OIL

No.	Concentration of calcium caseinate *Per cent*	Scale surviving at end of test* *Per cent*	Remarks
1	2	32.3	Many young alive. Oil absorbed by surplus emulsifier.
2	1	49.5	Many young alive. Oil absorbed by surplus emulsifier.
3	.5	38.3	Many young alive. Oil absorbed by surplus emulsifier.
4	.25	7.5	Sprayed surface slightly greasy. No young alive.
5	.125†	0.0	Oil film just visible on sprayed surface.
6	.0625	0.0	Oil film distinct on sprayed surface.
7	.031	0.0	Well developed oil film present.
8	.015	0.0	Well developed oil film present.
9	.0078	0.0	Well developed oil film present.

* The usual natural mortality, about 40 to 50 per cent, is necessarily included in the counts.
† This corresponds to 1 pound of calcium caseinate to 100 gallons of spray.

Nothing in common use will spread better than oil. Hence in a quick-breaking emulsion a spreader is not needed. The spreading of any liquid is facilitated by reduction in its surface tension. To make oil spread better would therefore require the introduction of an oil-soluble constituent which would reduce the surface tension of the oil itself. Casein and all other such substances customarily used as spreaders are water-soluble, being practically insoluble in oil. Hence any ''spreading effect'' which results concerns the water alone and not the oil. This confusion has arisen from the mistake of considering an oil emulsion as a ''solution'' instead of as a mixture of two independent liquids.

The use of mechanical mixtures would evidently overcome this inhibiting effect of emulsifying agents. The method is not used because reliance cannot be placed upon the mechanical agitators at present in common use. But by very slightly emulsifying the oil, ordinary spray tank agitation is capable of overcoming the natural buoyancy of the separated oil droplets and of maintaining a fairly uniform suspension of oil throughout the body of the liquid. The emulsifying agent is used in quantities just sufficient to separate the oil into relatively large droplets. The interfacial membrane is consequently weak and easily broken, thus liberating the enclosed oil. There is no danger that the stability of the system will be sufficient to withstand rupture upon impact with the leaf or fruit surface, and the maximum amount of oil is consequently freed and made available. On the other hand, the oil in the tank is maintained in the form of isolated droplets, there being no continuous sheet of oil to be broken up as would be the case with a mechanical mixture.

It has been found by observation that the individual globules of oil in the type of emulsion just described vary from about 0.1 mm. to 2.5 mm. in diameter, the smaller sizes largely predominating. The presence of oil droplets of the size indicated makes possible a very quick liberation of oil from the emulsion stage, while separation is very much slower in the stable type of emulsion made of extremely minute droplets. If the drops were uniformly 1 mm. in diameter, then in a 2-per-cent emulsion, 1 cc. would contain about 40 of these globules. Now, if 1 cc. be sprayed on a flat surface at a distance of 3 feet with an ordinary atomizer it will cover a circular area about 15 inches in diameter and the oil droplets will strike at widely separated spots, resulting in a typical "shotgun pattern." To form a film of oil over a given area, enough of the emulsion must be applied so that the droplets of oil will coalesce and form a film. In other words, the time spent while spraying becomes an important factor in application, for it is possible to increase the amount of oil on a surface by long or repeated sprayings. This factor varies with pressure, size of nozzle opening, and rate of discharge.

It has been found in practice that a 2-per-cent emulsion works very well in the field. If less than 2 per cent of oil is used, complete coverage will not be obtained without the use of excessive time in spraying. If more than 2 per cent is used there may be an undue accumulation of oil on the tree. In these sprays, raising the percentage of oil results merely in the liberation of more oil in the same period of time. The chief need in sprays of this type is the formation of a film of oil over the entire surface of the plant and the insect.

In the following test the emulsifier was varied from 5.0 to 0.0078 per cent while the oil remained constant. The emulsion was sprayed on a glass surface, the "run-off" collected and a quantitative determination of the oil present made.

Thus, as shown in table 4, the quantity of oil in the "run-off" from highly stable emulsions distinctly increased over that of the original concentration, so that the recovered drip was actually richer in oil than the original spray. It is only with quick-breaking emulsions that the oil percentage in the drip falls markedly below the original concentration. In the best of these, which corresponds to the one adopted for our general work, the drip even then contains 0.34 per cent of oil or about one-sixth of the original amount.

