A STUDY OF CERTAIN PHYSICAL FACTORS INVOLVED IN THE SPREADING OF SPRAY MATERIALS

THESIS FOR DEGREE OF M. S.

WILBUR HERMAN THIES

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A Study of Certain Physical Factors Involved in the Spreading of Spray Materials

Introduction

The development of the science of horticulture depends to a large extent on man's ability to control the insects and fungi which prey upon plant life. It is for this reason that the application of spray materials, as a protective measure, has assumed such an important place in the program of the fruit and vegetable growers of the present day.

Beginning with the work of Millardet in the eighties, research work in spray materials has attracted the attention of a vast corps of workers. Numerous independent efforts have been made to determine, the best kind of material to apply in each particular instance and also the most economical method of application. Whether the material be an insecticide or a fungicide, a thorough covering of the plant with a minimum of waste, is the goal to be attained.

It is the writer's purpose in this paper, first, to review the studies which have been made on the spreading of liquids in contact with solid surfaces and second, to discuss the question from the standpoint of certain physical factors, viz: (1) surface tension, (2) velocity and (3) size of drop.

Acknowledgment of many helpful suggestions pertaining to the tests is made to Professor V. R. Gardner of the Michigan Agricultural College, Horticulture Department, to Professor C. W. Chapman of the Physics Department and other members of the Physics Staff, also to Professor Louis Thompson of Kalamazoo College for counsel in connection with the calculation of air resistance.

Review of Literature

1. Historical Notes on Spreading

Many attempts have been made to increase the film-forming tendency of a spray solution and to make it "stick" better by the addition of adhesive substances.

One of the earliest is mentioned in Rapport au Ministre de l'Agriculture (1885). Davis, an investigator, used 6 kilograms of glue to 800 liters of copper sulfate solution, thinking that the glue increased its efficiency.

Soap or soap suds was early used in contact sprays with tobacco and other materials to insure spreading of the insecticide over the body of the insect.

Washburn (1891) used whale oil soap 6 lbs., to 50 gals. of a Paris Green suspension. Galloway (1892) used soap with different fungicides to increase spreading. Fairchild (1894) used soap with eau celeste, obtaining excellent spreading even on leaves with a heavy cuticle such as those of the pear. Galloway (1894) used resin soap with Bordeaux mixture, finding it just as effective in producing a continuous film on the leaf as ivory or whale oil soap.

Lowe (1896) encountered difficulty in spreading lead arsenate over the surface of willow leaves. He used glue, 2 qts. to 50 gals., successfully.

Mausier (1908) studied spreading of a number of liquids over different solids. He realized that spreading depends on the nature of the solid and of the liquid, but considered the difference as due principally to the surface tension of the liquid. A liquid which spreads over a particular solid in a certain definite way must have a certain definite surface tension value. If it has this value, it will spread regardless of the nature of the liquid. (A spray containing 30 gms. of soap to 10 liters of water with either 50 gms. of oil tar or 10 gms. of formaldehyde is considered as meeting the surface tension requirements of the leaf).

Gastine (1912) recommended the use of saponin to reduce the surface tension of spray materials and thus insure spreading.

Vermorel and Dantony (1912) conclude that surface tension of a liquid is not an index of its spreading power. Solutions with the same ability to spread may have different surface tensions. Two distinctions are made, (1) where the liquid is able to touch the surface, as water on a potato leaf, and (2) where the liquid rests on the surface without touching it, as water on a cabbage leaf, in which case there is a film of air between leaf and water. A solution of sodium oleate was found to spread on a cabbage leaf but not on grape leaf, while a saponin solution of higher surface tension than the sodium oleate spread readily on a grape leaf. They believed therefore that surface tension influenced spreading less than surface viscocity. The difference in the behavior of the above solutions is thought to be due to the surface concentration which takes place rapidly in the saponin solution after the film has formed, thus increasing the surface viscocity to such an extent that the solution was unable to collect in drops.

