

HILGARDIA

*A Journal of Agricultural Science Published by
the California Agricultural Experiment Station*

VOLUME 12

NOVEMBER, 1938

NUMBER 2

CONTENTS

THE DEPOSIT OF AQUEOUS SOLUTIONS AND OF OIL SPRAYS

W. M. HOSKINS and Y. BEN-AMOTZ

THE USE OF SELENIUM IN SPRAYS FOR THE CONTROL OF MITES ON CITRUS AND GRAPES

W. M. HOSKINS, A. M. BOYCE, and J. F. LAMIMAN

UNIVERSITY OF CALIFORNIA · BERKELEY, CALIFORNIA

THE DEPOSIT OF AQUEOUS SOLUTIONS AND OF OIL SPRAYS^{1, 2}

W. M. HOSKINS³ AND Y. BEN-AMOTZ⁴

INTRODUCTION

THE VALUE OF A SPRAY OIL as an insecticide is largely dependent upon the amount of oil deposited when an emulsion containing the oil is sprayed upon an insect or upon the surface of a plant infested by the insect. Care regarding the quality of the oil, uniformity of the emulsion, and thoroughness of application is obviously of little use if the deposition of oil over the sprayed surface is insufficient, excessive, or uneven.

Previous workers who have studied the behavior of spray-oil emulsions have laid emphasis upon various properties, such as surface tension of the aqueous phase, interfacial tension between the two phases, stability of the emulsion, size of the oil droplets, angle of contact formed when the emulsion or its aqueous phase is placed upon a solid, and other analogous properties. The experiments which have been in progress in this laboratory for several years have led to the opinion that the chief importance of these properties for the deposit of oil lies in their effects upon the relative ease with which the aqueous and the oil phases make and maintain contact with the surface sprayed. During the application of an oil emulsion to a solid, and for some time thereafter, there is competition for room upon the surface of the solid. If the aqueous phase either makes contact everywhere first or is able to displace oil which has reached the surface, the end result will be little or no deposit of the oil. On the other hand, if all the oil makes contact as fast as the emulsion is applied, the deposit will be pro-

¹ Received for publication May 18, 1938.

² This article is the fourth of a series having the general title: *Factors Concerned in the Deposit of Sprays*. For earlier numbers see Hensill and Hoskins (1935); Hoskins and Wampler (1936); Ben-Amotz and Hoskins (1937) in "Literature Cited" at the end of this paper.

³ Associate Professor of Entomology and Associate Entomologist in the Experiment Station.

⁴ Graduate student, University of California, August, 1933 to May, 1937.

portional to the duration of spraying ; and excessive or deficient amounts will be left on various regions according to how the spray is applied. The desired condition lies between these extremes, and the possibility of obtaining a satisfactory deposit of oil depends upon the correct adjustment of the ability of each phase to make the necessary contact with the solid which is sprayed. The object of the work to be reported here was to acquire information concerning the effects which certain water-soluble substances have upon the behavior of the aqueous and oil phases of spray emulsions as they are applied to the standard surface of beeswax which has been used in previous studies in this laboratory (Hensill and Hoskins, 1935 ; Ben-Amotz and Hoskins, 1937).⁵

The theory that during the application of an oil emulsion each liquid phase is acted upon by forces which result in displacement of one by the other to varying degrees and that the final amount of oil left as a deposit upon the surface is a resultant of the action of all the components of the emulsion has not been stressed by either physicists or entomologists who have worked with oil emulsions. More particularly, the behavior of the nonoil components of emulsions during the act of spraying has been neglected. Since the final result is necessarily influenced by the behavior of each part of the emulsion, a desirable means of study is the examination of the separate components under conditions which resemble as nearly as possible those which prevail during application of the whole emulsion. Such a plan was followed in the present work.

This paper includes an account of what happens to the water and the emulsifying and wetting agents in oil emulsions as well as to the oil itself during and shortly after spraying. From this information, an attempt is made to interpret oil deposit in terms of certain properties of the components taken both separately and together.

For both theoretical and practical reasons, measurements of the properties of spray liquids under static conditions are of little value as compared with measurements made under the conditions which prevail during application of the sprays, that is, under dynamic conditions. This principle cannot be consistently followed in studying all the properties of sprays : for example, no truly dynamic method for measuring the stability of emulsions is available as yet. As far as possible, the experiments with spray liquids reported in this paper have been conducted under conditions which at least approximate those of actual use. In certain cases, the corresponding behavior under static conditions was studied for comparison.

⁵ See "Literature Cited" at the end of this paper for complete data on citations, which are referred to in the text by author and date of publication.

The general scope of the investigation covered the following points: behavior of water and of aqueous solutions of the accessory substances when sprayed upon a surface, the amount of each deposited, the amount of accessory substances deposited, their distribution in the system, the angle of contact during spraying and at rest, the effect of rolling, the behavior of oil emulsions when sprayed, the wetting and spreading of the two phases, the effects of competition for space upon the solid surface, and other factors influencing the amount of oil deposited.

THEORIES OF BEHAVIOR OF LIQUID SPRAYS

The theoretical basis for interpreting the behavior of two liquids sprayed together upon a solid surface lies in the magnitudes of the various interfacial energies and in the mechanical effects resulting from violent impact of the liquids upon the solid. The behavior of a liquid upon a solid horizontal surface has been discussed in detail by so many writers—for example, Rideal (1926) and Adam (1930)—that only certain special features need to be mentioned here. In applying an insecticidal or fungicidal spray, the intent is to reach all parts of the solid surface concerned; as far as this objective is achieved, the surface, at least while the spraying continues, becomes covered with a film of the liquid.

If the liquid is either a pure compound or a solution, its behavior after spraying has ceased depends upon whether the sum of the liquid-surface energy, γ_1 , and the solid-liquid interfacial energy, γ_{1s} , is smaller or larger than the solid surface energy, γ_s . If $\gamma_1 + \gamma_{1s} < \gamma_s$, the liquid will remain in a film over the surface of the solid; but if $\gamma_1 + \gamma_{1s} > \gamma_s$, it will recede from the surface and gather into drops, whose area will be subject to the equilibrium condition that:

$$\gamma_s = \gamma_{1s} + \gamma_1 \cos \theta, \quad 1$$

in which θ is the equilibrium angle enclosed by the liquid at the edge of the drop. In spraying natural surfaces, variations in behavior are often noted between different regions of the same leaf or fruit. These are sometimes due to real differences in the nature of the surface at different points and sometimes to the presence of foreign material, such as dust. If finely divided material which is wet but poorly by the spray is on the surface, real contact may not be made with the surface; and the liquid will retreat very rapidly when spraying has ceased. In the special case when $\gamma_1 + \gamma_{1s} = \gamma_s$, the extent to which the liquid film extends will be particularly sensitive to mechanical disturbances. This condition is likely to occur only in certain regions rather than over any entire natural surface.

The introduction of a second liquid phase into the spray leads to greater or less contact of the new liquid with the solid surface and hence to competition for space between the two liquids and ultimately to partial or complete replacement of one liquid by the other. The energies concerned in these processes are those residing in the surfaces of the two

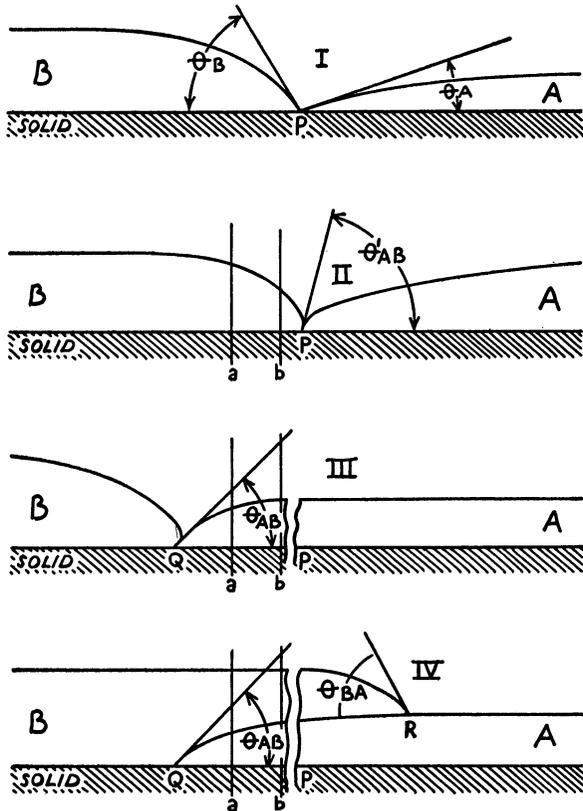


Fig. 1.—Displacement of one liquid from a solid surface by a second liquid.

