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DEPARTMENT OF REGISTRATION AND EDUCATION

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NATURAL HISTORY SURVEY
STEPHEN A. FORBES, *Chief*

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# Some Properties of Oil Emulsions Influencing Insecticidal Efficiency

BY

L. L. ENGLISH

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THE NATURAL HISTORY SURVEY DIVISION

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# FOREWORD

The first sprays used for combatting San Jose scale when it became established in the United States were made mainly from light oils, such as kerosene. Kerosene emulsion, one of the principal insecticides in use at that time, was first recommended for the control of San Jose scale by John B. Smith, of the New Jersey Agricultural Experiment Station, in 1897. During the next few years, when oil sprays were being tried for this purpose in many parts of the country, little attention was given to the standardization of the emulsion, and in some cases kerosene and water were applied in the form of a mechanical mixture made by forcing the two materials through a spray pump and mixing them in two jets discharged from the spray nozzle. Much injury resulted and many trees were killed, so that oil sprays as a class were more or less in disrepute for a number of years. Since 1917, however, there has been a marked increase in the use of oil sprays, due largely to the work of Federal and State entomologists with the so-called lubricating oil emulsions. These emulsions, made by several different formulae, have proved very effective and have largely taken the place of lime-sulfur in dormant spraying for the control of San Jose and other scale insects.

Entomologists and horticulturists generally have recognized that oil sprays as a class, while very effective, are dangerous to use unless properly prepared. In order to be sure that a spray is safe, we need to know its exact effect on insects and plants. This means that we must recognize differences in oils and differences in emulsifying agents, so as to learn what kind of emulsion to use for the result desired.

In the hope of throwing some light on these important questions concerning the use of oil sprays, the investigation herein reported by Mr. English was undertaken in February, 1925, on a Crop Protection Institute fellowship established by the Standard Oil Company of Indiana. The project was directed by a committee composed of W. P. Flint, J. S. Houser, J. J. Davis, and W. C. O'Kane, and the work was done at Urbana, Illinois, in cooperation with the Illinois State Natural History Survey.

December, 1927. W. P. FLINT.

# CONTENTS

# SOME PROPERTIES OF OIL EMULSIONS INFLUENCING INSECTICIDAL EFFICIENCY*

L. L. English

An insect's initial experience with an oil emulsion is physical. After the contact or the physical reaction, there may be chemical action. Oil, the killing agent used in emulsions, is not highly active chemically, and the oil globules are given a "coat" of material which usually is even less active chemically. As Woodman ('24) points out: "The failure of a spray is not usually due to a lack of toxicity but rather to the absence of certain desirable physical properties." These properties have been considered in the investigations of Cooper and Nuttall ('15), Moore and Graham ('18), and others, but their importance has not been given sufficient attention in actual spray practice.

The term "oil emulsion" is often used with the incorrect inference that all oil emulsions are alike. Some emulsions are suitable for application to foliage, while others are not. Some are more effective than others on scale insects, and those that are effective on scale insects may not be effective on aphids. The more the subject is investigated, the greater becomes the variety of oils and the larger the number of emulsifying agents encountered. Each oil, each emulsifier, and each class of insect pest introduces factors that must be considered more or less separately.

It is very difficult to isolate any one property of an emulsion and determine separately its action on insects. The physical and chemical properties of the oil, the kind and amount of emulsifying agent, and the stability of the emulsion are all so closely interlocked that one property usually cannot be varied without changing the others. There is good reason for believing that no two emulsions—and, very likely, no two lots of an emulsion made by the same formula—are *exactly* alike. The "individuality" of any emulsion will depend upon the way in which it is put together, the manner and duration of manipulation, the type and amount of emulsifying agent, the kind of oil, the quality of water, and the temperature at the time of dispersion. Ordinarily, with the same amount of

* This paper was submitted as a thesis for the degree of doctor of philosophy in entomology at Iowa State College of Agriculture, 1927.

emulsifying agent, and the same treatment, an oil of 80 to 100 viscosity* is easier to emulsify than one of 30 to 40 viscosity. Hence, the latter more nearly approaches the unstable, "quick-breaking" type of emulsion. Generally, the inert emulsifying agents, such as gums, calcium caseinate, glue, etc., at the usual concentrations, give less stable emulsions than fish-oil soaps or petroleum soaps. Everything else being equal, a reduction in the amount of emulsifier reduces stability.

The relative size of the globules of oil is an indication of the stability of an emulsion, and for lack of a better criterion this is used in correlating stability with efficiency. Very minute (1 micron or less), uniform globules, exhibiting pronounced Brownian movement, indicate a very stable emulsion. But a wide range in the size of the globules (from 1 micron to 30 or 40 microns) indicates a relatively unstable emulsion. The homemade, boiled emulsion of fish-oil-soap and lubricating oil is of this latter type. Such an emulsion may be less stable than one having relatively large (10 to 15 microns), uniform droplets. Two emulsions that look identical under the microscope may differ in stability; one may be more stable than the other because of an excess of emulsifier, a different emulsifier, or the kind of water used for dispersion.

The properties of oil emulsions which have been found to be important and which will be discussed are:

I. Physical properties—
  (1) Wetting ability of the emulsifying agent.
  (2) Volatility and viscosity of the oil.
  (3) Stability of the emulsion.

II. Chemical properties—
  (1) Saturated oils.*
  (2) Unsaturated oils.*

## THEORY OF WETTING

Various efforts have been made to establish criteria of wetting.† Robinson ('25) was unable to find a definite relation between the surface tension of the liquid and its spreading ability. Neither did he find the interfacial tension of an oil-water system to be a suitable indication. The same idea was used by Smith ('16) and by Cooper and Nuttall ('20). As there is no satisfactory technique for measuring the interfacial tension of a liquid in contact with a solid, these workers substitute a heavy oil for the solid. Measurements of this kind certainly give some indication

* See definitions, *Appendix A*.

† There are differences of opinion, especially among entomological workers, as to the distinction between wetting and spreading. Indeed, there is some doubt whether or not there is a real difference between the two phenomena. Consequently, there is no agreement as to what criterion should be used in determining the wetting ability of a spray. Woodman ('24) does not regard wetting and spreading as synonymous terms. He treats the contact-angle theory of wetting, but uses the amount of spray adhering to a glass slide as the measure of wetting. He states, however, that this is somewhat unsatisfactory. Moore ('21) and Nuttall ('20) also make a distinction between the two terms. But neither of the terms is well defined, and it is difficult to separate the two ideas, even if there is a real difference between them. For practical purposes, then, it may be just as well to continue to use both terms, although there seems to be no fundamental distinction. Freundlich ('22) uses the term "spreading" in speaking of liquid-liquid systems and the term "wetting" in speaking of liquid-solid systems, but exactly the same types of physical relations are involved in both.

of the relative wetting ability, but the index that is really wanted is the action of a particular spray on a particular solid. This index is expressed by the angle of contact.

The angle-of-contact theory is treated in various textbooks on physics and also by Freundlich and others of the authors previously mentioned. The discussion by Sulman ('20) is particularly good.

If a drop of liquid is in contact with a solid (Figure 1), three forces are involved: the surface tension of the liquid, $T_1$; the surface tension of the solid, $T_2$; and the interfacial tension of liquid-solid, $T_{12}$. The two latter, of course, are not measurable. The liquid meets the solid at a definite angle of contact at the point P. The forces $T_1$ and $T_{12}$ tend to draw the drop into a sphere. The force $T_2$ is acting in the opposite direction and tends to cause the liquid to spread out over the solid. When the liquid does not spread or does not contract, the system is in equilibrium and the forces acting in opposite directions are balanced. This is expressed by the equation, $T_2 = T_{12} +$ the component of $T_1$ which is acting in the same direction as $T_{12}$ and opposite to $T_2$. This component, by trigonometry, is $T_1 \cos \Theta$. The equation for equilibrium then becomes,

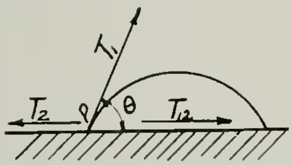


Fig. 1. Diagram of Forces That Determine the Ability of a Liquid to Wet the Surface of a Solid.

$$T_2 = T_{12} + T_1 \cos \Theta$$

If the equation is transposed,

$$\cos \Theta = \frac{T_2 - T_{12}}{T_1}.$$

Thus it will be seen that the angle $\Theta$ is a function of all three forces. For a condition of non-wetting, the angle of contact would be 180° and, theoretically, the drop of liquid would touch the solid at one point. For perfect wetting, the angle would be zero and the liquid would lie flat over the solid. Between zero and 180° there is partial wetting; and the smaller the angle of contact, the greater the wetting ability. For example, in Figure 2*A* where the system is in equilibrium at 60°, the wetting ability is about twice as great as in Figure 2*B*, where the angle is 120°.