Moore (1921) states that a concentration of material in the surface layer reduces surface tension and since different materials vary as to the time required to concentrate in the surface layer, measurements of surface tension by ordinary means are not comparable. Furthermore, if surface concentration takes place so rapidly as to cause the film to become viscous, a decided lowering of the surface tension should be apparent. No consideration is taken of the possibility of a concentration of materials at the interface of the leaf and the liquid. This should result in a lowering of the interfacial tension and thus tend to produce spreading.

Chappoz, G. (1913) recommends the use of saponin in preparing sprays, considering it superior to soap. He recognizes a general relation between spreading and drop number as determined by the Duclaux pipette.

Laforge (1913) points out that spreading and adherence are entirely different phenomena. Addition of saponin gives good spreading but not good adherence, while gelatin improves both.

Lefroy (1915) finds that spreading depends not only upon the surface tension of the spray, but also upon the surface tension of the leaf and of the tension at the interface of spray and leaf. He realizes that the latter two tensions cannot be measured and so recommends determination of the surface tension of the spray as an index of spreading quality. This should be as low as possible.

Cooper and Nuttall (1915) believe that certain factors may upset the relationship of the three forces which determine the tendency to spread. (1) Solvent action of liquid on solid, particularly in those cases where the surface is coated with wax or grease. (Moore shows that this solvent action of a liquid on a solid lowers the interfacial tension and therefore tends to aid spreading). (2) Surface concentration. (Cooper and Nuttall cite the experiments of Vermorel and Dantony on the good spreading of a spray with a high surface tension, owing to its high surface viscocity which results from a rapid surface concentration of the solute). The statement is made that the measurement of surface tension alone is insufficient to determine spreading qualities of a liquid. Cooper and Nuttall used sheep dips as the liquids, and substituted a heavy castor oil or vaseline for the solid. Then by means of a Donnan drop pipette, the tension at the interface of oil and dip was measured. They point out that this method is applicable only to soap solutions and will not give results with gelatin, saponin or similar solutions. Also the surface must be greasy (This eliminates its use in studying spreading on leaves). The conclusions of Cooper and Nuttall are as follows: If $\gamma s > \gamma l + \gamma ls$ the liquid will spread, and $\gamma s - (\gamma l + \gamma ls) =$ spreading power.

A-Drop
B-Surface

Diagrammatic Representation of Interfacial Tensions.

γl refers to tension at liquid-air interface

γ_{ls} refers to tension at liquid-solid interface
γ_s refers to tension at solid-air interface

γ_{ls} is of more significance in spreading than is γ_l, for, since interfacial tension varies inversely with drop number (Donnan's drop pipette), and also inversely with spreading, the drop number (which in reality is a measure of interfacial tension) must vary directly with the tendency to spread. For example, a high drop number means high spreading power, because of low interfacial tension. This conclusion evidently holds true for liquids of low surface tension such as soap solutions but does not hold true for all liquids that will spread.

Smith (1916) used Cooper and Nuttall's method of finding γ_{ls} in determining spreading power of various combinations of fish oil soap and nicotine sulfate. He found the relations of spreading and interfacial tension similar to those found by Cooper and Nuttall. But since oil was used to represent the solid surface, the experiment has no significance in a study of leaves.

Lee (1918) studied spreading of water, gelatin, casein, soap and paraffin emulsions on leaves of gooseberry and sea kale, and on leaves covered with gooseberry mildew. All gave spreading on gooseberry leaves, but only certain emulsions spread on the sea kale and on gooseberry mildew. No explanation was offered.

Lovett (1918) believes that the ability of a liquid to hold arsenates in suspension is a fair indication of its ability to spread. However, it is doubtful if this can be considered as an index of spreading over all surfaces. In a later paper (1920) Lovett says that although the suspension test is not an accurate index of spreading, it does indicate a physical quality in the solution much to be desired in a spreader.

Jacobson (1919) produced good spreading by use of the extract from 5 lbs. of alfalfa hay added to 100 gallons of spray solution. He does not state whether spreading is the result of increased surface viscocity, lowered surface tension, or to a concentration of materials at the leaf spray interface.

Ruth and Kelley (1922) report a series of experiments on the use of casein as an aid to the formation of a film. Their conclusions are that varietal and seasonal differences in leaf and twig surfaces exist, and that the ease of covering a surface varies with the season.