liquids, in the interface between the liquids, and in the interfaces between each liquid and the solid. In figure 1 are shown diagrammatically certain of the situations which have been observed when limited volumes of oil A, and aqueous solution B, were applied gently to adjacent areas of a surface. In section I, the advancing front of liquid A, which makes a small contact angle, θ_A , upon the solid S, meets liquid B, which is advancing in the opposite direction and which makes a larger contact angle θ_B . In section II, the depth of both liquids at the line of contact has increased,

and the interface between the two liquids has been established so that it makes the angle θ'_{AB} with the solid surface. This usually is not the equilibrium angle, and the system will change to a condition such as III or IV. Since liquid *B* has been replaced by liquid *A*, the changes in energy per square centimeter of solid surface in III, as in region *a-b*, are $(\gamma_A + \gamma_{SA}) - (\gamma_B + \gamma_{SB})$, which may be called the "replacement coefficient" for any case in which one liquid is pushed back by another and the one which is replaced does not spread over the other. Since limited volumes were assumed for each liquid, obviously the one which spreads will soon be in a very thin layer while the thickness of the other will become greater. At length an equilibrium will be reached whose geometrical characteristics will depend on whether contact is made upon a flat surface, within a trough, within a capillary tube, etc., but which will be characterized by an equilibrium angle θ_{AB} between the solid and the plane of contact of the two liquids where it meets the solid as at point *Q*. When equilibrium has been established, the relations at the line of maximum extension of liquid *A* will be expressed by the equation:

$$\gamma_{SB} = \gamma_{SA} + \gamma_{AB} \cos \theta_{AB}. \quad 2$$

The situation in which the displaced liquid spreads over the other is represented in section IV of figure 1. The energy change per unit area is $\gamma_B + \gamma_{AB} + \gamma_{SA} - (\gamma_B + \gamma_{SB})$, or $\gamma_{AB} + \gamma_{SA} - \gamma_{SB}$. The equilibrium condition will satisfy equation 2 and θ will have the same value as θ in III unless the layers of liquid are so thick that gravity has an appreciable effect. Liquid *B* may not spread entirely over liquid *A* but instead may assume an equilibrium angle, θ_{BA} , upon it. The equilibrium conditions at *R* may be expressed by the same kind of equation as for a liquid spreading upon a solid, in this case:

$$\gamma_A = \gamma_{AB} + \gamma_B \cdot \cos \theta_{BA}. \quad 3$$

Only under certain conditions is the above discussion rigidly valid for the behavior of an oil emulsion applied to a solid. The more important of these conditions are: (*a*) the surface is horizontal; (*b*) the effects of gravity are negligible; (*c*) the force with which the liquids strike the surface can be neglected; and (*d*) the effects due to emulsifying and wetting agents present in the emulsion are those for equilibrium conditions. Obviously in many situations none of these limitations hold. The numerous discrepancies between theory and fact in the use of sprays are largely due to the false assumption that an ideal system is being studied. In later sections, the practical effects of certain of the factors listed above will be discussed in detail.

In a system involving water, oil, a solid, and a soluble surface-active substance, the last-named may obviously exert its effect at any or all three of the possible interfaces—(a) water-oil, (b) water-solid, and (c) oil-solid. As a matter of fact, any actual substance of this nature tends to collect to varying extents at all three interfaces, but a distinction may be drawn between *emulsifying agents*, which primarily affect interface *a*, and *wetting* and *spreading agents*, whose chief effect is upon interfaces *b* and *c*.

The difference between wetting and spreading agents has been discussed by numerous workers, but the terms have not always been distinguished clearly. The various points concerned are covered satisfactorily in the following three sets of definitions: (1) A wetting agent is "any substance which causes a spray fluid to wet the sprayed surface so that 'running up' into drops on the surface is avoided;" a spreading agent is "any substance which tends to cause lenses of spray to spread over those portions of the plant surface which have not been hit directly by the spray" (Woodman, 1930). (2) "A wetting agent is any substance which increases the readiness with which a liquid makes real contact with a solid;" "a spreader is a material which increases the area that a given volume of liquid will cover on a solid or another liquid" (Hensill and Hoskins, 1935). (3) "Wetting properties are defined by the ability to form a persistent liquid-solid interface when excess of liquid is drained from the surface;" "spreading properties are defined by the ability of the liquid to form a liquid-solid interface solely by surface activity over the plane surface of the solid" (Evans and Martin, 1935). In order to avoid the use of long and awkward expressions in referring to materials added to the oil-water system for the purpose of altering its properties in one way or another, the term "accessory substance" will be used when no particular function is being emphasized.

The oil-water interface may be affected by a third component which is predominantly soluble either in oil or in water. Hence, both the stability of an emulsion and the relative ease of contact of oil and water with a solid surface may be affected by both water-soluble and oil-soluble accessory substances. The present work has been limited to those which are predominantly water-soluble. Chemically speaking, such substances will have an affinity for water, that is, the phase in which they are more highly soluble, but in order to be able to concentrate in the water-oil interface, they must possess a chemical group or groups which are soluble in the latter also. All emulsifying agents have an affinity for each of the liquid components of the emulsion. Similarly, a substance which aids a liquid to wet a solid must contain groups which have an affinity for

both the liquid and the solid, respectively. Since solids may or may not be similar in constitution to oils, a substance which is a good emulsifying agent for hydrocarbon oils will have different effects in promoting the wetting of various solids by water. A high emulsifying power is not necessarily accompanied by high wetting power and vice versa. Thus, proteins are effective wetting agents for beeswax surfaces, but are relatively poor emulsifiers for hydrocarbon oils, while soaps possess these properties in the reverse relation.

The extent to which a substance may effect the emulsifying, wetting, or spreading properties of a liquid or mixture of mutually insoluble liquids, such as an oil-water emulsion, is dependent upon the time allowed for it to migrate into the interfaces concerned; for the over-all concentration in the bulk of the liquid is usually low, and the marked effects exerted by surface-active substances are due to their ability to become concentrated in regions of transition from one kind of matter to another. The importance of time as a factor in the behavior of oil sprays was emphasized by Ben-Amotz and Hoskins (1937) and will be further illustrated in subsequent sections of this paper.

MATERIALS, APPARATUS, AND METHODS

Three water-soluble surface-active materials, a soap, blood albumin, and hemoglobin, were used as accessory substances. The soap was a so-called "neutral" powder, U.S.P. sodium oleate. It was finely divided, slightly yellow in color, and dissolved completely to give a practically colorless opalescent solution. A stock solution of known strength, made up fresh from time to time, was used in preparing the various solutions and emulsions.

The blood albumin was a commercial preparation of dried blood proteins known as Mapeo Blood Albumin. It was a brownish-red powder, containing approximately 3 per cent of insoluble material. A stock solution was used for preparing the various dilutions.

The hemoglobin was prepared in the laboratory from fresh beef blood according to the method of Morse (1927). Great care was taken to avoid conditions likely to cause chemical or physical changes in the hemoglobin, and the various preparations were kept at 0° C in aqueous solution. The concentration of each stock solution was determined by analysis for nitrogen and for iron. In each case the two methods agreed within 1 per cent.