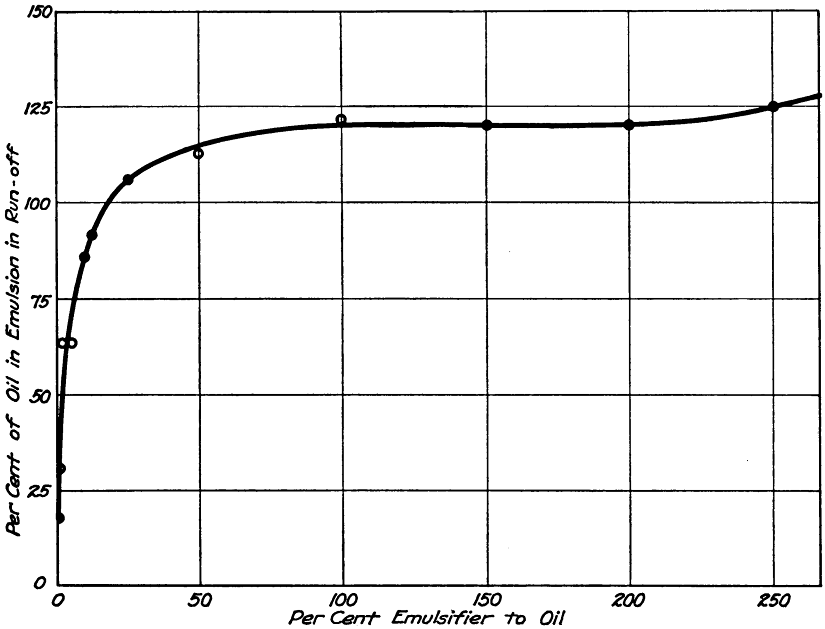

Fig. 2. Relation between amount of emulsifier used and the concentration of oil in the run-off from two-per-cent emulsions.

In experiments to obtain further evidence on the conditions of stability, emulsions were made as usual with Oronite Crystal oil. The standard emulsifier used was a mixture of powdered casein, selected for high solubility, and hydrated lime, the proportions being 1 to 4. Soap used in varying proportions as the emulsifier gave essentially similar results and hence these additional detailed data are not given.

A brief study brought out the following points in this connection. A stable emulsion containing 2 grams of oil to 98 grams of water was produced, (1) when 0.4 to 0.6 per cent of the 1 to 4 mixture of casein and hydrated lime was used; (2) when casein, dissolved in an amount of sodium hydroxide giving a hydroxyl concentration equal to that of the hydrated lime used in (1), amounted to 0.1 per cent, which corresponds approximately to 0.4 per cent of the 4 to 1 calcium casein mixture; and (3) when hydrated lime without casein was present in

TABLE 4

AMOUNT OF OIL IN RUN-OFF FROM A TWO-PER-CENT EMULSION MADE WITH VARYING AMOUNTS OF EMULSIFIER

Formula number	Calcium casein mixture *Per cent*	Ratio of emulsifier to oil *Per cent*	Ratio of concentration of oil in run-off to concentration in emulsion *Per cent*	Oil in run-off *Per cent*
1	5.0000	250.00	125.0	2.50
2	4.0000	200.00	120.0	2.45
3	3.0000	150.00	120.0	2.40
4	2.0000	100.00	122.0	2.44
5	1.0000	50.00	112.0	2.30
6	0.5000	25.00	106.0	2.20
7	0.2500	12.50	92.0	1.82
8	0.2000	10.00	86.0	1.70
9	0.1000	5.00	63.0	1.32
10	0.0500	2.50	63.0	1.24
11	0.0310	1.50	31.0	0.64
12	0.0078	0.39	17.0	0.34

the proportion of 0.6 to 0.8 per cent. The casein was found to be the more active emulsifying agent but the lime increased the general resulting stability. The principal value of the lime is in forming an alkaline solution, since casein dissolves in an acid or alkaline medium but not in a neutral one. A slight excess of lime also aids in neutralizing some of the soluble salts found in water which might hinder emulsification. Ordinary soap is now seldom used in spray practice for making emulsions, because the sodium base reacts with the calcium and magnesium salts in solution in many waters, forming insoluble soaps such as calcium oleate, thus causing the emulsion to break prematurely.

It was found, as the result of laboratory spray tests, that Oronite Crystal oil could be used effectively in emulsions of the quick-breaking type at two-per-cent concentration.

The following formula was finally developed as a standard for both laboratory and field use. The percentage values are obviously only approximate:

Oronite Crystal oil 2 per cent (2 gallons)
Calcium caseinate 0.0078 per cent (28.3 grams or 1 ounce, approximately)*
Water 98 per cent (98 gallons)

* As a result of field experience during the two years since this manuscript was originally prepared for publication it has been found that owing to the very general inefficiency of the average spray tank agitator, it is best and safest to use two to three times this quantity of emulsifier. This is not sufficient to noticeably affect insecticidal results, at least in the field.

In this formula the calcium caseinate is present in the proportion of 1 part to 200 parts of oil. In the laboratory the calcium caseinate is first dissolved in the water, then the oil is added and the whole violently shaken in order to produce emulsification. In the field a slightly different procedure is necessary. The calcium caseinate is first completely dissolved in about a quart of water. It is then added to from twenty-five to fifty gallons of water in the spray tank. The oil is next added and the agitator is started at the same time. The tank is then filled with water while the agitator is running. The emulsion is then ready to apply.

There is one point peculiar to this type of spray which is of considerable practical importance. The oil droplets are large and highly buoyant, and therefore quickly float to the surface of the water and form a definite layer or sheet of oil, which is, however, still emulsified. Vigorous agitation is, therefore, required to keep the spray of uniform consistency throughout. Only spray rigs which possess the most efficient type of agitator should be used to apply oil emulsions as quick-breaking as the one described above.

This spray has given 100 per cent kill of resistant red scale *in the laboratory*, where every scale insect was actually treated. In the field, owing to the impossibility of complete coverage and the possible effects of other factors this efficiency has never been attained.

FIELD TESTS OF A QUICK-BREAKING EMULSION

The quick-breaking Oronite Crystal oil emulsion previously described has been tested in the field. The formula found most satistory in the laboratory tests was used. As previously indicated, the resulting kills have never been as efficient(as might be expected) as those attained in the laboratory work. The results are shown in table 5.