Moore (1921) states that a solution containing 1/4 lb. of casein to 100 gallons of water gave good spreading on citrus leaves but failed unless applied with such force that the spray penetrated between the wax particles reaching the epidermis below. Incidentally, it may be stated that this is the only mention made, in any of the writings reviewed, of the effect of velocity on spreading.

Woodman (1924) of England, has carried on a piece of work on the physics of spray liquids in which he used glass as the surface because he believed that it resembled very closely in some of its characteristics the surface of a leaf. He defines a certain critical value for the surface tension of a liquid at which he says the maximum amount of spray material will be held. Failure to reduce the surface tension to this value results in imperfect wetting of the leaf. He found that reduction of surface tension beyond this point does not increase the wetting power.

The foregoing review of the work that has been done leaves considerable doubt as to the significance of the part played by surface tension in influencing the spreading of spray materials. It has long been assumed by many people that the surface tension of a liquid has a direct bearing on its tendency to spread when in contact with a solid surface. But several investigators have reported that certain other factors appear to have greater influence on spreading than does surface tension. It was, therefore, with the idea of throwing further light on this particular question that a series of tests was outlined. And since lime sulfur is used so commonly in spraying, that was the material selected.

I. Relation of SURFACE TENSION to Spreading

Plan of Procedure

A stock solution was made from Niagara Dry Lime Sulfur, 4 lbs. to 50 gallons and the five samples treated as indicated below.

Sample No. 1	Lime sulfur and fish oil soap.
Sample No. 2	Lime sulfur and saponin
Sample No. 3	Lime sulfur and calcium caseinate
Sample No. 4	Lime sulfur and Sun Oil
Sample No. 5	Lime sulfur

The surface tension of each sample was carefully measured with a du Nuoy instrument. This is a device made up of a steel wire and cross arm attachment to which is suspended a loop of platinum wire. One end of the steel wire is rigid, and as the dial is turned, the resulting stress raises the platinum loop, thus lifting the surface film. When the film breaks, the reading on the dial is observed. This is a measure of the force exerted by the film, or its surface tension. In this piece of work, these values were not converted into dynes per cm. because only relative values were desired. The dial readings are proportional to the surface tension in dynes. Hence the surface tension values given in Table 1 are merely degrees, read on the dial. It will be observed from this table that the treatment of the samples reduced the surface tension by varying amounts, Number 4 being only half that of the stock solution.

Spreading qualities were measured by dropping the liquids on glass, mica and paraffin. Although no one of these surfaces is exactly analogous to any kind of leaf or bark, the droplets behave on these surfaces in a way very similar to that on surfaces that are sprayed. This method therefore, puts to the test the question of influence of surface tension on spreading under different conditions.

The glass surface was cleaned very thoroughly with chromic acid and rinsed with distilled water. The mica surface was prepared by splitting along a cleavage plane. And the paraffin surface was cleaned and levelled by scraping with the edge of a plate of glass.

To transfer equal amounts of each solution to the above surfaces, a capillary tube was drawn on one end of a short piece of glass tubing and to the other end was attached a small rubber bulb. The end of the capillary tube was dipped in paraffin to prevent adherence of the solution. By means of the rubber bulb the solution was allowed to enter the capillary tube up to a given point. The tip of the tube was then held near the surface, all of the solution excluded at a single point on the surface, and allowed to spread naturally without disturbance. About twenty such areas were produced on each surface. The tube was then cleaned thoroughly, and the process repeated with the next sample.