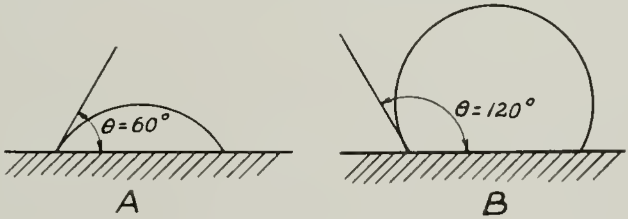


Fig. 2. Diagrams Contrasting the Wetting Abilities of Two Liquids.

## ANGLE-OF-CONTACT MEASUREMENTS

In practice it is difficult to measure the angle of contact of a drop of liquid. The force of gravity will flatten the drop somewhat; it is difficult to get drops of the same size; and the evaporation of small drops is rather rapid. Because of these difficulties it is not feasible to reflect the drop into a binocular microscope with a protractor in one barrel and measure the angle of contact. This method was tried and discarded for the simple method used by Stellwaag ('24).*

The apparatus is simple, and the method is quite rapid and entirely practical. The necessary pieces of equipment are: (1) a container for the liquid, (2) a device for holding the object to be tested, so that it can be turned, raised, and lowered into the liquid, and (3) a protractor etched on a mirror. For this particular work a museum jar (8x15x13 cm.) was used, and a device for holding the object was made from an old microscope stand. (See Figure 3.)

The jar should be perfectly level, and its rim should be coated with paraffin, so that the liquid will stand flush with the top or a little above it. Before testing, the surface of the liquid should be freshly cleaned with a glass rod. Leaves and other objects to be tested should not be handled, of course, and should be placed in the holder in a manner that will give as uniform a surface as possible. The liquid should be kept at a constant temperature.

As the object is slowly lowered, the liquid either will be depressed by it or will rise to it, forming a meniscus. The object is turned until the surface of the liquid is exactly horizontal at the point of contact. Then the angle of contact is read by means of the protractor, care being exercised to see that the bottom of the protractor coincides with the surface of the liquid and that the midpoint coincides with the point of intersection of the liquid by the object.

Suppose the liquid meets the leaf perpendicularily as in Figure 4*A*, the angle of contact is 90°. If, however, the liquid is depressed (Figure 4*B*), the angle is greater than 90°, and the leaf must be rotated to the left until the liquid meets it horizontally (Figure 4*C*).

The leaf should be inserted at an angle smaller than the proper angle of contact and slowly rotated until the liquid meets it on a horizontal

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* So far as known, Stellwaag is the first entomologist to use the angle of contact for measuring wetting ability, and much credit is due him for pointing out the action of liquids on plant leaves of different kinds and structures, and the importance of wetting in the control of aphids. This method was also used by Adam and Jessop ('25) in determining the polarity of various solids.

Trappman ('26) criticizes Stellwaag's method and prefers surface tension measurements. It is quite true that the determination of the angle of contact on leaves and twigs, no two of which are exactly alike, is subject to more variability than surface tension measurements in which nothing biological is involved. Another disadvantage of Stellwaag's method is that the surface of the liquid must be kept uncontaminated. Also, this method is not well adapted for use with coarse suspensions. But it is fundamentally correct, and, by careful and repeated observations, it affords a means of working out some of the underlying principles of spray practice.

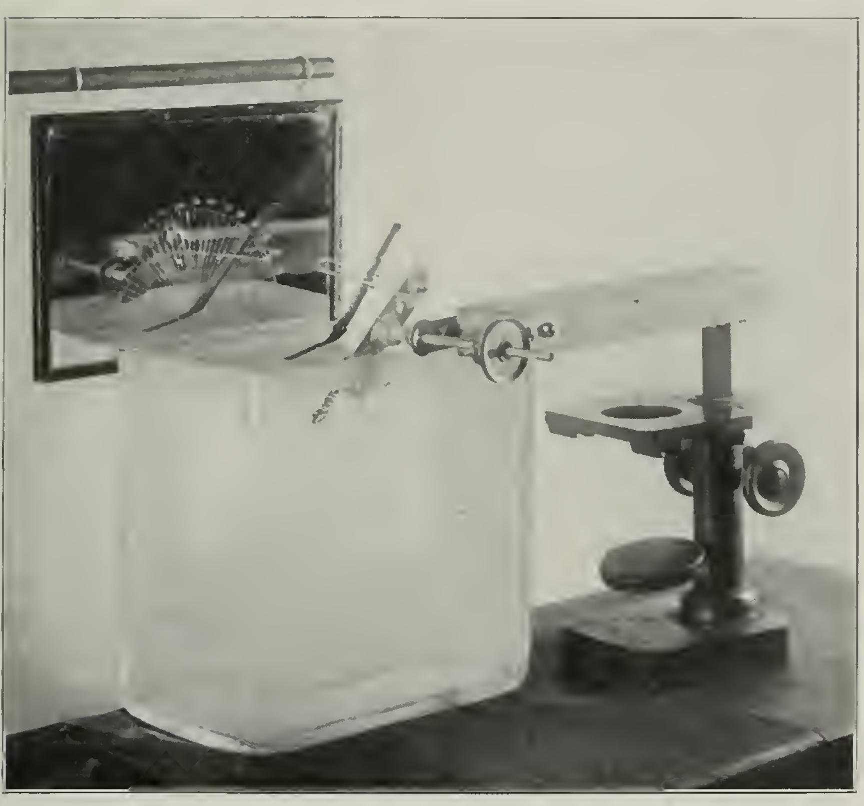


FIG. 3. APPARATUS USED IN MAKING ANGLE-OF-CONTACT MEASUREMENTS.
*(Photo by K. F. Auden.)*

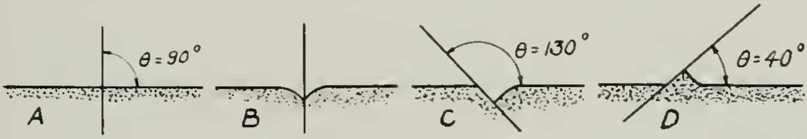



FIG. 4. DIAGRAMS SHOWING INSERTION OF A LEAF INTO LIQUIDS AT DIFFERENT ANGLES IN ORDER TO MEASURE WETTING ABILITY.

In *A*, where the liquid is neither elevated nor depressed at the point of contact, the angle is 90°. In *B*, where the liquid is depressed, the angle of contact is greater than 90°, and the leaf must be rotated to the position shown in *C*. *D* represents the position to which the leaf must be rotated when the liquid is elevated at the point of contact, the angle being less than 90°.

plane. This may necessitate several trials, especially if the angle is considerably smaller than 90°. Figure 4*D* shows the position at an angle of 40°.

It is difficult to make angle-of-contact measurements with oil emulsions because of the very thin film of oil which persistently appears on the surface; consequently, it was thought better to make a study of the emulsifying agents that were used in several emulsions. The objects to be tested were always selected fresh, and the measurements were carried out as soon after collection as possible. The liquids were kept at a temperature of 25° C. throughout the tests. From three to ten observations were made of each object in contact with the liquids at each dilution. The dilutions ranged from 1 per cent to 1/16 of one per cent. (For analysis of the water used for dilution, see *Appendix C*.)

It is not to be supposed that data thus obtained on the angles of contact represent fixed values, but they do represent relative conditions from which reliable deductions can be made.

No attempt was made to study the effect of time or repeated contact on the value of the angles. Indeed, it may be that the determinations which were made should be regarded as indications of the *initial* wetting ability. The hysteresis of liquid-solid systems is a study within itself.