These kills resulted from very careful application. The percentage surviving from average commercial spraying with the same material would no doubt often be above these figures. The results given are based on counts made on the fruit. Less satisfactory results occur on the twigs, possibly because of their greater oil-absorptive capacity, thus resulting in a less permanent oil film.

The criterion of effective application is complete coverage resulting in the presence of a visible film of oil over the entire surface of the plant, after the water carrier has evaporated.

TABLE 5

MORTALITY OF RED SCALE IN FIELD TESTS OF A QUICK-BREAKING TWO-PER-CENT EMULSION OF ORONITE CRYSTAL OIL

Place	Per cent of scale† surviving on fruit at end of test
Riverside, Calif.	5.05 and 2.94 (2 plots)
Whittier, Calif.*	7.95
La Habra, Calif.*	2.96
Santa Ana, Calif.*	2.13 (On purple scale, *Lepidosaphes beckii* (Newman), 2.00)
Tustin, Calif.*	3.43
Santa Barbara, Calif.	5.86 and 3.90 (2 plots)
Lindsay, Calif.	7.8 and 0.0 (2 plots) (on the citricola scale *Coccus pseudomagnoliarum* Kuwana)
Average	4.0

* Resistant-scale areas.

† The red scale *Chrysomphalus aurantii* (Mask.) is meant except as otherwise noted.

EXPERIMENTS RELATING TO THE NATURE OF THE INSECTICIDAL ACTION OF NEUTRAL OILS

The following test illustrates the essential blandness and "neutrality" characteristic of these white, highly refined petroleum oils, a fact which finds further confirmation in that it is this type of oil which is utilized in human medicine. Coleman's mealybug (*Phenacoccus colemani* Ehr.) were continuously immersed in Oronite Crystal oil and examined twice a day until all had died. Death was assumed to take place concurrently with cessation of all bodily movements, as determined by absence of response to stimulation by a needle.

Table 6 includes the combined results of two distinct tests. The same data are shown graphically in figure 3.

Some supplementary data on other insects were obtained which check very well with the results recorded above.

Thus with cabbage aphis (*Aphis brassicae* Linn.), out of eight individuals which were tested two were still alive after 18 hours' immersion in the oil. There is little doubt that aphids on the whole are more susceptible than mealybugs.

Larvae of the orange tortrix (*Tortrix citrana* Fern.) likewise survive a considerable period of immersion in this oil. In one test involving two individuals, one specimen was dead at the end of the 72nd hour and the other at the end of the 96th. In this case cessation of the pulsation of the dorsal vessel was taken as indicative of death.

In the case of ladybird beetles (*Hippodamia convergens Guerin*) visible movements cease in from 3 to 7 minutes.

TABLE 6

SURVIVAL OF COLEMAN'S MEALYBUG IMMERSED IN ORONITE CRYSTAL OIL

Hours elapsed since beginning of test	Insects dead	Insects still living
0	0	40
68	1	39
72	6	33
77	4	29
96	1	28
114	4	25
120	5	20
144	2	18
148	1	17
160	1	16
166	1	15
184	4	11
240	3	8
264	1	7
288	2	5
294	2	3
312	1	2
336	1	1
384	1	0
Totals (end of test)	40	0

Average time of lethal immersion, $\frac{6524}{40} = 163$ hours, or nearly 7 days.

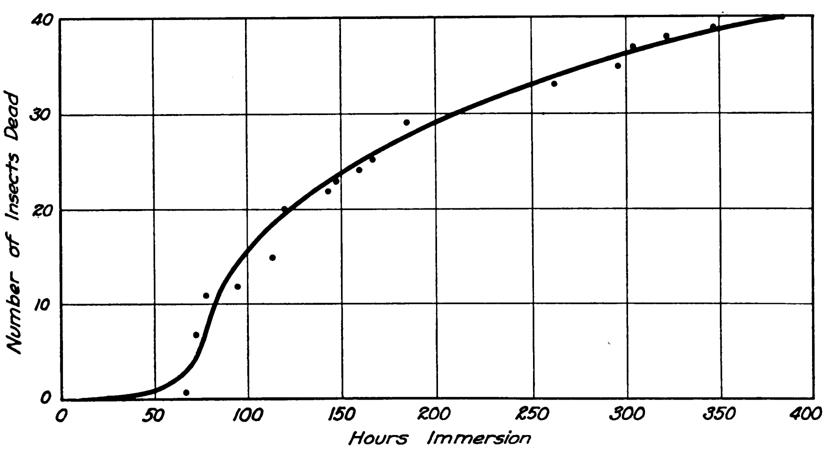

Fig. 3. Lethal curve of Coleman's mealybug, *Phenacoccus colemani* Ehrhorn, immersed in Oronite Crystal Oil.

The contrast between the long period of immersion required for mealybug and the shorter one for beetles was puzzling. As a check, beetles were immersed in tap water, and the apparent anomaly was then explained. Furthermore, there were obtained some data confirming our belief that the lethal effects of these highly refined oils could be explained almost solely upon the basis of suffocation.

Beetles were floated to the top of a water-filled, inverted test tube, and it was found that all visible movements ceased within practically the same length of time as in the oil. That cessation of movement in this instance was not indicative of death was clearly shown when beetles that had been immersed in water for several hours revived very rapidly upon being warmed and dried. This indicates that with these insects at least, cessation of movement is not a definite criterion of death.