The accessory substances were used at concentrations varying from zero to 0.0225 per cent by weight. For convenience, actual measurements were made in milligrams per gallon of spray and are so given in the

graphs. The relations of milligrams per gallon, per cent by weight, and ounces per 100 gallons are as follows :

Milligrams per gallon	Per cent by weight	Ounces per 100 gallons
71	0.0019	$\frac{1}{4}$
142	0.0037	$\frac{1}{2}$
284	0.0075	1
568	0.0150	2
852	0.0225	3

The oil used in all experiments was a "white neutral" tank-mix stock oil of 80 seconds Saybolt viscosity, 92 per cent unsulfonatable residue, and 0.85 grams per cc density. It was secured from the refinery at intervals and kept in closed cans to minimize the changes that take place during storage. This oil was used at 2 per cent by volume in all the emulsions.

The water was ordinary Berkeley tap water whose pH is 8-9 and degree of hardness 45-50 p.p.m. CaCO_3 . The temperature of the spray liquids when ready for use was 16-20° C.

The surface to which the sprays were applied was a commercial white beeswax, which, for application, was dissolved in carbon tetrachloride at 35° C to a concentration of 4.5 per cent by weight. Oil sample bottles 13.6 cm in height and 3.6 cm in diameter (total lateral area 153 sq. cm) and glass plates $3\frac{1}{4}$ by $4\frac{1}{4}$ inches were dipped in the wax solution and then set on a rack to dry for 24 hours. A very thin hard coating was left which appeared to be uniform in properties and whose weight was constant thereafter. The bottles and plates were used as soon thereafter as possible, for after a few days the surface became split by fine cracks and behaved differently when sprayed.

Measurements Made under Static Conditions.—Surface tensions were determined with the du Noüy interfacial tensiometer. All measurements were made by pulling the ring upward. In preparing for a test, care was taken to disturb the surface to a minimum extent in order that the experimental result might be an accurate measure of the tension of a surface of the given age.

Angle of contact was determined by placing a small drop of the liquid upon a horizontal waxed plate and photographing it from the side.

Replacement of one liquid by another was studied by placing drops of each very close together and visually following the changes in position after the drops touched.

Emulsifying power was studied by agitating for 1 minute with a milk-shake mixer equal volumes of oil and a solution of the chosen accessory substance. The emulsions were then allowed to stand in tall cylinders

and the time required for 50 per cent of the oil to escape and collect at the top was determined.

Measurements Made under Dynamic Conditions.—The extent of wetting of a surface as spray is applied to it was determined by taking photographs with 0.001 second exposure (Craig, 1936). By doing this at intervals, the sequence of events can be followed as a spray is applied.

The shape assumed by drops as they roll down a vertical or inclined surface was also studied by the photographic method.

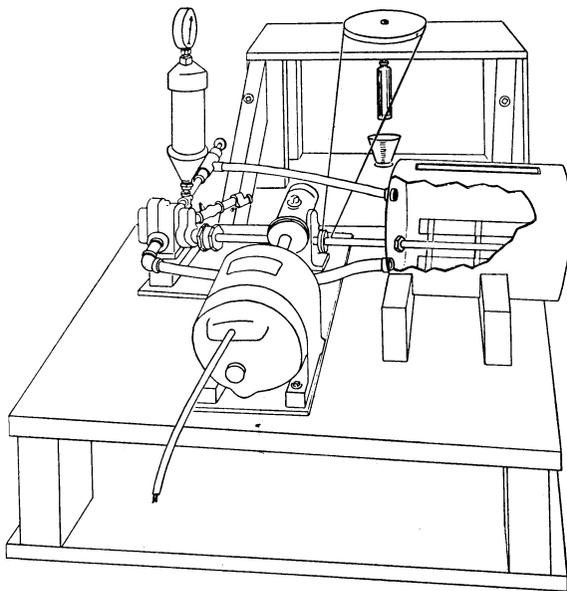


Fig. 2.—Apparatus used in spraying.

The important distinction between the *advancing* and *retreating angles of contact* made by rolling drops is brought out clearly by photographs.

The spraying apparatus consisted of a small gear pump attached to a horizontal 2-gallon tank equipped with an agitator having long flat blades of the ice-cream-freezer type, which revolved 240 times per minute. The nozzle was of the Vermorel design with a disk opening $\frac{1}{32}$ inch in diameter. By properly setting the pin, a solid cone of spray of uniform density can be secured. The objects to be sprayed were placed in a hood 55 cm distant from the nozzle and centered in the spray cone. The bottles were attached by means of a cork to the lower end of a vertical iron rod which rotated at 15 r.p.m. The entire apparatus is shown diagrammatically in figure 2.

The sprays were prepared by putting 1 gallon of water in the tank with the required amount of accessory substance. The agitator was set in motion and oil in the standard amount of 2 per cent by volume was added. After agitation had continued for 5 minutes, the pump was started and the emulsion was recirculated to the tank under a pressure of 80 pounds to the square inch for 1 minute. Sufficient spray was then wasted to flush out the pipes and the waxed bottles were sprayed as rapidly as possible.

The volume of spray applied to each bottle was regulated by catching the runoff in a funnel and graduated tube set closely beneath the bottle. Spraying was continued until the volume of the liquid was 20 cc. At a pressure of 80 pounds per square inch very little liquid is knocked off the bottle, and consequently that which drains from the bottom is a reliable index of the total volume which struck the surface. By means of a shutter set in front of the nozzle, the volume of the spray which reaches the bottle can be controlled to within 1 cc. The corresponding variations in deposit are negligible.

Four bottles were sprayed for each deposit test, and the tests were repeated several times for each condition.

The amount of oil deposited was determined by the difference in weight before and after spraying, 48 hours being allowed for all water to evaporate.

The amount of aqueous solution or of entire emulsion deposited was determined also by the difference between weights before and after spraying, but in these cases the bottles were taken from the spray chamber, placed for 5 minutes in a compartment saturated with water vapor in order that excess liquid might drain off, and then weighed as rapidly as possible.

For studying the amount of accessory substance left upon the surface under various conditions, hemoglobin was used and estimated by analysis for nitrogen by a micro-Kjeldahl method.

RESULTS

Effects of the Accessory Substances upon the Wetting and Depositing Powers of the Aqueous Phase.—The study of the separate components of the emulsions was begun with the aqueous phase since it is the only one in which the surface-active added substances are soluble and which, therefore, may be expected to reveal most simply the effects of their presence.

In figure 3, *A*, the behavior of water and of solutions of blood albumin, hemoglobin, and sodium oleate during application to waxed bottles is shown by photographs taken with 0.001 second exposure according to the method of Craig (1936). When the pictures were taken, spraying had