Figure 5 shows the results obtained in tests with corn, oat, and cabbage leaves. These leaves were chosen because the hair-like structures on the corn and oat leaves and the waxy covering of the cabbage leaf make them difficult to wet; and the angle-of-contact measurements for each emulsifying agent against these three kinds of leaves were averaged in preparing the graphs of Figure 5. From these graphs it will be noted that the soaps give much lower angles than calcium caseinate or glue. This is to be expected, after reviewing the work of Harkins, Davies and Clark ('17) ; for glue, calcium caseinate, and such materials are not strongly polar, and are not as readily adsorbed as soaps, nor are they thrown into an interface as easily. So far as wetting ability is concerned, the soaps are in a class by themselves, both theoretically and practically, *unless* the spray mixture is of such composition as to destroy the soap.

## RELATION BETWEEN WETTING ABILITY AND TOXICITY TO APHIDS

That aphids are not readily killed by a spray that does not wet them, is well known. One of the reasons for adding soap to nicotine sulfate is to give the spray wetting ability. Stellwaag states that the effectiveness of a spray on aphids is almost entirely dependent on its wetting ability.

The curve for soap No. 15 in Figure 5 shows almost the same angle of contact at all the dilutions used. With potash-fish-oil soap and soap No. 55, the angle begins to increase quite rapidly at dilutions of ½ and ¼ per cent, as these soaps begin to precipitate out with hard water;* and at

* See analysis of water, *Appendix C.*

weaker dilutions there is insufficient soap left to give good wetting. Dilution causes no appreciable change in the angle of contact with calcium caseinate and glue. The angles with these materials are not much below those obtained with water.

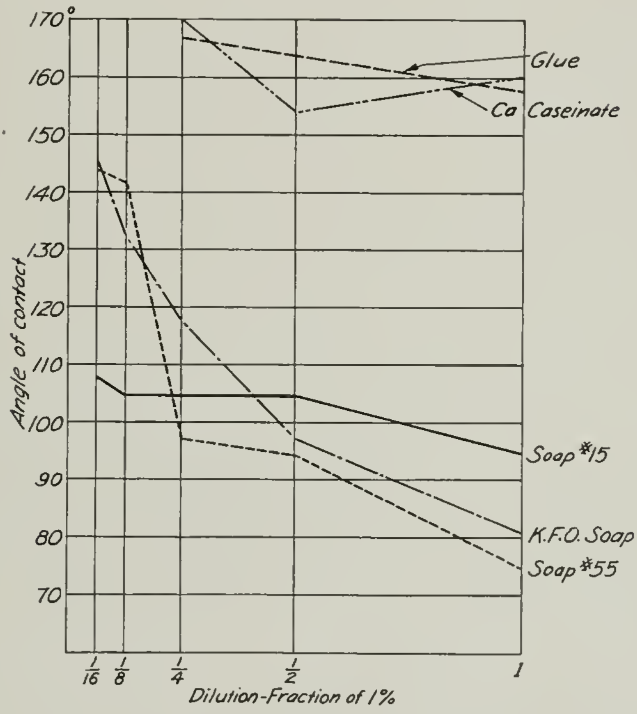



FIG. 5. CHART SHOWING CHANGES IN ANGLE OF CONTACT CAUSED BY INCREASED DILUTION.

Soap No. 15 is a petroleum product used in the preparation of soluble oils. Soap No. 55 is used for the same purpose but is made up largely of sodium oleate. KFO soap is potash-fish-oil soap.

The results of laboratory tests with three species of aphids are given in Table I. (For definitions of terms and methods of tests, see Appendix *A* and *B*.) The emulsions were diluted with tap water and were used at a strength of 2 per cent on *Hesteroneura setariae* Thos., 1 per cent on *Tritogenaphis ambrosiae* Thos., and 0.5 per cent on *Aphis pomi* De G. Here it will be noted that stock emulsion No. 5, made with an inert emulsifying agent, killed a relatively low per cent of the aphids. Homemade

TABLE I.

SUMMARY OF 17 TESTS ON APHIDS, SHOWING THE RELATIVE EFFECTIVENESS OF VARIOUS OIL EMULSIONS.

| Item | Emulsion | Emulsifying agent | Aphids killed | Aphids used | Per cent killed |
|---|---|---|---|---|---|
| 1 | Stock No. 5 | Inert [1] | 3491 | 4449 | 78.46 |
| 2 | Homemade | KFO soap [2] | 3675 | 4738 | 77.56 |
| 3 | Sol. oil No. 56 | Soap No. 55 | 2712 | 4166 | 65.09 |
| 4 | Soap No. 55 | | 3654 | 4149 | 88.07 |
| 5 | Soap No. 15 | | 3749 | 4355 | 86.08 |
| 6 | Sol. oil No. 90 | Soap No. 15 | 4074 | 4606 | 88.44 |
| 7 | Water check | | 540 | 4179 | 12.92 |
| 8 | Untreated check | | 290 | 4326 | 6.70 |

[1] Materials such as glue, calcium caseinate, and gums are classed as inert.
[2] KFO soap is potash-fish-oil soap.

TABLE II.

SUMMARY OF 5 TESTS ON *Aphis spiraecola* PATCH.
Dilution of Sprays 0.5 per ceut by weight.

| Item | Spray | Tap water | | | Distilled water | | |
|---|---|---|---|---|---|---|---|
| | | Aphids killed | Aphids used | Per cent killed | Aphids killed | Aphids used | Per cent killed |
| 1 | Soap No. 15 | 770 | 999 | 77.0 | 871 | 1032 | 84.2 |
| 2 | Soap No. 55 | 750 | 1068 | 70.3 | 951 | 1158 | 82.2 |
| 3 | KFO Soap | 358 | 1037 | 34.6 | 761 | 1024 | 74.3 |
| 4 | Ca. Caseinate | 184 | 955 | 19.3 | 157 | 968 | 16.2 |
| 5 | Water Check | 61 | 997 | 6.1 | 61 | 997 | 6.1 |

TABLE III.

SUMMARY OF 5 TESTS ON *Aphis spiraecola* PATCH.
Dilution of Sprays 1 per ceut by Volume.

| Item | Spray* | Tap water | | | Distilled water | | |
|---|---|---|---|---|---|---|---|
| | | Aphids killed | Aphids used | Per cent killed | Aphids killed | Aphids used | Per cent killed |
| 1 | Sol. Oil No. 90 | 1254 | 1346 | 93.3 | 854 | 1007 | 84.9 |
| 2 | Sol Oil No. 17 | 1194 | 1239 | 96.4 | 924 | 1057 | 87.3 |
| 3 | Sol. Oil No. 56 | 816 | 1046 | 78.3 | 657 | 962 | 68.3 |
| 4 | Stock No. S15 | 748 | 980 | 76.3 | 645 | 989 | 65.3 |
| 5 | Stock No. 5 | 581 | 991 | 58.6 | 367 | 803 | 45.7 |
| 6 | Water Check | 129 | 817 | 15.8 | 129 | 817 | 15.8 |

* Soluble oils Nos. 90 and 17 are emulsified with soap No. 15; soluble oil No. 56, with soap No. 55; stock emulsion No. S15, with potash-fish-oil soap; and stock emulsion No. 5, with a material similar to calcium caseinate.

emulsion and soluble oil No. 56, which are made with soaps that precipitate out with hard water, also show inefficiency.

It is quite striking that soluble oil No. 56 shows a kill of only 65 per cent, while its emulsifying agent (Soap No. 55), alone, shows a kill of 88 per cent. Soluble oil No. 56 consists of about 20 per cent of soap No. 55 and 80 per cent oil; hence, the spray contains only one-fifth as much soap as No. 55 at the same dilutions. From Figure 5 it will be seen that soap No. 55 at a dilution of 1 per cent still shows a low angle of contact. But soluble oil No. 56, being so much weaker, has soap precipitated from it quite rapidly and, hence, is low in wetting ability. Soap No. 15, by contrast, does not precipitate out so readily, and its soluble oils maintain their efficiency.