There is little doubt that oil-immersed beetles would likewise revive rapidly and completely if the adhering oil could be dissipated as completely and rapidly as the water. The fact that they do not do so indicates that enough oil adheres permanently to the body and completely covers the spiracles so that the insect cannot be removed from its oil bath.

Mealybugs were likewise treated with water as a lethal agent. Four insects so immersed for four hours and apparently dead, all movement having ceased, revived completely. In a succeeding check test ten mealybugs were kept under water for a period of five hours. Of these only two revived. These results indicate a very much lower average lethal immersion limit for water than for oil. Movement ceases much sooner in water than in oil.

As a final test of the "oxygen-deprivation hypothesis" eighteen mealybugs were placed in an atmosphere of pure hydrogen, which is essentially inactive so far as living organisms are concerned. Impurities due to the processes of generation were doubtless present in some degree, but on the whole the results check very well with those previously given. Of the eighteen specimens treated eleven were dead at the end of 24 hours; four more at the end of 48 hours and the remainder (thirteen) at the end of 72 hours. This is an average lethal immersion period of 64 hours, approximately two and one-half days.

In view of the foregoing data, it may be stated that death of scale insects through the action of white neutral oils may be ascribed almost entirely to suffocation. At least, this one factor offers a satisfactory explanation for all the known facts.

After the completion of the original draft of the manuscript of this paper it was found that we had overlooked two important articles bearing upon this same subject, written by George D. Schafer (13, 14) in 1911 and 1915 respectively. It is unnecessary to review his conclusions relative to our work, which was done entirely independently, but it is worth while to note that our results bear practically the same implications and are confirmatory of his conclusions on the subject of oxygen deprivation.

TABLE 7

RELATION OF VISCOSITY OF OIL TO ITS EFFECT ON RED SCALE

No. of test	Oil description	Viscosity	Percentage of oil in emulsion	Per cent scale surviving test*	Remarks
1	Castor oil	1840	2	48.0	No more than natural mortality.
2	No. 6, a heavy lubricating oil	364	2	0.0	
3	Oronite Crystal oil	100	2	0.0	
4	A special light lubricating oil (specifications not given)	38	2	2.0	This oil was just below the lethal viscosity limit.
5	No. 4a, a refined kerosene	21+	20†	19.0	

* The basis for scale counts ranged from 200 to 600 insects.

† In spite of the high percentage here used only a very poor kill was obtained; at 2 per cent only the natural mortality would have been found.

In laboratory tests, oils within a rather wide range of high viscosity, other things being equal, gave complete control. Below the minimum of this range, the lighter an oil the less certain will be the kill. On the other hand, extremely high viscosities are likewise ineffective. These facts are illustrated in table 7, which is based upon laboratory tests.

Under the heading "viscosity" are given a series of values which are approximate only. Oronite Crystal oil was arbitrarily taken as a standard and assigned a value of 100. The values were determined by measuring the time of flow of 50 cc. of the oil from a small burette at a constant temperature.

These tests were made with the resistant red scale (*Chrysomphalus aurantii*). All emulsions were of the quick-breaking type.

These oils (excepting castor oil) are all almost entirely non-toxic, and castor oil even with its toxicity fails to kill. Evidently castor oil and oil 4a are ineffective for different reasons. In the case of castor oil the cause is probably mechanical, as this oil is apparently too viscous to spread evenly and form a continuous film. In the case of oil 4a, on the other hand, the oil evaporates so quickly that a film is not maintained long enough to kill the more resistant individuals. The minimum viscosity[7] limit for complete killing evidently lies somewhere between Oronite Crystal oil and the "special light lubricating oil" used in this test.

Dilution tests (table 8) were then made and found to conform in general to the conclusion just stated. Kerosene distillate was used in making these viscosity reductions. These tests are not conclusive and must later be greatly extended, particularly toward the lower limits.

TABLE 8

EFFECTS OF DILUTING HEAVY OILS WITH KEROSENE DISTILLATE

Oil	Viscosity	Percentage of oil in emulsion	Percentage scale surviving test
Castor oil plus kerosene distillate	74±	2	0.0
Oronite Crystal oil plus kerosene distillate	45±	2	0.0
Oil 6 plus kerosene distillate	100	2	0.0

Kerosene distillate is of itself ineffective, but when its viscosity is increased by the addition of castor oil (or vice versa) a kill is immediately obtained. Toxicity is of paramount importance in assigning practical limits to degrees of volatility (viscosity) permissible in a given oil. For instance, an oil which might be volatile enough to disappear completely in one hour, if also sufficiently toxic to penetrate and kill the most resistant individual scales treated in thirty minutes, would obviously be entirely effective as a spray material. On the other hand a non-toxic oil which would volatilize completely in ten days would not suffice to kill red scale. The importance of these two factors lies not so much in their *absolute* as in their *relative* values.

[7] The terms 'low viscosity' and 'high volatility' cannot be used interchangeably in all cases. Oils from a similar source, distilled at the same range of temperature will be quite uniform in viscosity, but in the process of refining, the viscosity changes enormously, while volatility may remain constant. The blending of oils of different viscosities may also destroy the correlation between viscosity and volatility.