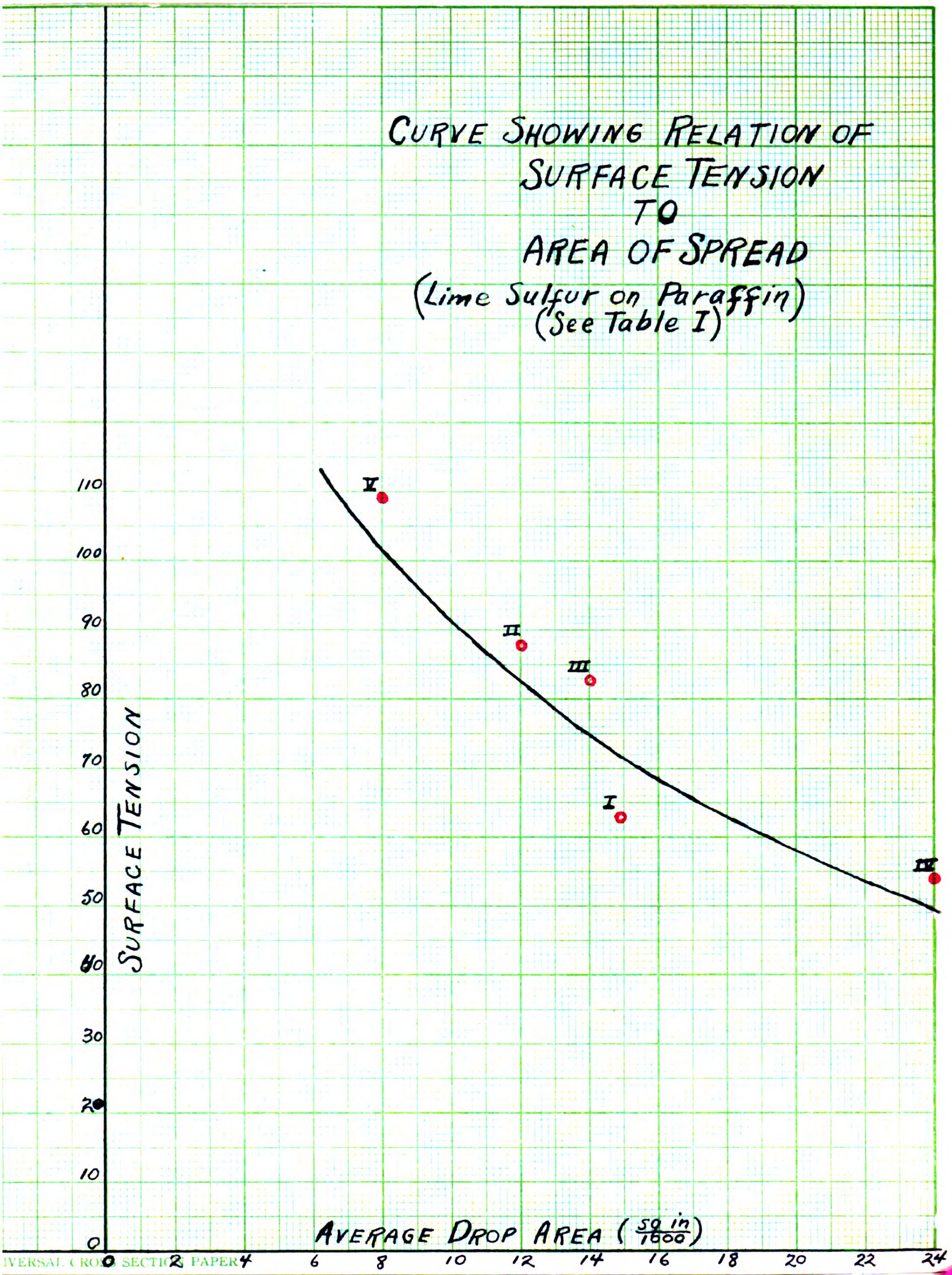
When the areas had completely dried, measurements were made with a planimeter, first discarding any area which was not circular. The figures in Table 1 show averages of such measurements.

Similar tests were made of these five solutions on leaves of cherry and pear. But on account of indistinctness of margin, and tendencies to spread along the leaf veins, the only conclusion drawn was that spreading is slightly greater on the upper surface than on the lower surface of the leaf. This was true for each solution and for both kinds of leaves tested.

TABLE I Showing Relation of Surface Tension To Area Covered by Drops of Uniform Size on Three Surfaces,--Glass, Mica, and Paraffin.