In view of the fact that fish-oil soap and soap No. 55 precipitate out in hard water, it would be logical to predict a higher per cent kill if these soaps were dispersed in distilled water instead of tap water. This prediction is borne out by Table II. While there are varying increases with all of the soaps, the increase from 34.6 per cent to 73.3 per cent with fish-oil soap is particularly noteworthy. Calcium caseinate shows very little difference, as would be expected.

Since the soaps are more effective with distilled water, it seems that the emulsions made from them should be more effective. This, however, is not true, as will be seen in Table III, where the per cent kill for distilled water is in no case higher than the per cent kill for tap water. Here the effect of the water on the type of emulsion is introduced. If tap water precipitates out some of the soap, an emulsion dispersed in it naturally is not as stable as one dispersed in distilled water. With the exception of emulsion No. S15 there is very little difference in stability of those diluted with tap water and those diluted with distilled water, as determined by centrifuging. There is no perceptible difference in the size of the globules of the tap water emulsions and the distilled water emulsions. If, however, the diluted emulsions are allowed to stand in cylinders for a few days, those made with tap water show a distinct separation of oil. Soluble oil No. 90 is very stable, and the difference in stability with tap and distilled water is insufficient to be preceptible in a photograph. If drops of the emulsions are compared under a binocular microscope, those diluted with tap water seem to have more oil at the surface of the drop than the corresponding emulsions diluted with distilled water. This adsorption of oil may be a factor in the wetting of aphids and the retention of spray by them. Drops of a poor wetting spray bounce off the aphids, and very little is retained. Much additional work is needed to clear up the relation of wetting ability and stability to the possible concentration of the oil on plants and insects.

## RELATION OF CHEMICAL PROPERTY OF OIL AND STABILITY OF EMULSION TO EFFECTIVENESS AGAINST APHIDS

The kind of oil and the amount of emulsifying agent in an emulsion produce differences in efficiency, as shown in Table IV. (See Figure 6.) The emulsions under items 1 and 2 in this table are relatively ineffective. These emulsions are of the quick-breaking type, but they do not have the necessary wetting ability. The emulsions under items 3, 4, 5, and 6 have the necessary wetting ability, but vary in stability. Soluble oil No. 18, an extremely stable emulsion, the globules of which cannot be seen with the ordinary high power of the microscope, is the least effective of these four, its per cent kill being only 86.8. Soluble oil No. 90, the globules of which can barely be seen in the photograph, gives a kill of 88.4 per cent. When the amount of emulsifying agent is reduced as in No. 17, making a less stable emulsion, the kill is 94.6 per cent. Soluble oil No. 16 has the same amount of emulsifying agent as No. 90, but it is made from a saturated oil, which in this case gives an emulsion having about the same stability as No. 17, and the kill is in very good agreement. That emulsions having globules of different sizes would have different properties was indicated by Moore ('23), and the size of globules has been correlated with toxicity to aphids in recent work by Griffin, Richardson, and Burdette ('27).

As to instability, this theory is offered: The less stable the emulsion, the greater the amount of oil thrown to the surface of the spray drops, or adsorbed by them; and a very unstable emulsion thus approaches a water-in-oil type of spray, with a consequent increase in the amount of oil adhering to the plant or insect.

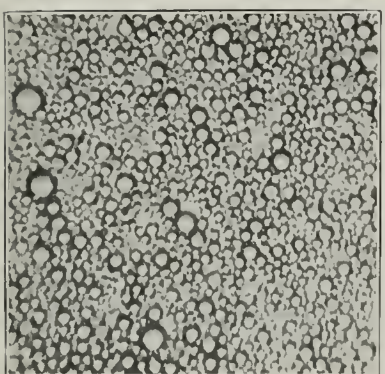
The chemical difference between the saturated and unsaturated oils in these emulsions appears to be of minor importance. The dominating factors are the wetting ability and the instability of the emulsion. The experimental data indicate that the most effective emulsion on aphids

TABLE IV.

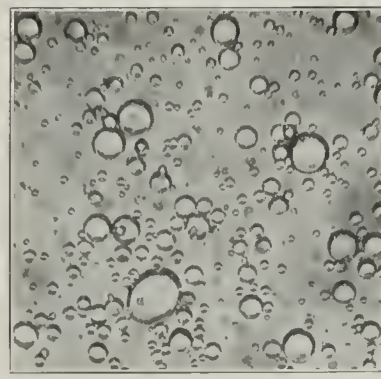
SUMMARY OF TESTS ON THREE SPECIES OF APHIDS *(T. ambrosiae, H. setariae,* AND *A. pomi)*, SHOWING INFLUENCE OF CHEMICAL PROPERTY OF OIL AND STABILITY OF EMULSION.

| Item | Emulsion | Oil | Emulsifying agent | | Aphids killed | Aphids used | Per cent killed |
|---|---|---|---|---|---|---|---|
| | | | Kind | Amount | | | |
| 1 | Stock No. 5 | Sat.[1] | Inert. | Reduced | 3491 | 4449 | 78.46 |
| 2 | Homemade | Unsat.[2] | K.F.O. Soap | Normal | 3675 | 4738 | 77.56 |
| 3 | Sol. Oil No. 18 | Unsat. | Soap No. 15 | Excess | 4300 | 4952 | 86.83 |
| 4 | Sol. Oil No. 90 | Unsat. | Soap No. 15 | Normal | 4074 | 4606 | 88.44 |
| 5 | Sol Oil No. 17 | Unsat. | Soap No. 15 | Reduced | 4721 | 4986 | 94.68 |
| 6 | Sol. Oil No. 16 | Sat. | Soap No. 15 | Normal | 4837 | 5174 | 93.48 |
| 7 | Water Check | | | | 540 | 4179 | 12.92 |
| 8 | Untreated Check | | | | 290 | 4326 | 6.70 |

[1] Sat. = Saturated oil.
[2] Unsat. = Unsaturated oil.
} See definitions, *Appendix A.*

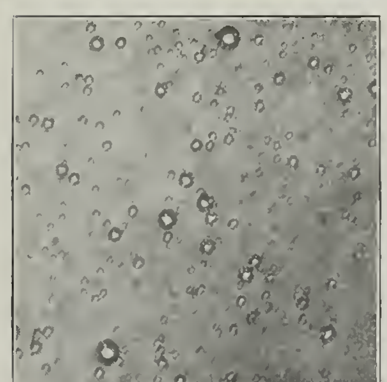


*A.* Stock emulsion No. 5.

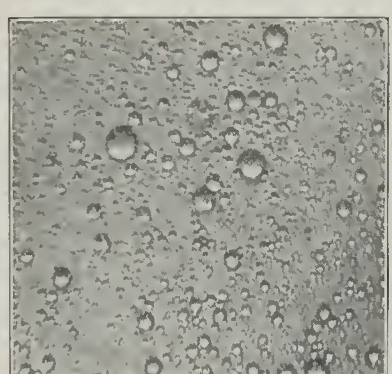


*B.* Homemade lubricating-oil emulsion.

*C.* Soluble oil No. 90.



*D.* Soluble oil No. 17.



*E.* Soluble oil No. 16.

FIG. 6. MICROPHOTOGRAPHS OF EMULSIONS USED IN EXPERIMENTS. (× 290)

would be one that is relatively unstable and has high wetting ability. But antagonistic factors are encountered; for the emulsions that have high wetting ability are injurious to foliage, and chemically inert emulsions do not have high wetting ability.

### Relation between Wetting Ability and Toxicity to San Jose and Oyster-shell Scale (in the Dormant Stage)

Good wetting ability, which was shown to be an important requisite of emulsions for use on aphids (Table I), is not so important in the case of oyster-shell scale and San Jose scale. In this case, the emulsions that certainly have poor wetting ability are just as effective as those having good wetting ability. This can be seen from a series of laboratory experiments on oyster-shell scale* (Table V) and a typical field test on San Jose scale* (Table VI). It is not necessary to discuss this point at length or to present a great many data, for similar results have been obtained by

Table V.