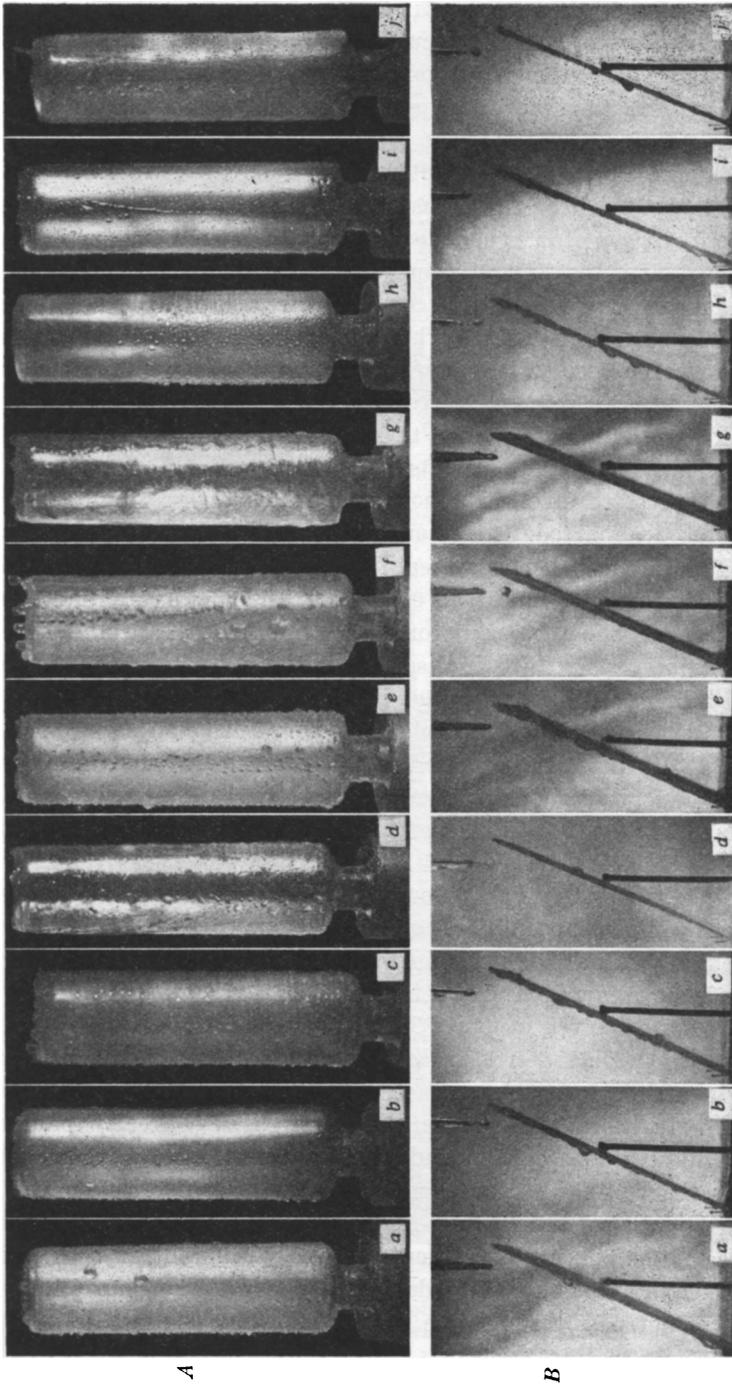


Fig. 3.—4, Behavior of aqueous solutions of the accessory substances during spraying; B, behavior of drops of aqueous solutions of the accessory substances as they move down an inclined wax surface. Composition of the solutions: a, water; b-d, blood albumin; e-g, hemoglobin; h-j, sodium oleate. Each of the accessory substances is in a series of increasing concentrations—35, 142, and 568 mg per gallon.

A

B

been in progress for 10 seconds, during which time approximately half the standard runoff of 20 cc had occurred. The appearance at corresponding concentrations of the two protein solutions is somewhat similar and is in sharp contrast to that prevailing with the soap. At equal concentrations, hemoglobin gives somewhat better wetting than the commercial blood albumin. The lowest concentration of each substance causes the solutions to wet but little better than water; but thereafter the proteins cause the formation of broad shallow drops, which coalesce to run down in streams. With the highest concentration illustrated (568 mg per gallon), wetting is fairly well accomplished and broad sheets cover a considerable portion of the area. The soap solution at the highest concentration shown forms only a few narrow streams and no sheets. As a matter of fact, comparable wetting scarcely occurs with solutions of sodium oleate six times as concentrated as those of the proteins.

The contrast between the effects of the two types of accessory substances is illustrated further by photographs taken several minutes after spraying was completed. These conditions are shown in figure 4. The transition from small hemispherical drops to broad shallow drops and eventually to complete coverage of the wax surface by a continuous sheet of solution is shown clearly for the two proteins. On the other hand, even the highest concentration of soap causes only limited formation of streams and no continuous coverage.

The observations and photographs made both during and after spraying leave no doubt that as measured under actual conditions of use, soap solutions are very poor wetting agents for beeswax surfaces, whereas the two protein solutions, particularly the hemoglobin, are excellent for that purpose.

A quantitative study of the amounts of solution left upon the surface was made by allowing each tared bottle to drain for 5 minutes in a chamber practically saturated with water vapor and then weighing it. Very little drainage occurred after this interval.

The results are given in figure 5. They bring out the important fact that whereas the formation of shallow drops tends to increase the amount of liquid remaining upon the surface, as soon as conditions are such that complete wetting occurs, the amount remaining is very greatly reduced. This result is in accord with the finding of Evans and Martin (1935) that the better the wetting the less the maximum amount of spray that could be applied before runoff occurred. Although the conditions of their work and those of the present experiment were very different, in both cases improvement in wetting led to decreased deposit. The soap solution, which does not pass through the state of forming shallow drops but

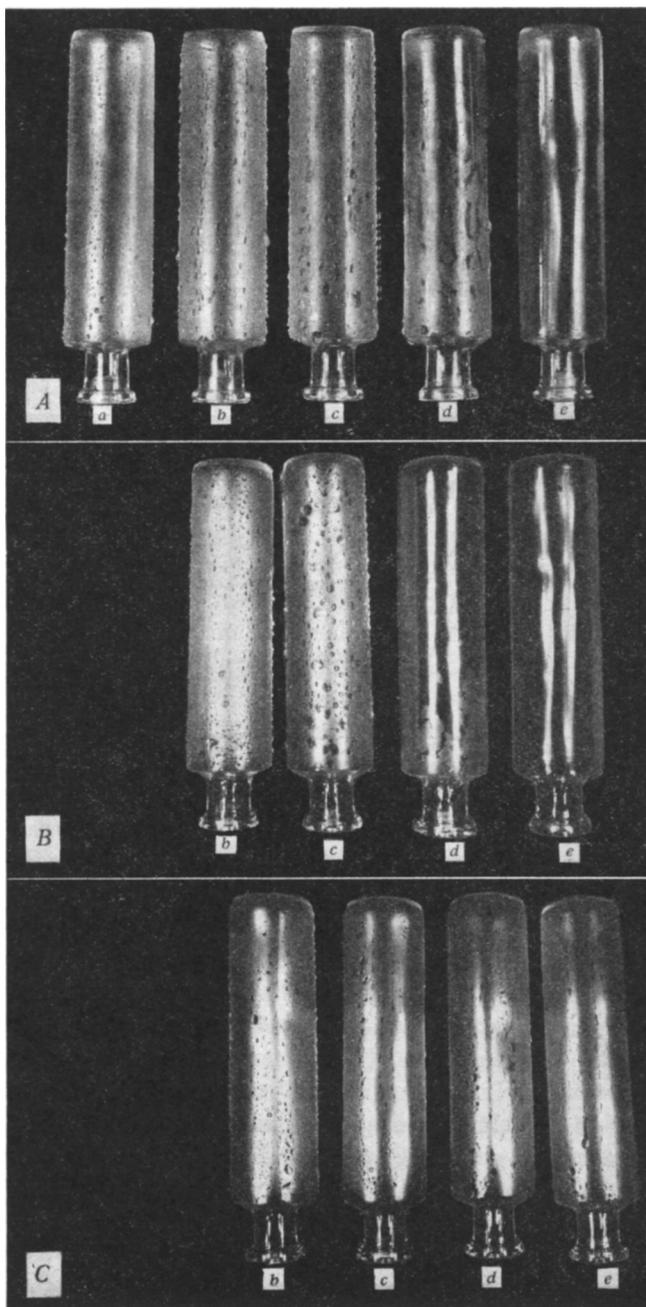


Fig. 4.—Appearance of bottles several minutes after spraying with aqueous solutions of the accessory substances: *A*, *a*, water; *b–e*, blood albumin; *B*, hemoglobin; *C*, sodium oleate. Each of the accessory substances is in a series of increasing concentration—*b*, 71 mg per gallon; *c*, 142 mg per gallon; *d*, 284 mg per gallon; *e*, 568 mg per gallon.

forms very narrow streaks instead, remains upon the surface in continuously decreasing amounts as more solute is used.