Number and Surface Tension of Sample

Surface	IV(ST=53)	I(ST=60)	III(ST=82)	II(ST=87)	V(ST=109)
			Area of spread in square inches		
Glass	.05	.03	.028	.032	.032
Mica	.082	.076	.08	.096	.086
Paraffin	.024	.015	.014	.012	.008



CURVE SHOWING RELATION OF SURFACE TENSION TO AREA OF SPREAD
(Lime Sulfur on Paraffin)
(See Table I)

A study of the above data fails to reveal any correlation between surface tension and spreading, except in the case of paraffin. On a paraffin surface the solution with the highest surface tension spread over the least area and vice versa. It would seem the reason for this is that none of the solutions were strongly adsorbed by the paraffin, or in other words the force of adhesion was weak. A drop of liquid, therefore on such a surface, will remain spherical if the surface tension is high or flatten out if the surface tension is low.

But in the case of either glass or mica, surface tension seems to be a negligible factor in spreading, or to be more explicit, no direct relation is apparent. This fact seems to offer experimental evidence that surface tension as such, need not be considered as a factor of fundamental importance in determining the spreading ability of spray drops on all types of surfaces. And although it is undoubtedly operative when a liquid is applied to certain surfaces, such as lime sulfur on paraffin, the virtue of a low surface tension value in spray materials is probably due to the greater facility with which such a material may be broken into small droplets. The importance of the size factor will be pointed out in a later portion of this paper.

It is a well known fact that if a liquid is adsorbed at a solid surface, it forms a liquid film and we say that it "wets" the solid. If the liquid is not adsorbed by the solid no wetting takes place. The phenomenon of adsorption depends upon the nature of both liquid and solid because it has to do with the molecular forces between the two. No measurements, therefore, which we can make of the forces between the molecules of the liquid, such as the force of surface tension, will throw any light on the forces of adsorption. The phenomena of adsorption, then, must be of fundamental importance in a study of the spreading of spray materials. The tests already mentioned bear out this contention.

It seems only reasonable to infer that this molecular affinity termed by Langmuir as "secondary valence," which is undoubtedly electrical in its nature, is largely responsible for the behavior of spray drops as they strike a solid surface. And to the extent that spreading is determined by adsorption, the composition of the spray material must be of prime importance. This is a problem for the manufacturer of spray materials rather than for the grower who uses them.

Historical Notes on Adsorption

"For a liquid to wet a solid in the presence of air, the liquid must be adsorbed more strongly than the air and must displace it. Since the adsorption of liquids is selective, it follows that one liquid will be adsorbed more by a solid than will a second liquid and that consequently the first will displace the second from contact with the solid. No systematic study of this phenomenon seems to have been made.("Bancroft's "Colloid Chemistry")

Even though the principles which underlie the phenomenon of adsorption are not fully understood, its application to every day life and also its bearing on the behavior of spray materials are very evident from the illustrations here given.

Lord Rayleigh (1902) states that in his opinion the contact angle is zero, if the liquid is actually adsorbed by the solid surface. The same idea is expressed by Harkins and Brown (1919). If this is true it is obvious that no adsorption takes place between lime sulfur and paraffin.

Kerosene will displace water in contact with copper and water will displace kerosene in contact with quartz (Pockels, Wied. Ann. 67, 669, 1899). This explains the reason for using a rag dipped in alcohol with which to wipe off a lamp.

Alcohol will displace oil in contact with metals. (Hofman, Zeit, Phys. Chem. 83, 385, 1913).

Linseed oil will displace water in contact with white lead (Cruikshank and Smith in in The Manufacture of Paint, 92, 1915). This shows the function of vaseline in preventing the rusting of metals.

In the kitchen, housewives wet moulds before putting in corn starch or gelatin, they butter pans before making fudge, and grease griddles before making flapjacks. These are all cases of selective adsorption. It is claimed that aluminum griddles do not need to be greased because the air in the oxide film keeps the cake from sticking.

Some of the methods of removing grease spots from clothing depend upon selective adsorption (Lake, Journ. Phys. Chem. 20, 701, 1916).

Gelatin is adsorbed so strongly by glass that on drying it may tear off the surface of the glass. On the other hand, it will not adhere to plates of mica or calcite. (Bancroft)

Certain plastic clays, high in silica, adhere to iron in a remarkable way (Trans. Am. Ceramic So. 14, 610, 1912).

Graham (1867) reports that fifteen times as much oil of sweet almonds was retained by palladium foil as of water.