Summary of Tests on Oyster-shell Scale, Showing Influence of Wetting Ability.

| Item | Emulsion | Emulsifying agent | *Per cent killed at dilution of | | | |
|---|---|---|---|---|---|---|
| | | | 5% | 10% | 10% | 10% |
| 1 | Stock Emul. No. S 15 | K. F. O. Soap | 36.3 | 99.4 | 99.8 | 97.3 |
| 2 | Stock Emul. No. 5 | Inert | 96.2 | 90.9 | 99.8 | 99.5 |
| 3 | Soluble Oil No. 17 | Soap No. 15 | 47.3 | 93.3 | 99.4 | 99.8 |
| 4 | Soluble Oil No. 90 | Soap No. 15 | 41.7 | 92.8 | | 96.4 |
| 5 | Checks | | 0.0 | 0.0 | 0.0 | 0.0 |

* Check basis.

Table VI.

Summary of Tests on San Jose Scale, Showing Influence of Wetting Ability.

| Item | Emulsion | Emulsifying agent | Per cent live scale | |
|---|---|---|---|---|
| | | | 2% solution | 1% solution |
| 1 | Stock Emul. No. S 15 | K. F. O. Soap | 2.4 | 5.9 |
| 2 | Stock Emul. No. 5 | Inert | 3.0 | 7.4 |
| 3 | Soluble Oil No. 16 | Soap No. 15 | 0.2 | 4.7 |
| 4 | Soluble Oil No. 90 | Soap No. 15 | 7.7 | 28.5 |
| 5 | Checks | | 66.6 | 66.6 |

* For methods, see *Appendix B*.

TABLE VII.

ANGLES OF CONTACT (MEAN VALUES), SHOWING RELATIVE EASE OF WETTING VARIOUS LEAVES AND TWIGS.

| Object | Liquid | | |
|---|---|---|---|
| | K. F. O. soap | Glue | Tap water |
| Oat Leaf—Upper side | 113 | 171 | 180 |
| Corn leaf—Upper side | 126 | 175 | 180 |
| Cabbage leaf—Upper side | 104 | 127 | 167 |
| Apple skin—Ben Davis (Green) | 89 | 107 | 130 |
| Apple leaf—Upper side (Jonathan) | 44 | 64 | 55 |
| Peach leaf—Upper side (Elberta) | 35 | 65 | 60 |
| Apple twig—(Jonathau)* | 27 | 41 | 40 |
| Peach twig—(Elberta)* | 45 | 50 | 50 |
| Poplar twig*† | | | 5 |
| Lilac twig *† | | | 0 |

* Dormant.
† Incrusted with Oyster-shell scale.

Chandler, Flint and Huber ('26) on San Jose scale;* by List ('24) on oyster-shell scale; and by Flint and Bigger ('26), Hawley ('26), Wakeland ('25), and Melander ('24) on the fruit tree leaf roller.

There are two reasons why these insects are controlled by oil emulsions that do not necessarily have high wetting ability:

(1) Apple, peach, poplar, and lilac twigs are not difficult to wet, as is shown in Table VII. Tap water wets them rather easily. This, by the way, may be responsible for a higher "runoff" with "good-wetting" sprays than with sprays of poor wetting ability, as is indicated in deOng's ('26) figures showing an increase in the amount of oil in the "runoff" with an increase in the amount of emulsifying agent. With other sprays Ruth and Kelley ('22) show, by weighing, that the amount of spray retained will vary with both the surface sprayed and the spray used.

(2) In comparing the effect on aphids with that on scales, it should be considered that scales are sessile, while aphids are not. Aphids become quite active when disturbed by spraying, and they have been observed to crawl out of a drop of liquid or to rid themselves of a globule by moving around. This, of course, applies only to sprays that do not wet them.

Therefore, wetting ability is not an important factor in the control of San Jose scale, oyster-shell scale, and apparently leaf-roller eggs, for the simple reason that the host plants, being easily wetted, retain sufficient spray to insure an oil film coverage as soon as the emulsion breaks. From the results of deOng ('27), Yothers ('24), and Woglum ('25), it seems that the same principle holds for citrus scales.

* In a private communication, B. A. Porter reports similar results.

## RELATION OF VOLATILITY AND VISCOSITY OF OIL TO EFFECTIVENESS AGAINST SCALE INSECTS.

The theory formulated by deOng from his work on citrus scales may be applied also to oyster-shell and San Jose scales. The data in Table VIII demonstrate that a spray containing an oil of 60 viscosity and 5.3 per cent volatility is not as effective against oyster-shell scale as a corresponding spray containing an oil of slightly higher viscosity and lower volatility. Likewise, a refined kerosene of 32 viscosity and 35.1 per cent volatility, emulsified with potash-fish-oil soap, is very ineffective. If the toxicity were due to penetration alone, a light oil of this nature should be more effective than heavier oils. With this in mind, a series of laboratory tests were run with oyster-shell scale to determine the action of unemulsified, or "straight", oils on the scale (Table IX). Neither the refined nor the unrefined kerosene was effective. Oil No. 31, of 60 viscosity and 5.3 per cent volatility, which was run as a check, gave practically a perfect

TABLE VIII.

SHOWING RELATION OF VOLATILITY AND VISCOSITY OF OIL TO EFFECTIVENESS ON OYSTER-SHELL SCALE.—DORMANT.

| Item | Emulsion | Emulsifying Agent | Properties of the oil | | | Per cent killed at dilution of | |
|---|---|---|---|---|---|---|---|
| | | | Kind | Viscosity *Sec.* | Volatility *Per cent* | 5% | 10% |
| 1 | Soluble Oil No. 34 | Soap No. 37 | Sat. | 60 | 5.3 | 0.0 | 74.1 |
| 2 | Soluble Oil No. 35 | Soap No. 37 | Unsat. | 83 | 1.0 | 38.7 | 86.4 |
| 3 | Soluble Oil No. 33 | Soap No. 37 | Sat. | 83 | 1.0 | 69.6 | 94.1 |
| 4 | Stock Emul. No. S 7 | K. F. O. Soap | Sat. | 32 | 35.1 | | 13.5 |
| 5 | Stock Emul. No. S 8 | K. F. O. Soap | Sat. | 60 | 5.3 | 6.0 | 90.8 |
| 6 | Stock Emul. No. S 9 | K. F. O. Soap | Sat. | 83 | 1.0 | 9.6 | 99.9 |
| 7 | Stock Emul. No. S10 | K. F. O. Soap | Unsat. | 104 | 0.2 | 36.3 | 99.4 |
| 8 | Checks | | | | | 0.0 | 0.0 |

TABLE IX.

SHOWING INEFFECTIVENESS OF UNDILUTED VOLATILE OILS ON OYSTER-SHELL SCALE.

| Item | Oil | Properties of the oil | | | Per cent killed | | |
|---|---|---|---|---|---|---|---|
| | | Kind | Viscosity | Volatility | A | B | C |
| 1 | Refined No. 9 | Sat. | 32 | 35.10 | 9.0 | 4.0 | 52.7 |
| 2 | Perfection Kerosene | Unsat. | 32 | 54.28 | | 41.7 | 67.7 |
| 3 | Oil No. 31 | Sat. | 60 | 5.30 | | | 99.9 |
| 4 | Checks | | | | 0.0 | 0.0 | 0.0 |

kill. An hour or two after twigs are treated with these light oils, there is no evidence of oil present; whereas a distinct residue of the heavier oil persists for a week or more. Analogous results were obtained on San Jose scale, as will be seen from Table X. The light oil of high volatility was not effective when emulsified with fish-oil soap or with an inert agent or when incorporated in a soluble oil.

There may be a wide range of viscosity (from 80 up to 250 or 300) without any appreciable change in volatility. When the viscosity drops as low as 60, there is a rise in volatility and a decrease in effectiveness. It is believed that a suitable oil for scale control should not fall below 80 viscosity and should not have a volatility of over 1 per cent.