It was very easy to notice during the act of spraying that the various solutions made widely differing angles of contact with the solid; to some extent these effects can be seen in the photographs of figure 3, *A*. In order to study this behavior to better advantage, photographs with 0.001-sec-

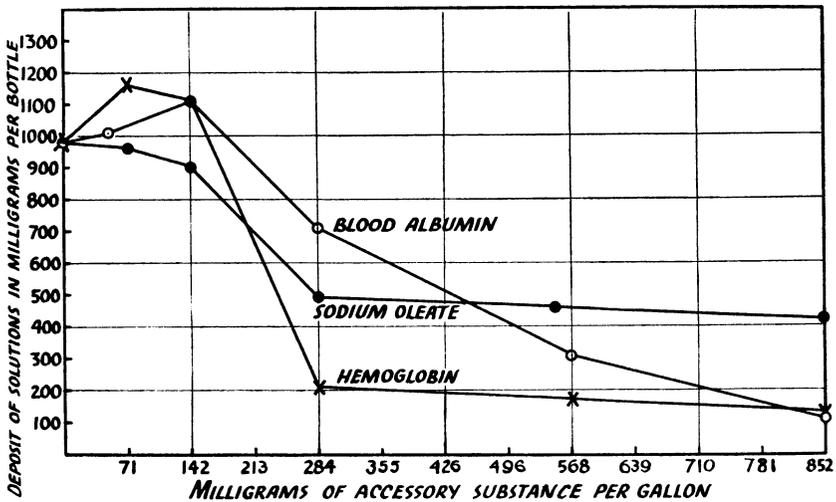


Fig. 5.—Total deposit of solutions of the various accessory substances.

ond exposure were taken of drops of the solutions as they rolled down a waxed slide set at an angle of 24° to the vertical.

The results are shown in figure 3 *B*. Since the drops were made to fall very rapidly from the tip of the burette, they were of nearly uniform size, and several could be photographed at once as they moved down the slide. The following significant differences in behavior of the solutions may be noted: moving drops of the water and of all the soap solutions assume approximately the same shape; but with successively higher concentrations of protein, drops of these solutions flatten, and with the greatest amounts present (fig. 3 *B*, *d* and *g*), a continuous sheet so thin that it cannot be seen from the side is formed by coalescence of the successive drops.

A somewhat similar method of studying spray liquids was suggested by Heranger (1936) who allowed drops to move down the underside of an inclined tube. Under those conditions, the drops are distorted on account of the shape of the solid. For this reason, the present method seems to approximate more closely conditions of normal use of sprays.

The difference between the advancing and retreating angles established during movement of drops down a wax surface is brought out clearly in figure 3 *B*. In the case of water and the soap solutions, the advancing angle is somewhat greater than 90° , whereas the retreating angle is considerably less. However, the important point is not the precise magnitude of these angles but the fact that the latter have a finite magnitude, that is, the drops move as a whole and do not leave a layer of solution behind them. By contrast, the protein solutions, particularly that of hemoglobin, form long tails and, with the higher concentrations, spread from one drop to the next and make a zero retreating angle with the wax surface.

Since this ability of the protein solutions to adhere strongly to the surface is entirely due to the solute, it was of great interest to learn if the proteins become concentrated upon the wax. This was done in the following manner: bottles were sprayed in the usual way, taken from the stand, and shaken several times very vigorously. By this procedure most of the liquid was mechanically removed, and a fairly uniform weight of about 125–150 mg was left as a thin film in all cases. The amounts of protein in these strongly adherent portions of the spray solutions, as calculated from micro-Kjeldahl determinations of nitrogen, are given in columns 2 and 3 of table 1. From the original concentrations in the spray solutions, the amounts of protein in this weight of solution may be calculated approximately, by assuming unit density, to vary from 0.0025 to 0.031 mg. Upon dividing the first and last numbers in columns 2 and 3 of table 1 by these figures, it is found that the blood albumin is from 60 to 25 times as concentrated in the strongly adherent film upon the bottles as in the original solutions and the hemoglobin from 140 to 20 times as concentrated, depending upon whether the weakest or the strongest solutions are compared. As is usual with adsorption processes, the greater relative effect is found with the more dilute solutions.

To gain further information regarding the collection of protein at the wax-liquid interface, analyses were made to determine the amount of blood albumin in all the solutions which remained upon the bottles after spraying, that is, those shown in figure 4. The amounts are given in column 4 of table 1. Comparison of columns 3 and 4 shows that most of the protein remained upon the bottles when they were shaken, though for the lower concentrations at least 80 per cent of the adhering liquid was shaken off. Hence, this experiment also indicates that the protein accumulated at the solid-solution interface.

On account of the emphasis placed by certain writers upon the importance of surface tension as a measure of the wetting or spreading

properties of spray solutions, determinations were made of the surface tensions of the various solutions of blood albumin, hemoglobin, and sodium oleate used in the spraying experiments. All measurements were made upon surfaces 15 seconds old since this is about the least time in which trustworthy tests can be carried out with the du Noüy instrument.

The results are given in table 2. Apparently the differences in behavior of the various solutions during spraying cannot be correlated with the surface tension measured in this way. The tension of older surfaces, such

TABLE 1
WEIGHTS OF PROTEINS IN SPRAY REMAINING UPON WAXED BOTTLES

Concentration of accessory substance in spray liquid	Weight of protein on bottle			
	From solution			From emulsion (not shaken): hemoglobin
	After shaking		Not shaken: blood albumin	
	Hemoglobin	Blood albumin		
1	2	3	4	5
<i>mg per gal.</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>
71.....	0.35	0.15	0.25	0.22
142.....	0.41	0.31	0.41	0.23
284.....	0.47	0.47	0.66	0.26
568.....	0.54	0.63	1.14	0.30
852.....	0.59	0.70	0.70	0.34

as are ordinarily used for such measurement, are even less likely to be related to the wetting power of spray liquids during application.

Effects of the Accessory Substances upon the Behavior of the Oil Phase and of the Complete Emulsion.—The introduction of oil into an aqueous spray liquid leads at once to the situation previously described, that is, competition between the two phases for room upon the surface sprayed. The extent of separation of oil and water during the time an emulsion is passing through the air from nozzle to surface is apparently not known; but since this period is very short with the arrangement used in the present work, most of the surface of the spray drops is probably aqueous. Accordingly, after impact of the spray, there is opportunity for migration of the accessory substance to the solid-aqueous interface, and wetting occurs to an extent dependent upon the concentration of the wetting agent and the nature of the solid.

Photographs of the behavior of various emulsions during spraying are shown in figure 2 of the previous article in this series (Ben-Amotz and Hoskins, 1937). Comparison of these pictures with those for the solutions

containing no oil (fig. 3, *A*, of this paper) reveals that the emulsions wet the surface less easily than the corresponding solutions of the accessory substances. When the aqueous phase wets poorly—for example, in the absence of accessory substances or with soap solutions—the droplets grow in size upon the surface during spraying until under the influence of gravity, they begin to move downward. Their shape is similar to that

TABLE 2
SURFACE TENSION* OF SOLUTIONS OF THE VARIOUS
ACCESSORY SUBSTANCES
(All surfaces were 15 seconds old)

Accessory substance	Concentration	Surface tension, γ
None.....	<i>mg per gal</i> 0 (tap water)	<i>dynes per cm</i> 74.0
Blood albumin.....	{ 71 142 284 568 852	65.0 62.6 59.5 57.5 56.4
Hemoglobin.....	{ 71 142 284 568 852	70.5 67.4 64.4 61.6 53.8
Sodium oleate.....	{ 71 142 284 568 852	69.9 66.6 63.5 58.9 49.1

* These data are as read on the du Noüy tensiometer. To reduce them to absolute values of γ , multiply by factor 0.943, calculated by method of Harkins and Jordan (1930).

shown in figure 3, *B*, *a*, *h*, *i*, and *j*. At no time is there a large area of contact between the emulsion and the surface, and consequently a comparatively small portion of the available oil ever reaches the solid. If a drop of such an emulsion is allowed to move down the surface of a waxed slide or bottle, the oil which separates upon the solid can be seen as isolated spots. Complete coverage can be secured only by allowing many such drops to roll down a given portion of the surface.

When the aqueous phase has moderately good wetting power—for example, with the protein solutions containing 35 to 142 mg per gallon—the drops of emulsion elongate as they move and form long tails in which the oil droplets congregate. Opportunity is thus afforded for oil to deposit upon the surface if it is able, first, to make real contact, and second, to

displace the aqueous phase. As far as these actions occur, the surface changes from the original solid wax to liquid oil. An oil surface is wet by protein solutions much less readily than is wax. For this reason, the emulsions have more difficulty in remaining extended upon the surface as the latter is progressively converted to oil. At some characteristic concentration for each protein, conditions will be such that maximum oil will reach the sprayed surface. With higher concentrations, the aqueous phase has so much wetting power that oil has excessive difficulty in displacing it from the surface; hence, less oil may be expected to be deposited.