PRELIMINARY TESTS OF TOXICITY OF INSECTICIDAL MATERIALS

Table 9 gives data relating to the toxicity of a series of oils and other substances. These values should be self-explanatory in view of the preceding discussion. The tests were not all made in the same way and on the whole can be relied upon to give an idea of relative toxicity, but not of the minimum lethal limit, which is ultimately the most important factor. Five mealybugs, *Phenacoccus Colemani* (Ehrhorn), were used in making each of the determinations. Substances are listed according to toxicity, the more toxic ones coming first.

The possibility of imparting toxicity to otherwise neutral oils through the addition of toxic constituents (fatty acids or unsaturated hydrocarbons, for instance) and hence permitting higher volatility and shortening the time of insect kill may be of great importance in future work. This raising of the volatility is also of considerable significance in decreasing plant injury. Long persisting oils may tend to upset the metabolic processes of the plant even where no immediate effect is noticeable.

TRACHEAL PENETRATION OF INSECTICIDES AND SIGNIFICANCE OF SOLUBILITY OF WAX IN OILS

A study was made of the penetration of different fractions of petroleum oils, some of the vegetable oils and other spray materials, into the tracheal system of the red scale. This work was somewhat similar to that of Moore(7) on tracheal penetration.

For this purpose specimens were chosen that had passed through the second moult but had not yet reached maturity. At this stage of development the insect is free from the scale covering and can be lifted out intact. The detached insect is placed on a slide, ventral side up, and when it is immersed in liquid the tracheal system becomes plainly visible. The low refractive index of the air-filled trachea causes them to show as black lines under the microscope. If penetration of the liquid occurs, it causes an increase in the refractive index of the liquid-filled portion with a consequent lowered visibility, and the degree of penetration becomes plainly visible.

Figure 4 is a photomicrograph showing the main branches of the tracheal system of the red scale. It will be noted that the spiracles

TABLE 9

RELATIVE TOXICITY OF INSECTICIDAL SUBSTANCES TO MEALYBUGS AS INDICATED BY PERIOD OF LETHAL IMMERSION

Rank	Substance	Time of lethal immersion	Remarks
1	Benzol	3 seconds	Chemically pure
2	Ether	10 seconds	Chemically pure
3	Grain alcohol	90 seconds	95 per cent pure
4	"Zero" rosin oil	3 minutes	Georgia Rosin Products Co.
5	Double Run Zero rosin oil.	3 minutes	Georgia Rosin Products Co.
6	Triple Zero rosin oil	3 minutes	Georgia Rosin Products Co.
7	Turpentine	3.5 minutes	Commercial
8	Double-distilled coconut fatty acid.	6 minutes (average)	Armour & Co.
9	London rosin oil	7 minutes	Georgia Rosin Products Co.
10	Oleic acid	7–12 minutes	Commercial
11	Shale oil	12 minutes (maximum)	California distilled
12	Petroleum oil 1†	17 minutes (maximum)	Standard Oil Co. of Calif. (lubricating-oil distillate)
13	Furfural	10–13 minutes	Insects only partially immersed, vapors evidently toxic.
14	Special "X" rosin oil	20 minutes (average)	Georgia Rosin Products Co.
15	Liquid asphalt.	30 minutes*	Standard Oil Co. of Calif.
16	Unsaturated hydrocarbons removed from kerosene	43 minutes (average)	Standard Oil Co. of Calif.
17	Vaseline plus water white distillate.	60 minutes*	Vaseline 1 part, kerosene 5 parts.
18	Petroleum oil 3†	60–360 minutes	Standard Oil Co. of Calif. (lubricating-oil distillate)
19	Petroleum oil 1a†	60–1200 minutes*	Standard Oil Co. of Calif. (kerosene distillate)
20	Petroleum oil 3a†	108 minutes (average)	Standard Oil Co. of Calif. (kerosene)
21	Petroleum oil 2a†	120 minutes*	Standard Oil Co. of Calif. (kerosene)
22	Petroleum oil 4a†	120 minutes*	Standard Oil Co. of Calif. (the least toxic of the kerosenes)
23	Whale oil	210 minutes*	Crude. Highly toxic.
24	Petroleum oil 2†	240–720 minutes	Standard Oil Co. of Calif. (lubricating-oil distillate)
25	Cottonseed oil	13–1400 minutes	Crude

* The definite meaning (whether average, maximum or approximate survival limit) of the value given is unknown.

† See table 1 for further specifications.

TABLE 9—(*Continued*)

Rank	Substance	Time of lethal immersion	Remarks
26	Linseed oil	30–1300 minutes	Commercial
27	Petroleum oil 4†	240–1400 minutes	Standard Oil Co. of Calif. (lubricating oil)
28	Castor oil	1400 minutes*	Refined
29	Fish oil	1400 minutes*	Commercial
30	Petroleum oil 4x†	1400 minutes*	Standard Oil Co. of Calif. (lubricating oil)
31	Olive oil	2500 minutes*	Refined
32	Petroleum oil 6†	2500 minutes*	Standard Oil Co. of Calif. (lubricating oil)
33	Petroleum oil 5x†	2500 minutes*	Standard Oil Co. of Calif. (lubricating oil)
34	Petroleum oil 7†	1200–5760 minutes	Standard Oil Co. of Calif. (lubricating oil)
35	Petroleum oil 5† (Oronite Crystal oil)	9780 minutes (average)	Standard Oil Co. of Calif. (lubricating oil)

* The definite meaning (whether average, maximum or approximate survival limit) of the value given is unknown.