Table X.*

Showing Relation of Volatility and Viscosity of Oil to Effectiveness on San Jose Scale.

| Item | Emulsion | Emulsifying agent | Properties of the oil | | | Per cent live scale at dilution of | | |
|---|---|---|---|---|---|---|---|---|
| | | | Kind | Viscosity *Sec.* | Volatility *Per cent* | 3% | 2% | 1% |
| 1 | Stock Emulsion | K.F.O. Soap | Unsat. | 104 | 0.19 | 0.9 | | |
| 2 | Stock Emulsion | K.F.O. Soap | Sat. | 83 | 1.00 | 0.2 | | |
| 3 | Stock Emulsion | K F.O. Soap | Sat. | 32 | 35.10 | 36.2 | | |
| 4 | Stock Emulsion | Inert | Unsat. | 104 | 0.19 | 2.0 | | |
| 5 | Stock Emulsion | Inert | Sat. | 83 | 1.00 | 0.2 | | |
| 6 | Stock Emulsion | Inert | Sat. | 32 | 35.10 | 11.6 | | |
| 7 | Soluble Oil No. 56 | Soap No. 55 | Unsat. | 83 | 1.07 | | 4.8 | 27.7 |
| 8 | Soluble Oil No. 47 | Soap No. 55 | Sat. | 32 | 35.10 | | 21.3 | 35.6 |
| 9 | Checks | | | | | 43.0 | 66.6 | 66.6 |

* Data under items 1 to 6, inclusive, are by S. C. Chandler, of the Illinois State Natural History Survey.

## Relation of Chemical Property of Oil and Stability of Emulsion to Effectiveness against Scale Insects

Data in some of the preceding tables suggest differences in the effectiveness of saturated and unsaturated oils on scale insects. With a slight repetition of some of the data an attempt will be made to demonstrate these differences.

Table XI shows data on oyster-shell scale obtained with the emulsions shown in the photographs of Figure 7. The first two emulsions listed here have the same oil content, and the emulsifying agent in both is a potash-petroleum soap, but No. 35 contains an unsaturated oil and No. 33 a saturated oil. The latter, being a quicker-breaking emulsion, gave a higher per cent kill than No. 35. Soluble oils Nos. 16 and 45 (items 3 and 4 in Table XI) are made from the same oil, but No. 45, having 40 per cent less emulsifying agent than No. 16, is a very unstable emulsion, and the difference in kill at a dilution of 5 per cent is very striking: 97.7 per cent kill for the unstable emulsion against 26.3 per cent for the stable one. Nos. S9 and S10, although made from different oils, are both quick-breaking emulsions. Here, apparently, the unsaturated oil seems to be slightly more effective than the saturated oil. If reference is made to Table IX, showing the toxicity of undiluted volatile oils to oyster-shell scale, it will be noted that the saturated oil gave kills of 4.0 per cent and 52.7 per cent in two separate experiments, whereas the unsaturated oil gave kills of 41.7 per cent and 67.7 per cent in the same experiments. The data under items 5 and 6 in Table XI also indicate that the unsaturated

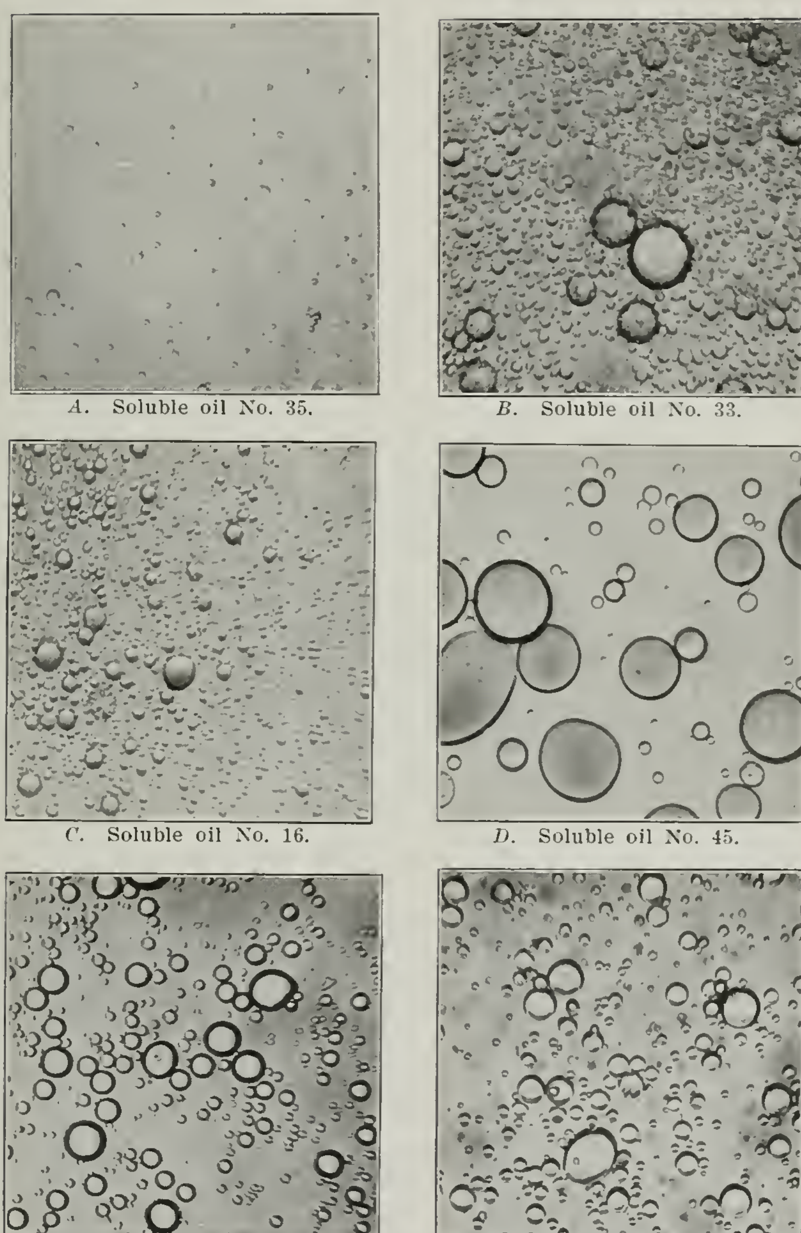
Table XI.

Showing Relation of Chemical Property of Oil and Stability of Emulsion to Effectiveness on Oyster-shell Scale.

| Item | Emulsion | Emulsifying agent | Properties of the oil | | | | Per cent killed at dilution of | |
|---|---|---|---|---|---|---|---|---|
| | | | Kind | Loss to $H_2SO_4$ *Per cent* | Viscosity *Sec.* | Volatility *Per cent* | 5% | 10% |
| 1 | Soluble Oil No. 35 | Soap No. 37 | Unsat. | 9.0 | 83 | 1.0 | 38.7 | 86.4 |
| 2 | Soluble Oil No. 33 | Soap No. 37 | Sat. | 1.0 | 83 | | 69.6 | 94.1 |
| 3 | Soluble Oil No. 16 | Soap No. 15 | Sat. | 0.0 | 83 | 0.2 | 26.3 | 98.9 |
| 4 | Soluble Oil No. 45 | Soap No. 15 | Sat. | 0.0 | 83 | 0.2 | 97.7 | 99.8 |
| 5 | Stock Emulsion No. S 9 | K.F.O. Soap | Sat. | 1.0 | 83 | 1.0 | 9.6 | 99.9 |
| 6 | Stock Emulsion No. S 10 | K.F.O. Soap | Unsat. | 7.0 | 104 | 0.2 | 36.3 | 99.4 |
| 7 | Checks | | | | | | 0.0 | 0.0 |

oil is slightly more effective. Thus, the unsaturated oil may be more effective if the emulsion is quick-breaking; otherwise, the saturated oil may be more effective because of its influence on stability.

The influence that saturated and unsaturated oils may have on the stability of an emulsion, together with their relative effectiveness, is further indicated by the results on San Jose scale shown in Table XII. (See Figure 8.) Soluble oils Nos. 90 and 16 are made from equal amounts of the same emulsifying agent, but No. 90 is the more stable, probably on account of the fact that the oil from which it is made is not so highly refined as the oil in No. 16. It will be seen that No. 90 is relatively less efficient on San Jose scale on peach, as well as on apple. Soluble oil No. 17 made with the same oil as No. 90, but with a reduced amount of emulsifier, is relatively more effective. The influence that saturated and unsaturated oils may have on the stability of the emulsion and its effectiveness is indicated to a slight extent when the oils are emulsified with an inert material. It will be noted from the photographs in Figure 8 that stock emulsion No. 210 is slightly more stable than No. 200.