Additional information concerning the phenomena which occur during the application of emulsions to wax surfaces was secured by a study of the amounts of the various components deposited during the process of spraying. The total was determined by allowing the tared bottles to drain in the humidity chamber for 5 minutes before weighing, just as in the determination of total deposit of the solutions. The results are shown in figure 6. In this same figure are shown the amounts of oil deposited per bottle from 20 cc runoff of each emulsion. The difference between total deposit of emulsion and oil deposit is the amount of aqueous phase left upon the surface. Obviously the curves representing the deposits of the aqueous phase are in general similar in shape and close to those for total deposit.

As was mentioned above, the photographs of the spraying process show that the various emulsions wet the surface more and more poorly as the deposit of oil increases. The deposits of the entire emulsions and of the aqueous phases bear out this observation.

Thus the decided increase in total deposit with higher concentrations of blood albumin is consistent with the abrupt decrease in the amount of oil deposited, for the surface is thereby wetted more easily. At the same time, the formation of a thin film of the aqueous phase is not possible, so that no decrease in deposit occurs from that cause as occurred with the aqueous solutions alone (fig. 5).

In the case of hemoglobin, the increase in total deposit with small amounts of the protein is caused by increased ease of wetting even in the presence of the oil; but thereafter the uniformly large amount of oil on the surface causes the deposit of emulsion to remain nearly constant as the concentration of hemoglobin increases.

The nearly constant small amount of emulsion deposited in the case of sodium oleate may be explained as a consequence of the very poor wetting properties of this material over the concentration used, together with the fairly constant deposit of oil.

A comparison of figures 5 and 6 will show that with the higher concentrations of accessory substances, more of the aqueous phase containing the proteins remains upon the surface than when only the solutions are used, whereas the reverse is the case with soap. This shows clearly that

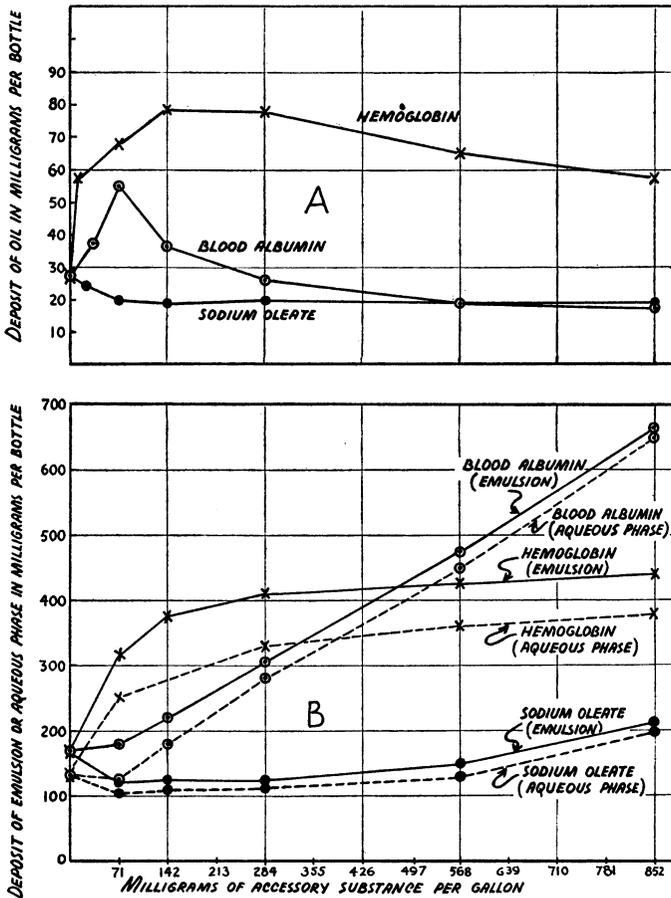


Fig. 6.—Deposit of oil, total emulsion, and aqueous phase resulting from different concentrations of accessory substances.

the greater difficulty in wetting an oil surface and consequent formation of drops instead of sheets increases the amount of the aqueous phase which adheres to the surface. Since the soap solution is not able to form continuous sheets on either wax or oil, a similar reversal would not be expected.

Further information regarding the behavior of oil emulsions during

spraying was obtained by analyses to determine the amounts of accessory substance left upon the wax surface during the process of spraying. Comparison of the data in columns 5 and 2 of table 1, shows that hemoglobin was present in amounts somewhat over half as great as when no oil was in the spray. Thus less accessory substance was deposited from the emulsion than from the aqueous solution; but since drops of the emulsion clung to the oily surface, this experiment shed no light on whether the hemoglobin was still upon the wax, that is, beneath the oil, or whether it was all in the aqueous phase. In order to determine this point, two kinds of experiments were performed.

In the first experiment, upon bottles which had been sprayed with an emulsion containing hemoglobin, the locations of the adherent drops of the whole emulsion were marked, and the spray was then allowed to dry. The spot-test reagent of Lucas (1935) was then applied to various regions of the surface. This reagent is a solution of sodium perborate and benzidine in glacial acetic acid, and it changes from pale straw color to blue in the presence of extremely small amounts of hemoglobin. The results were very clear-cut; for even the smallest drop of the whole emulsion gave an unmistakable response, but the rest of the surface gave no color. It is scarcely possible that the oil covered over any hemoglobin and prevented a reaction; for after standing several hours, as in some of these experiments, the oil enters into the wax layer and leaves the surface exposed again. Furthermore, when a drop of hemoglobin was allowed to dry upon the wax surface and a thin film of oil was added and allowed to stand for a time, the test was very positive. This experiment indicates that hemoglobin follows the aqueous phase and does not remain behind when water is displaced by oil.

The second test of this theory consisted of placing drops of oil and of hemoglobin solution adjacent to one another upon a waxed slide. The areas in which the solution was replaced by oil gave no test for hemoglobin.

No direct study of the behavior of blood albumin or of sodium oleate could be made since similar simple tests are not available. There is every reason to believe that blood albumin acts like hemoglobin. In fact, during the replacement of their solutions by oil, both proteins may be observed to pile up in front of the oil as it advances. Probably not even a unimolecular layer of the water-soluble proteins is left upon wax as the latter becomes covered by hydrocarbon oils. A definite conclusion can scarcely be drawn for soap, which has much more affinity for oil. However, the very poor wetting power of soap solutions for wax is an indication that soap also will follow the aqueous phase.

A number of experiments were made to study the displacing power of oil for the various solutions of accessory substances placed upon waxed plates. In the case of water and of any of the soap solutions within the concentration range used in the spraying work, displacement was complete. The oil crept around and beneath the aqueous drop, which eventually floated upon the oil in the form of a flattened sphere. Probably because water is heavier than oil, the latter was present beneath the drop of water only in a very thin but continuous film.

When a protein solution was used, the initial rate of displacement was slower, and equilibrium was reached in some one of the positions indicated in figure 1. The higher the protein concentration the less the replacement and the more closely the equilibrium state resembled figure 1, II. On account of its great importance in connection with all oil emulsions, the replacement of one phase by the other merits further detailed study.

DISCUSSION

In spite of the importance of the quantity of liquid left upon a plant or other sprayed surface when an aqueous solution of an insecticide or fungicide is applied, very little information on the subject has been recorded. Emphasis is usually laid upon complete wetting of the surface; and of course the importance of reaching each part, at least during the application of the spray, cannot be denied. Unfortunately, however, as shown by Evans and Martin (1935) and in the present investigation, the state of complete wetting is also that of low retention of liquid. The discovery that dissolved proteins become concentrated in the adhering liquid suggests that toxic materials, for example, nicotine or polysulfide, may be held in a similar manner. If this should prove to be the case, then wetting agents would probably affect such behavior, and the possible helpful or harmful effects in this respect of various accessory substances would offer a fruitful field of investigation.