† See table 1 for further specifications.

are connected with each other by four large tracheal trunks. In addition a large number of smaller branching tubes ramify to all parts of the body. For purposes of comparison the spiracle-connecting trunks of the tracheal system are divided into three areas designated as A, B and C.

That portion of the trunk extending from the opening of the spiracle to the point where the trachea first branches is designated A. About one-third of the distance between the spiracles along the main tracheal trunk is designated B, and the entire distance C. In figure 4, these distances are shown from one spiracle only. When the oil penetrates far enough to fill the four trunks it has usually, at the same time, completely filled the smaller branches.

Table 10 shows that neither lime-sulfur solution (in ordinary dilution) nor Bordeaux 5–5–50 showed any penetration at all. When lime-sulfur and a proprietary miscible oil were combined there was a fair degree of penetration. All emulsions of the lubricating-oil type, as well as the lubricating oils themselves, gave good penetration, filling the entire tracheal system. The kerosenes, on the other hand, were very erratic in behavior. Initial penetration (2–8 minutes) was in nearly all cases very rapid but in a considerable number of instances this gradually ceased, and movement of the liquid was reversed so that the tube emptied itself. Apparently the insects have the power of expelling these light oils from the tracheae. Furthermore, they are then able to keep these oils from penetrating for more than 30 to 40 minutes. This ability of the insect, particularly when taken

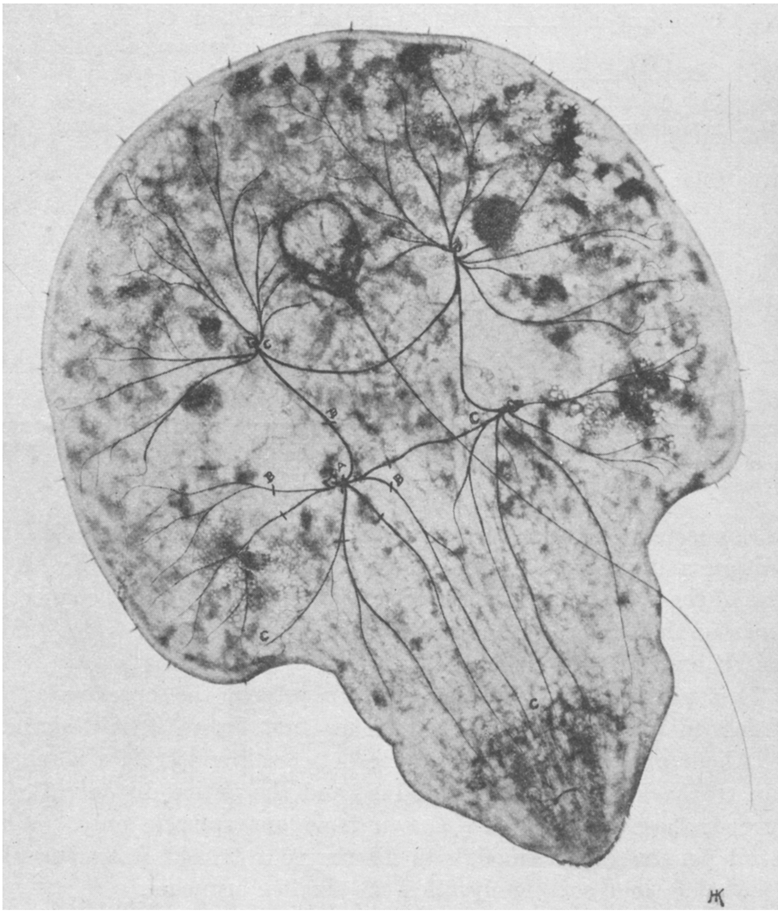

Fig. 4. Ventral aspect of the red scale, *Chrysomphalus aurantii* (Maskell), showing the tracheal system.

in connection with the high volatility of the oils, excludes the kerosenes from the class of satisfactory scalecides even though their toxicity is relatively high compared with that of neutral lubricating oils.

In these tests it was found that soaps, oils, stable emulsions and water-glue solutions were capablé of penetrating into the tracheae of these detached insects. In some cases, as in highly stable oil emulsions and lime-sulfur oil mixture, the penetration seemed to be that of the emulsion itself. This seems to raise a question, considering the emphasis previously laid upon the necessity of oil liberation. It is obvious that anything, whether a pure oil or an emulsion, which would completely clog the spiracles would ultimately suffocate the insect.

TABLE 10

TRACHEAL PENETRATION OF RED SCALE BY INSECTICIDAL SUBSTANCES

Material	Tracheal penetration
Sprays:	
Lime sulfur, 2 per cent	None
Lime sulfur, 10 per cent	None
Lime sulfur, 20 per cent	A
Lime sulfur, undiluted	A
Bordeaux, 5-5-50	None
Miscible oil, 2 per cent and lime sulfur, 1 per cent	B
Commercial oil emulsion, 5 per cent (standard type)	C
Fish-oil soap and Oronite Crystal oil emulsion, 6 per cent	C
Fish-oil soap and No. 6 petroleum oil emulsion, 6 per cent	C
Fish-oil soap and kerosene distillate (Oil No. 1a) emulsion, 6 per cent	Erratic, initially rapid
Fish-oil soap and kerosene oil No. 2a emulsion, 6 per cent	Erratic, initially rapid
Bordeaux and Oronite Crystal oil emulsion, 6 per cent	C
Ferrous sulfate and Oronite Crystal oil emulsion, 6 per cent	C
Oils (pure):	
Oronite Crystal oil (No. 5)	C
Petroleum oil No. 6	C
Kerosene, No. 2a	C
Kerosene distillate, No. 1a	C
Cottonseed oil (Crude)	C
Oleic acid	B
Turpentine	B
Linseed oil	C
Miscellaneous:	
Tap water	None
Sodium silicate (water glass)	A
Xylol stained with Sudan III	Erratic, ultimately complete
Xylol (pure)	C