*A.* Soluble oil No. 35.

*B.* Soluble oil No. 33.

*C.* Soluble oil No. 16.

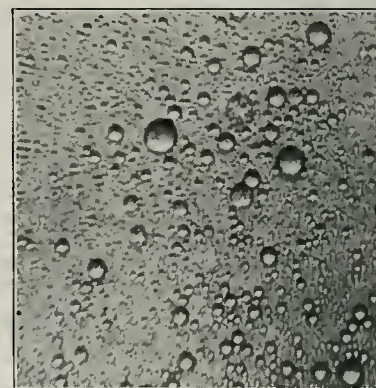
*D.* Soluble oil No. 45.

*E.* Stock emulsion No. S9.

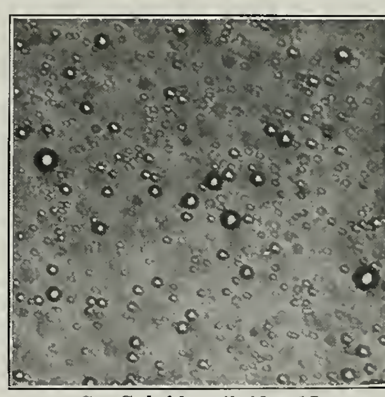
*F.* Stock emulsion No. S10.

FIG. 7. MICROPHOTOGRAPHS OF EMULSIONS USED IN EXPERIMENTS. (× 290)

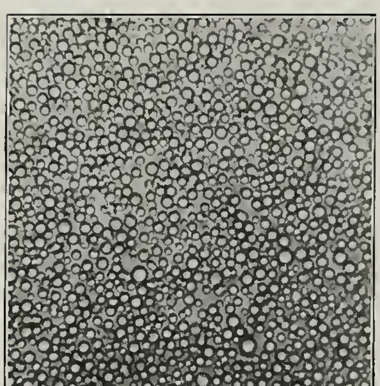
*A.* Soluble oil No. 90.



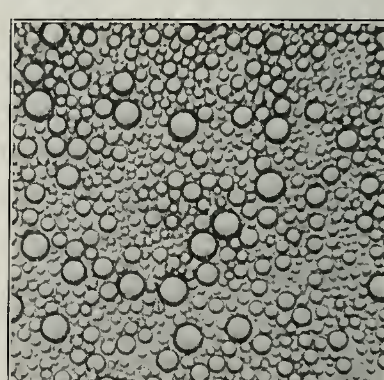
*B.* Soluble oil No. 16.



*C.* Soluble oil No. 17.



*D.* Stock emulsion No. 210.



*E.* Stock emulsion No. 200.

FIG. 8. MICROPHOTOGRAPHS OF EMULSIONS USED IN EXPERIMENTS. (× 290)

The results on scale insects corroborate deOng's work by indicating that the action of an oil emulsion in producing death is largely a physical one, causing suffocation. If the action is due to penetration alone, then the oils of low viscosity should be more effective, because of their greater mobility. But high volatility is usually associated with low viscosity, and if death is to be effected by penetration, the oil should persist. The ineffectiveness of light volatile oils has been demonstrated by Moore and Graham ('18), who state that such oils may evaporate too quickly to cause

TABLE XII.

SHOWING RELATION OF CHEMICAL PROPERTY OF OIL AND STABILITY OF EMULSION TO EFFECTIVENESS ON SAN JOSE SCALE.

| Item | Emulsion | Emulsifying agent | Properties of the oil: Kind | Loss to $H_2SO_4$ *Per cent* | Viscosity *Sec.* | Volatility *Per cent* | Per cent live scale at dilution of | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | 2% | 1% |
| | **On Peach** | | | | | | | |
| 1 | Soluble oil No. 90 | Soap No. 15 | Unsat. | 9.0 | 83 | 1.0 | 7.7 | 28.5 |
| 2 | Soluble oil No. 16 | Soap No. 15 | Sat. | 0.0 | 83 | 0.2 | 0.2 | 4.7 |
| 3 | Check | | | | | | 66.6 | 66.6 |
| | **On Apple** | | | | | | 3% | 1.5% |
| 4 | Soluble oil No. 90 | Soap No. 15 | Unsat. | 9.0 | 83 | 1.0 | 0.2 | 4.9 |
| 5 | Soluble oil No. 17 | Soap No. 15 | Unsat. | 9.0 | 83 | 1.0 | 0.6 | 1.5 |
| 6 | Soluble oil No. 16 | Soap No. 15 | Sat. | 0.0 | 83 | 0.2 | 0.4 | 0 0 |
| 7 | Check | | | | | | 40.0 | 40.0 |
| | **On Peach** | | | | | | 3% | 2% |
| 8 | Stock Emul. No. 210 | Inert | Unsat. | 9.0 | 83 | 1.0 | 1.7 | 2 6 |
| 9 | Stock Emul. No. 200 | Inert | Sat. | 0.0 | 83 | 0.2 | 0.6 | 1.3 |
| 10 | Check | | | | | | 12.6 | 12.6 |

Note: Emulsifying agent in Sol. oil No. 17, reduced.

death. It has been observed by deOng ('27) that scale insects may actually expel the lighter oils from their tracheal systems. If the action were mainly chemical, the unsaturated oils, which are more active chemically, would be more effective. The important point in scale control is to apply an emulsion that will release quickly an oil of sufficiently high viscosity and low volatility to give a residue that will persist for sometime.

## INJURY TO PLANTS

As a general rule, the higher the viscosity and the lower the volatility of an oil, the more likely it is to cause injury to plants, whether it is saturated or unsaturated. It is quite possible to apply a volatile, unsaturated kerosene without much danger of injury, but with oils that give a persistent residue it is necessary to increase the degree of refinement in order to insure safety to foliage. Wherever a persistent residue is required, therefore, the difference between saturated and unsaturated oils is the most important consideration with respect to plant injury.

In tests on apple foliage it has not been found necessary to use an oil of medicinal quality, i. e., an oil that shows *no* loss to 97 per cent sulfuric acid. An oil having a loss of 1 per cent to sulfuric acid and a viscosity of 83 has been found quite safe on apple foliage at dilutions as high as 4 per cent when emulsified with some inert material. But the incorporation of a saturated oil, even of medicinal quality, in a soluble oil did not prove safe, nor did it apparently decrease the injury below that of the corresponding unsaturated oil. Although the saturated oil itself and the petroleum soap were relatively innocuous when applied separately, a safe combination of the two could not be worked out. Replacing sodium with potassium in the soap did not reduce injury; neither did an entire change of emulsifying agent. The incorporation of a highly volatile saturated oil in a soluble oil did reduce injury considerably, but the combination was not entirely safe and was not of satisfactory insecticidal efficiency. (Tables VIII, IX, X.)

In the early stages of the work, various oils were applied undiluted, or "straight", to apple twigs in order to determine their liability to cause injury. The results of a typical test are seen in Table XIII.

TABLE XIII.

INJURY TO APPLE FOLIAGE BY UNDILUTED OILS.

| Item | Viscosity | Volatility | Loss to $H_2SO_4$ | Estimated per cent injury observed after | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *Per cent* | *Sec.* | *Per cent* | 20 hrs. | 25 hrs. | 2 da. | 4 da. | 6 da. | 10 da. |
| 1 | 32 | 35.1% | 0.0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 83 | | 1.0 | 0 | 0 | 0 | 0 | 0 | 10* |
| 3 | 83 | 0.2% | 0.0 | 0 | 0 | 0 | 0 | 0 | 10* |
| 4 | 32 | 54.3% | 3.0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 83 | 1.0% | 9.0 | 0 | 40 | 80 | 90 | 100 | 100 |
| 6 | 104 | 0.2% | 7.0 | 0 | 40 | 80 | 90 | 100 | 100 |

* Finally, yellowing and defoliation.

Tests of this kind illustrate strikingly the acute injury done by unsaturated oils. Twigs treated with unsaturated oils show almost complete blackening of the tissue within 48 hours, while it may be several days before the saturated oils cause injury, and even then the injury is not "burning" but "yellowing" and defoliation. The latter seems to be the result of suffocation of the cells in the tissue, while the action of the unsaturated oils appears to be chemical for the most part. The very volatile oils leave the plant without causing injury. The important point in selecting an oil emulsion for spraying foliage is to use one that is as nearly inert chemically as possible. Such an emulsion is obtained with a saturated oil and an inert emulsifier. This conclusion is in harmony with deOng's.