Difficulties in Experimental Work.—Efforts to gain information about the behavior of sprays during actual use must be made under two kinds of handicap. Theory has been developed extensively for static but not for dynamic conditions. At least two additional forces must be introduced into the expressions for the behavior of a liquid sprayed against a solid, that is, gravity and impact pressure. The steady increase in the pressure under which sprays are being applied as more powerful pumps are developed causes the latter factor to be of more and more importance. Until such theoretical advances are made, recourse must be had almost entirely to empirical methods. Here the second difficulty arises; for the necessary technique has been developed but slightly. The complete failure of the

drop method for measuring dynamic angles of contact was pointed out by Ben-Amotz and Hoskins (1937) and illustrated by photographs. The rotating cylinder method of Ablett (1923) is undoubtedly an improvement and merits trial with spray solutions. The ordinary method of changing the angle of incidence of a slide introduced into the liquid has been shown by Evans and Martin (1935) to give results suitable for correlation with deposit of solution formed by their special method of spraying only up to runoff, but it does not apply to the method of overspraying ordinarily used.

Importance of Dynamic Retreating Angle and Static Advancing Angle.—A distinction must be drawn between the situations in which the advancing angle and those in which the retreating angle is of prime importance. When the degree of wetting achieved by a liquid over the surface sprayed and the amount of the liquid retained are the chief considerations, as in the present work, the retreating angle is a controlling factor. Contact having been made with the surface by spraying under pressure, the behavior of the liquid thereafter depends upon its tendency to draw back and roll off. Contact brought about in this way may not be wetting at all in the sense of a meeting of molecules which have a marked degree of affinity for each other.

If the spray is a pure liquid or a solution, that is, consists of one phase only, the amount which will remain upon the solid will not be influenced seriously by the manner in which excess liquid leaves the surface during spraying, but it will be affected greatly by the behavior of that which is present just as spraying is stopped. For this situation, the best criterion is the retreating angle of contact measured under dynamic conditions simulating those prevailing at the time concerned. The migration of solute molecules to an interface and their orientation there are functions of time. Hence a measurement made after more or less prolonged contact, as is the usual method, does not represent the behavior of a spray in ordinary use; for drainage under the influence of gravity occurs rapidly.

The spreading of a spray beyond the limits to which it is driven during application may be of great importance, for example, in reaching beneath the covering of a scale insect or between the petals of an unfolding bud. Such extensions of a liquid usually occur rather slowly. Hence measurements of the advancing angle of contact made under static conditions may be entirely appropriate for study of such behavior.

In short, the static advancing angle is a valuable measure of the ability of a liquid to spread, and the dynamic retreating angle is an equally valuable criterion of its ability to wet. In each case the indication is valid only for the solid upon which the measurement was made, though spread-

ing is more sensitive to surface conditions than is wetting (Bartell and Wooley, 1933). The rapidity with which a liquid changes in shape or position is, of course, dependent also upon its viscosity (Woodman, 1924; Research Staff of General Electric Company, 1922).

Effect of Stability of Emulsion.—The foregoing discussion of the behavior of liquids applies to any single-phase spray, though, in the present work, interest was centered in the aqueous phase largely because it is the carrier for the emulsified oil. The introduction of a second, finely divided liquid, such as oil, broadens the range of variation in the system by at least three additional factors: stability of the emulsion, competition for space upon the solid, and alteration of the surface as oil increases in amount upon it. Of these, the first was discussed by Ben-Amotz and Hoskins (1937), who showed that the more stable an emulsion, other things remaining equal, the less oil will be deposited from a given volume of it. As the stability increases, the individual oil droplets make contact with the solid surface with greater and greater difficulty and fewer of them escape from the layer of emulsifying agent which has collected in the oil-water interface. The ideal method of measuring stability in this case would evaluate this ability of oil to escape from the emulsion to the solid. Such a method, separated completely from wetting phenomena of the aqueous phase, does not seem to have been developed.

The arguments advanced earlier regarding the importance of the dynamic retreating angle of contact as a factor which determines the amount of a homogeneous liquid which will remain upon a sprayed surface must be emphasized from yet another point of view in the case of emulsions. When the aqueous phase has moderately good wetting power, the drops elongate as they roll and in the tails the droplets of oil congregate. They are thereby brought close to the solid, and their chances of making contact with it are enhanced. As emphasized before, at some certain concentration of each accessory substance which allows sufficient wetting, maximum oil will be left upon the surface. This condition is realized with the two proteins but not with the soap; for solutions of the latter do not have pronounced wetting power except at concentrations so high that the deposit, because of the great stability of the emulsion, is extremely low. How much the conditions of replacement of the aqueous phase by oil are influenced by the pressure with which the spray liquid strikes the surface apparently has not been investigated. Until this information is available, experiments on replacement under static conditions cannot be used for quantitative comparison of various emulsions, but they certainly permit qualitative comparison.

Primary and Secondary Deposit.—The gradual alteration in the

sprayed surface from the original solid through spotted attachment and spreading of oil droplets to the final continuous layer of oil affords opportunity for division of the process into steps. The terms "primary" and "secondary" deposit were used by Smith (1933) and with slightly modified meaning by Hensill and Hoskins (1935). In the light of certain ideas developed in this report, they may be further elaborated. The primary deposit really consists of two parts. In the beginning, oil droplets are

TABLE 3
FRACTIONAL PART OF TOTAL OIL DEPOSIT CONTRIBUTED BY SECONDARY DEPOSIT

Concentration of accessory substance	Weight of aqueous phase left			Minimum weight of oil corresponding to aqueous phase			Total oil deposit (from fig. 7)			Minimum fraction of total oil deposit from secondary deposit		
	Blood albumin	Hemo-globin	Sodium oleate	Blood albumin	Hemo-globin	Sodium oleate	Blood albumin	Hemo-globin	Sodium oleate	Blood albumin	Hemo-globin	Sodium oleate
<i>mg per gal.</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.....	140	140	140	2.4	2.4	2.4	28.0	28.0	28.0	9	9	9
71.....	125	250	155	2.1	4.2	2.6	55.0	68.0	20.0	4	6	13
142.....	180	300	165	3.1	5.1	2.8	37.0	78.5	19.5	8	6	14
284.....	280	330	175	4.8	5.6	3.0	26.0	78.0	20.0	18	7	15
568.....	450	360	205	7.7	6.1	3.5	19.0	65.0	19.0	41	9	18
852.....	650	380	300	11.0	6.5	5.1	17.5	57.5	19.0	63	11	27

placed upon wax and in almost innumerable points a thin coating is developed as the oil spreads. This may be called the first stage, during which the wetting power of the aqueous phase for wax determines the manner and extent of contact between spray and solid. Displacement of the aqueous phase by oil corresponds in general to that found when a drop of oil and a drop of solution of the accessory substance are placed adjacent to one another upon a waxed slide. As the surface becomes changed from wax to oil, the first stage merges into the second, in which the wetting power of the aqueous phase for a surface of oil determines the degree of contact. Displacement of the aqueous phase by additional oil from the spray is very rapid and complete. Hence the major portion of the primary deposit is laid down during this period.

Secondary deposit is that part of the total oil which reaches the surface from adhering drops or sheets of emulsion when the water in the latter evaporates. The data needed for determination of its magnitude are given in figure 6, *if the assumption is made that the aqueous phase which is left upon the bottles at the conclusion of spraying has the same composition as the original emulsion.* The results are given in table 3.

With low concentrations of the accessory substances, only a small portion of the total oil is contributed by the secondary deposit; but at higher concentrations, this is increasingly important, particularly in the case of blood albumin.

There is evidence from visual observation that the assumption made in these calculations is not valid in all cases; for the residue of emulsion resembles the product formed by creaming, particularly when the larger amounts of accessory substances are present. That is, under the circumstances in which the drops elongate as they roll down the surface, the emulsion becomes enriched and more oil is left as a secondary deposit than is calculated from the weight of emulsion upon the surface. Hence the data of table 3 on secondary deposit should be taken as minimal values.