The paradox is explicable, however, when we consider the penetration of the trachea of an insect *in situ*. Here the armored scale (red scale), which was the subject of discussion in connection with the liberation of oil from quick-breaking emulsions, is completely protected by both a dorsal and a ventral waxy scale covering. For the insecticide to come into actual contact with the spiracles necessitates first of all penetration of this scale covering. Water is not a wax solvent and is hence completely excluded from penetrating this covering. The same consideration applies to any water mixture, including stable emulsions wherein water is the continuous phase and where little or no oil liberation takes place. Free oils on the other hand are not only capable of tracheal penetration but are wax solvents as well and hence capable of penetrating the scale covering. In a stable emulsion the oil is kept largely locked up and hence can exert no independent effect upon the wax.

This explanation is borne out by the fact that miscible oils (as is found in current practice in the field) may be fairly effective against the unarmored black scale (*Saissetia oleae* Bernard), where the spray is able to gain unobstructed access to the tracheal opening, while they fail in large degree in the case of red and other armored scales.

VEGETABLE OILS

In addition to the petroleum oils, certain vegetable oils were tested as spray materials. These include cottonseed, linseed, castor, and rosin oils. These are all much more toxic to insects (as indicated in table 9) than neutral white oils, no doubt on account of their fatty-acid content. These fatty acids seem in general to correspond to the unsaturated hydrocarbons of the petroleum oils. Like the latter, they are toxic to plants as well as to insects, although in many instances at least, to a less degree.

The most promising of the vegetable oils tested was cottonseed oil. In the field this gave an excellent kill of scale, but defoliation was considerably more severe than was the case with Oronite Crystal oil. There is a great field for future investigation of vegetable oils in connection with insecticidal spray work.

COCONUT FATTY ACID

In view of the widespread interest in the recent development of the use of coconut-oil fatty acids by Siegler and Popenoe(15), it is well to call attention to the fact that while they undoubtedly have marked insecticidal properties, they are also exceedingly toxic to plant tissue when used in concentrations even remotely approximating those necessary to kill armored scale insects of citrus. The following test shows this conclusively.

An emulsion was made with equal parts of fatty acid and gasoline, as recommended in the reference quoted, but the amount of glue was reduced so as to make an emulsion of the quick-breaking type. This mixture was diluted with water until the emulsion contained 2 per cent of the fatty acid. A potted citrus plant was sprayed with this emulsion with disastrous effect. It was completely defoliated and both the leaves and the twigs were badly burned and spotted.

Lemons infested with red scale were sprayed with the same emulsion. The fruit was burned and shriveled, but only 97 per cent of the scale was killed. Furthermore, at the time the examination was made (ten days after spraying) young were hatching and settling on the fruit. In this instance, although severe injury resulted to the plant and fruit, the scales were not all killed. This failure is probably due in large part to lack of wax solubility, with consequent inability to penetrate the scale covering. This material would probably be much more effective against the unarmored black scale (*Saissetia oleae*).

On diluting the emulsion one-half, so that it contained 1 per cent of fatty acid, a mortality of only 83.4 per cent was found and the fruit was again shriveled.

The test was repeated without the gasoline in order to get the full effect of the undiluted fatty acid. An application of a two-per-cent emulsion left only 0.66 per cent of the scale alive but severely injured both the fruit and plant.

Finally a stock emulsion was applied, made according to the formula recommended, with its full complement of glue (giving a stable emulsion) and containing 2 per cent of fatty acid (or 80 times as strong as recommended for aphids). No injury to the plant resulted from this application. When the determination of insect mortality was made, there could be found no indication that an insecticide had been applied, the count showing mortality of 43.6

per cent, which is equivalent to natural mortality only. The spray had proved totally ineffective. Young scale were found crawling freely about within two days after the application.

These tests again confirm the conclusions previously reached regarding the necessity of a quick-breaking emulsion in order to liberate the insecticidal agent for effective use.

SUMMARY

1. Petroleum oils of the kerosene and "stove-distillate" type (28°–32° A.P.I.) have been occasionally used as insecticides over a period of many years in citrus orchards, with varying results as to insecticidal effects and injury to the tree and fruits.

2. Non-viscous oils of a low boiling point, such as the kerosenes, are safer to use on the tree than those of high boiling points, but are unsatisfactory as scalecides because of relatively low toxicity combined with high volatility.

3. Highly refined, white lubricating oils are probably the most advisable for use on citrus trees, especially at summer temperatures. Oils of a low viscosity are apparently safer to use on trees than those of high viscosity. This is due to the more rapid disappearance of the former.