## Conclusions

Emulsifying agents used in making oil emulsions for spray purposes vary in wetting ability, as measured by Stellwaag's angle-of-contact method, and consequently cause variations in the effectiveness of the emulsions. This is especially important in the control of aphids.

The stability of oil emulsions, which is indicated to some extent by the size of the globules, is one of the principal factors in insecticidal efficiency. The type of oil emulsified, the kind and amount of emulsifying agent, the quality of water used for dilution, and other factors commonly considered unimportant, are capable of causing changes in stability and consequent fluctuations in efficiency.

Increased effectiveness may or may not be accompanied by an increase in the size of globules. Increased size of globules is the result of desirable qualities in an emulsion rather than the cause of effectiveness.

For use against aphids, the most effective emulsion is one that has high wetting ability coupled with instability. Either of these factors may vary so as to be dominant. A relatively "poor-wetting", unstable emulsion may be more effective on aphids than a "good-wetting", stable emulsion. If the stability of two emulsions is about the same, then the one with the greater wetting ability is the more effective on aphids.

In the control of scale insects, the instability of the emulsion is the primary consideration. The less stable the emulsion, the greater its efficiency. High wetting ability is not necessary for the control of San Jose scale and oyster-shell scale, because of the comparative ease with which their host plants are wetted. The emulsions used for the control of these insects should release quickly an oil of sufficiently high viscosity and low volatility to give a persistent residue.

A saturated oil, because of its influence in some cases on the stability of the emulsion, may be more effective than an unsaturated oil.

The amount of oil adhering and taking proper effect on the insect is dependent upon both the wetting ability and the instability of the emulsion. Inadequate wetting is a common cause of inefficiency, but excessive wetting, which results in some of the emulsion running off from objects that are easily wetted, is also a possible cause of inefficiency. These conditions are dependent on the kind of emulsion and the insect involved.

In order to be innocuous to plant foliage, an emulsion should be as inert chemically as possible. Soaps and unsaturated oils tend to injure foliage.

Each oil emulsion should be considered as a particular *individual* insecticide, having properties peculiar to itself and giving results that other emulsions may not.

### Acknowledgments

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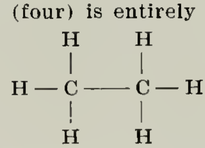
## *Appendix A*

### DEFINITIONS OF TERMS

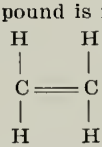
A **saturated hydrocarbon** is a compound of hydrogen and carbon in which the normal valence of carbon (four) is entirely satisfied.

Example: ethane



An **unsaturated hydrocarbon** is one in which the normal valence of carbon is not satisfied; hence, the compound is more active chemically than a saturated hydrocarbon.

Example: ethylene



A **saturated oil**, or white oil, is one from which the unsaturated hydrocarbons have been removed by treatment with sulfuric acid. A saturated oil is practically inert chemically.

An **unsaturated oil** is not as highly refined as the white oils. While au oil of this kind may consist largely of saturated hydrocarbons, not all the unsaturated hydrocarbons have been removed in refining it.

**Loss to Sulfuric Acid.*** The loss in volume of an oil as a result of treatment with sulfuric acid is an index to the unsaturated hydrocarbon content. The greater the loss, the more unsaturated the oil. There is a standard method of procedure for this test.

**Viscosity.*** This is simply defined as resistance to flow, or negative fluidity. The standard of comparison used for oils is the Saybolt test. The units used are seconds, and they represent the time required for a given volume of oil to flow through a given orifice at a definite temperature.

**Volatility.†** This is an arbitrary test which expresses as per cent by weight, the evaporation of a given quantity of oil at 212°F for 8 hours.

**"Soluble Oil" and "Stock Emulsion".** For purposes of discussion, a distinction is usually made between "soluble oil" and "stock emulsion", although there is no basic difference between them, both being oil emulsions. "Soluble oils," which are more or less transparent because of the extremely fine degree of dispersion of the oil phase, are compounded petroleum products which form milky-white emulsions when diluted with water. Dendrol and Sunoco are examples. The term "stock emulsion" is used with refereuce to a concentrated emulsion, such as Volck, Sherwin-Williams Free-mulsion, homemade lubricating oil emulsion, etc.

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* The determinations of loss to sulfuric acid and of viscosity were made by the Standard Oil Company (Indiana), according to United States Government Specifications for Lubricants and Liquid Fuels and Methods of Testing, U. S. Bureau of Mines, Technical Paper 323 A., March 18, 1924.

† Refer to British Engineering Standards Association, Tentative British Standard Specifications 148 (1923), pages 9-10, Section 14b.

## *Appendix B*

### EXPERIMENTAL METHODS

**Tests on aphids.** *Aphis pomi* De G. was obtained on the water sprouts of apple; *Aphis spiraecola* Patch on *Spiraea vanhouttei* Zabel; *Hesteroneura setariae* Thos. on a grass (*Echinichloa crus-galli* L.); and *Tritogenaphis ambrosiae* Thos. on wild lettuce (*Lactuca canadensis* L.). The infested shoots were cut from the plants a short time before spraying. Nearly all the leaves were removed so that the aphids would not be protected. The shoots were then placed vertically on a revolving stand and sprayed thoroughly with a hand sprayer having bottom feed. An excessive amount of spray on the aphids was insured, i. e., as much as would adhere. After treatment, the shoots were inserted in holes in the tops of pill boxes filled with water and isolated on squares of paper bordered with tree tanglefoot. After approximately 24 hours, the aphids were carefully removed with a camel's hair brush and counted.

**Tests on oyster-shell scale.** For the laboratory tests with oyster-shell scale, *Lepidosaphes ulmi* Linn., infested poplar (*Populus deltoides* Marsh) twigs were used. These were trimmed uniformly, and all scales were removed except 25 to 50, the number varying with separate experiments, but never within one experiment. Five of these twigs were treated with each material, and several untreated checks of five twigs each were carried through each experiment. After treatment, the twigs were placed in a moist sand bench to grow. A ring of tanglefoot around each prevented the escape of "crawlers" at the time of hatching. Throughout the hatching period, the twigs were examined daily with a binocular microscope, and the crawlers were removed as counted. The checks usually hatched very uniformly, and the hatch on the treated blocks was calculated to "check basis". About 3,000 to 3,500 eggs hatched from each check block of five twigs.

**Tests on San Jose scale.** All of the tests of sprays on San Jose scale (*Aspidiotus perniciosus* Comstock) were conducted in the field. In some cases, large infested branches were treated; in others, several entire trees were used in each block. The usual procedure of taking San Jose scale data was followed. A month or six weeks after treatment, twigs were collected from the various blocks, and a count of 1,000 scales was made to determine the percentage of survival. In making the counts, the scale was turned over in order that the insect itself might be seen. Robust, lemon-colored ones were recorded as "alive". Brown, black, shriveled, or "off color" ones were recorded as "dead."

## *Appendix C*

### ANALYSIS OF TAP WATER USED IN EXPERIMENTS

Illinois State Water Survey, Sample No. 51728, June 28, 1924

| Determinations | | Parts per million |
|---|---|---|
| Iron | Fe | 1.2 |
| Manganese | Mn | 0.0 |
| Silica | $SiO_2$ | 14.1 |
| Nonvolatile | | 1.8 |
| Alumina | $Al_2O_3$ | 0.0 |
| Calcium | Ca | 66.9 |
| Magnesium | Mg | 31.4 |
| Ammonia | $NH_4$ | 5.3 |
| Sodium | Na | 34.8 |
| Potassium | K | 4.1 |
| Sulfate | $SO_4$ | 1.2 |
| Nitrate | $NO_3$ | 1.4 |
| Chloride | Cl | 4.0 |
| Alkalinity as $CaCO_3$ | | |
| Phenolphthalein | | 0.0 |
| Methyl Orange | | 376.0 |
| Residue | | 380.0 |