In general, high secondary deposit is undesirable, for such oil will be left in very localized regions and can contribute to the general deposit only by spreading upon the surface. While this may occur to some extent with oil, it is impossible in the case of a suspended solid such as bordeaux mixture or lead arsenate. Consequently the secondary deposit of such substances is of little value, except with such pests as are attracted to spotty deposits of toxic material—for example, the walnut husk fly, *Rhagoletis completa* Cresson.⁶

The nature of the curves relating total deposit with concentration of accessory substance can be qualitatively explained for blood albumin, hemoglobin, and sodium oleate in terms of the wetting power of the aqueous phase, ease of replacement of the aqueous phase by oil, and stability of the emulsions. The characteristic differences between typical wetting agents and typical emulsifiers are consistent with their relative abilities to deposit oil. The above properties, however, are complex in nature and give no final answer to the problem.

The information gathered from these experiments indicates the possibility of formulating a theory in terms of three fairly simple properties of an oil emulsion:

1. The retreating angle of contact of the aqueous phase upon the chosen solid. This must be determined under dynamic conditions, and at present high-speed photography seems to offer the best approach.
2. Ease of escape of oil from the minute droplets of the emulsion onto the surface. The difficulty in testing this property is separation of it from wetting power of the aqueous phase.
3. Rate of replacement of the aqueous phase by the oil. Theoretically this is involved in equation 2, $\gamma_{SB} = \gamma_{SA} + \gamma_{AB} \cos \theta_{AB}$. Direct measure-

⁶ Personal communication from Dr. A. M. Boyce.

ment of θ_{AB} , which may be called the angle of replacement, is very difficult under dynamic conditions, and the displacement method of Bartell and Osterhof (1927) and Bartell and Whitney (1932) is complicated in the present case by the solubility of oil in the beeswax.

Wetting Agents as Spreaders of Oil.—The question of the rôle of water-soluble wetting agents in promoting the spread of oil has been discussed by certain previous workers (de Ong, Knight, and Chamberlain, 1927; Smith, 1933; Knight and Cleveland, 1934). Smith, who used the term “spreader” in the same sense in which “accessory substance” is used in this report, said: “It appears that one function of a spreader is to cause the oil to spread on surfaces upon which it will not spread otherwise” and “As the water evaporates, the spreader lays down a coating over the surface over which the oil spreads in a uniform film.”

The truth of the second statement is substantiated by the experimental observation that oil spreads over a region in which a protein solution has dried on beeswax several times as fast as upon the untreated beeswax. The protein, however, must be dry. Hence the effect can occur with oil emulsions only after the water has evaporated. The evidence from the replacement experiments indicates that water-soluble accessory materials promote wetting by the aqueous phase only. But there are differences in the tendencies of proteins and of soaps to collect in the various interfaces. Thus, sodium oleate has a strong affinity for the oil-water interface and forms very stable emulsions, which wet wax but poorly because the soap has less affinity for the wax-water interface. Blood albumin and hemoglobin promote wetting by water very strongly but emulsify oil poorly. Possibly an accessory substance somewhat soluble in both water and oil would be retained sufficiently by the oil to promote the spread of the oil upon wax during the time of spraying, but this would necessitate the presence in the molecule of three groups having affinities for water, oil, and wax, respectively.

SUMMARY

The application of a spray is a dynamic process, and hence attempts to relate the deposit of oil obtained from various emulsions should be based upon measurements made under conditions approximating those of use. With a standard surface of beeswax as the solid sprayed and a standard method of spraying, a study has been made of the relations between concentration of blood albumin, hemoglobin, or sodium oleate and the following properties: amount of the aqueous solution and of the accessory substance deposited in the absence of oil; deposit of oil, of aqueous phase, of accessory substance, and of all components when emulsions were used;

ease of wetting of wax by solutions of the accessory substances and by the entire emulsion; replacement of aqueous phase by oil; and stability of the emulsions.

The amount of oil deposit can be explained at least qualitatively as follows: When only oil and water are present, the emulsion wets poorly, and drops roll on the surface with minimum area of contact. Addition of a protein promotes wetting and opportunity for oil to reach the surface. Hence deposit is increased until formation of large sheets of the aqueous phase upon the surface and resistance to displacement of the aqueous phase by oil lead to a decrease in oil deposit with higher concentration of protein. Soap promotes wetting so little that a corresponding increase in oil deposit does not occur. With all three accessory substances, the increase in stability of the emulsions diminishes oil deposit. Water-soluble substances follow the aqueous phase and increase spreading of oil only after the water has evaporated.

LITERATURE CITED

ABLETT, R.

1923. An investigation of the angle of contact between paraffin wax and water. *Phil. Mag. and Jour. Sci.* **46**(6):244-56.

ADAM, N. K.

1930. *The physics and chemistry of surfaces*. 332 p. Clarendon Press, Oxford.

BARTELL, F. E., and H. S. OSTERHOF.

1927. Determination of the wettability of a solid by a liquid. *Jour. Indus. Engin. Chem.* **19**:1277-80.

BARTELL, F. E., and C. E. WHITNEY.

1932. Adhesion tension. A receding angle, pressure of displacement method. *Jour. Phys. Chem.* **36**:3115-26.

BARTELL, F. E., and A. D. WOOLEY.

1933. Solid-liquid-air contact angles and their dependence upon the surface condition of the solid. *Jour. Amer. Chem. Soc.* **55**:3518-27.

BEN-AMOTZ, Y., and W. M. HOSKINS.

1937. Factors concerned in the deposit of sprays. III. Effects of wetting and emulsifying powers of spreaders. *Jour. Econ. Ent.* **30**:879-86.

CRAIG, R.

1936. A simple device for short photographic exposure. *Science* **84**:296.

DEONG, E. R., H. KNIGHT, and J. C. CHAMBERLIN.

1927. A preliminary study of petroleum oil as an insecticide for citrus trees. *Hilgardia* **2**(9):351-84.

EVANS, A. C., and H. MARTIN.

1935. The incorporation of direct with protective insecticides and fungicides. I. The laboratory evaluation of water-soluble wetting agents as constituents of combined washes. *Jour. Pomol. and Hort. Sci.* **13**:261-94.

HARKINS, W. D., and H. F. JORDAN.

1930. A method for the determination of surface and interfacial tension from the maximum pull on a ring. *Jour. Amer. Chem. Soc.* **52**:1751-72.

HENSILL, G. S., and W. M. HOSKINS.

1935. Factors concerned in the deposit of sprays. I. The effect of different concentrations of wetting agents. *Jour. Econ. Ent.* **28**:942-50.

HERANGER, S. F.

1936. La persistance des liquides et le mouillage des vegetaux. *Rev. Vit.* **85**:449-53.

HOSKINS, W. M., and E. L. WAMPLER.

1936. Factors concerned in the deposit of sprays. II. Effect of electrostatic charge upon the deposit of lead arsenate. *Jour. Econ. Ent.* **29**:134-43.

KNIGHT, H., and C. R. CLEVELAND.

1934. Recent developments in oil sprays. *Jour. Econ. Ent.* **27**:269-89.

LUCAS, A.

1935. Forensic chemistry and scientific criminal investigation. 376 p. Longmans, Green & Co., New York, N. Y.

MORSE, W.

1927. Applied biochemistry. 2d ed. 988 p. W. B. Saunders & Co., Philadelphia.

RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON.

1922. A problem in viscosity: the thickness of liquid formed on solid surfaces under dynamic conditions. *Phil. Mag. and Jour. Sci.* **44**(6):1002-14.

RIDEAL, E. K.

1926. Surface chemistry. 336 p. University Press, Cambridge, England.

SMITH, R. H.

1933. The tank mixture method of using oil spray. *California Agr. Exp. Sta. Bul.* **527**:1-86. Revised ed.

WOODMAN, R. M.

1924. The physics of spray liquids. I. The properties of wetting and spreading. *Jour. Pom. and Hort. Sci.* **4**:38-58.

1930. Wetting and spreading and emulsifying agents for use with spray fluids. *Jour. Soc. Chem. Indus.* **49**:93-98.