4. Severe injury to the citrus trees from the use of lubricating oil is associated with the presence of a high percentage of unsaturated hydrocarbons. Refining petroleum oil with sulfuric acid removes the following injurious constituents: aromatics, olefins, resins, and sulfur.

5. The filtration of petroleum oils through Fuller's earth has not shown itself effective in reducing the amount of injurious constituents present.

6. Gross symptoms of injury to citrus trees from the use of unrefined petroleum oils, include defoliation, fruit spotting and dropping and the killing of twigs and branches. In addition to these injuries, there is an apparent interference with the normal plant functions of transpiration and respiration.

7. A quick-breaking emulsion utilizes to the maximum degree the insecticidal agent. Two per cent non-volatile lubricating oil with 98 per cent of water as a carrier has, when applied as a quick-breaking emulsion in the laboratory, produced a complete kill of red scale on lemons. Stable oil emulsions using the same ingredients are ineffective against this scale at strengths of from 4 to 8 per cent actual oil.

8. The "quick-breaking" action in an emulsion is greatest when the average size of the dispersed oil globules is greatest, and that size is greatest when the proportion of emulsifier to oil is least.

9. The concentration of oil in the run-off from sprays containing 2-per-cent concentration of oil varied from 2.5 per cent for the stable type of emulsion to 0.39 per cent for the quick-breaking type in laboratory tests on glass plates.

10. The insecticidal action of unrefined lubricating oils seems to be the result of two principal lethal factors. These are suffocation and toxic action, or poisoning. The former results chiefly from non-volatility (film permanence), the latter chiefly from the action of unsaturated hydrocarbons in the case of unrefined petroleum oils, or that of free fatty acids in the case of vegetable oils.

11. The wax solubility of oils is one of the important factors determining the insecticidal effectiveness of lubricating oils against the red scale. In the quick-breaking emulsions the free oil dissolves the waxy scale covering and enables the oil to penetrate to the spiracles; stable emulsions, with which the liberation of free oil does not readily occur, lack this feature to a great extent and are therefore not so effective.

12. The lethal immersion period varies from a few seconds for the most toxic substance tested to sixteen days for the least toxic.

13. Volatility limits of oil range from a few minutes or hours to several weeks.

14. Various physiological disturbances, which are highly characteristic and little understood, are induced in citrus trees by the use of "neutral" white oils in quick-breaking emulsions. These disturbances are evidenced by special types of leaf and fruit drop but not by actual burning or spotting (except possibly in rare instances).

15. Free fatty acids—while highly effective as insecticides for aphids—are not suitable for use in quick-breaking emulsions at the high concentration required for the control of scale insects, because of the injurious effects on plant tissue of such concentrations of the acids.

16. The present paper is published as a progress report on a special investigation, the results of which, while highly suggestive and important, should not be construed as constituting a recommendation for practical orchardists.

LITERATURE CITED

1. QUAYLE, H. J.
   1922. Resistance of certain scale insects in certain localities to hydrocyanic acid fumigation. Jour. Econ. Ent. **15:** 400.
2. GRAY, GEO. P., AND E. R. DEONG
   1925. Laboratory and field tests of California petroleum insecticides. Indus. Eng. Chem. **18:** 175–180.
3. VOLCK, W. H.
   1903. Spraying with distillates. California Agr. Exp. Sta. Bul. **153:** 1–31.
4. MAGNESS, J. R., AND A. M. BURROUGHS
   1921–22. Apple storage investigations. Marble Lab., Canton, Pa., Rept.
5. BURROUGHS, A. M.
   1923. Effects of oil sprays on fruit trees. Proc. Amer. Soc. Hort. Sci. **1923:** 269–277.
6. EDELEANU, L.
   1914. Refining petroleum by liquidified sulfur dioxide. Amer. Inst. Min. Eng. Bul. **93:** 2313.
7. MOORE, WM.
   1918. A study of the toxicity of kerosenes. Jour. Econ. Ent. **11:** 70–75.
8. FAWCETT, HOWARD S.
   1916. A spotting of citrus fruits due to the action of oil liberated from the rind. California Agr. Exp. Sta. Bul. **266:** 261–269.
9. TINKLE, P., H. D. DRAPER, AND J. H. HILDEBRAND
   1923. The theory of emulsification. Jour. Amer. Chem. Soc. **45:** 2780–2788.
10. BHATNAGAR, S. S.
    1921. Studies in emulsions. Jour. Chem. Soc. **119:** 61.
11. PARSONS, LEON W., AND O. G. WILSON, JR.
    1921. Some factors affecting the stability and inversion of oil-water emulsions. Jour. Indus. Eng. Chem. **13:** 1116–1123.
12. DEONG, E. R., AND HUGH KNIGHT
    1925. Emulsifying agents as an inhibiting factor in oil sprays. Jour. Econ. Ent. **18:** 424.
13. SCHAFER, GEO. D.
    1911. How insecticides kill. Parts 1 and 2. Michigan Agr. Exp. Sta. Tech. Bul. **11:** 1–65.
14. SCHAFER, GEO. D.
    1915. How insecticides kill. Part 3. Michigan Agr. Exp. Sta. Tech. Bul. **21:** 1–67.
15. SIEGLER, E. H., AND C. H. POPENOE
    1925. The fatty acids as contact insecticides. Jour. Econ. Ent. **18:** 292–299.

Transmitted June, 1926.

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