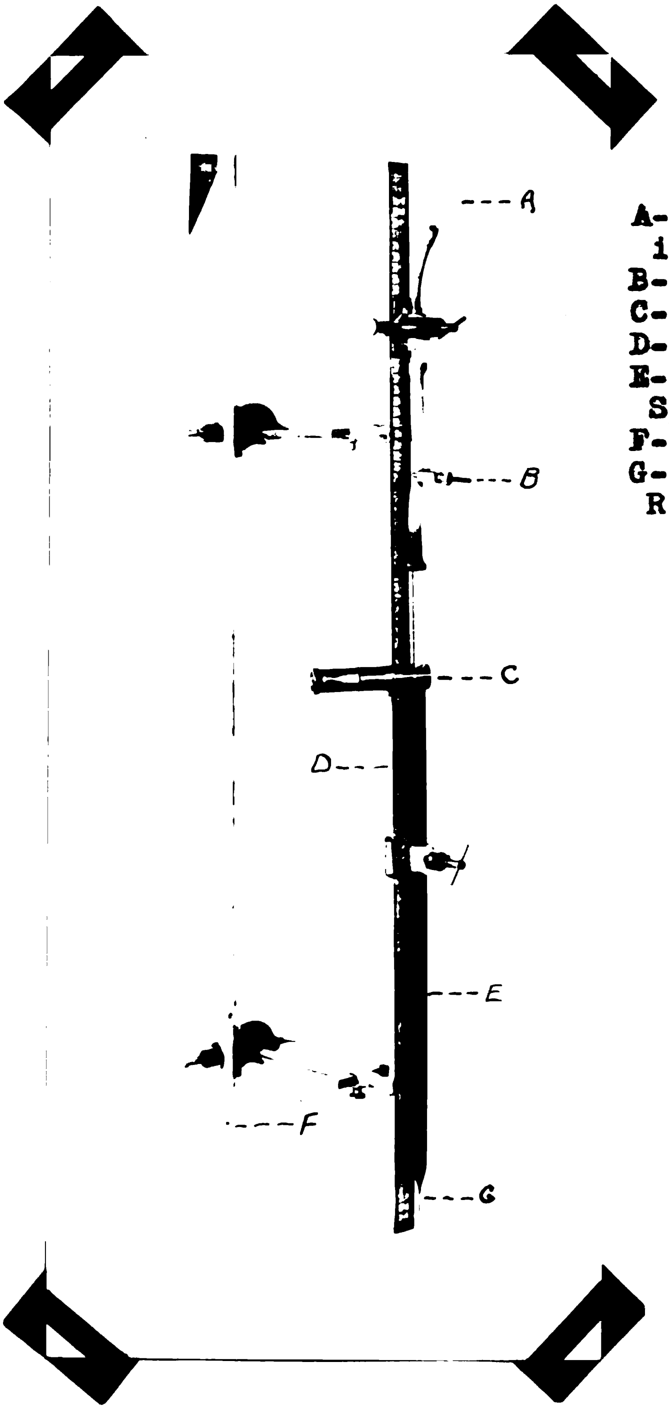
The foregoing observations of the phenomena of adsorption will suffice to emphasize the close relation between the behavior of sprays and the composition of liquid and solid.

The following tests were outlined with the idea of determining what influence, if any, the velocity of a drop has upon its tendency to spread. For within certain limits velocity is under the grower's control and it is important for him to understand how it contributes to the effectiveness of the spraying operation.

2. Relation of VELOCITY to Spreading

On account of the physical impossibility of studying the effect of velocity of drops on spreading where a large number are released at once (as from a spray nozzle), the device shown in Figure 2 was used.

A capillary tube similar to the one previously described was drawn from the lower end of



A- Capillary Tube for inlet of Air
B- Pinchcock
C- Telescope
D- Scale
E- Burette containing Spray Material
F- Standard
G- Capillary Tube for Release of Drops

Fig. 2 Apparatus used in Studying Effect of Velocity on Spreading a burette. The upper end was fitted with a rubber tube and a second capillary tube with pinchcock, to regulate the rate at which drops were released.

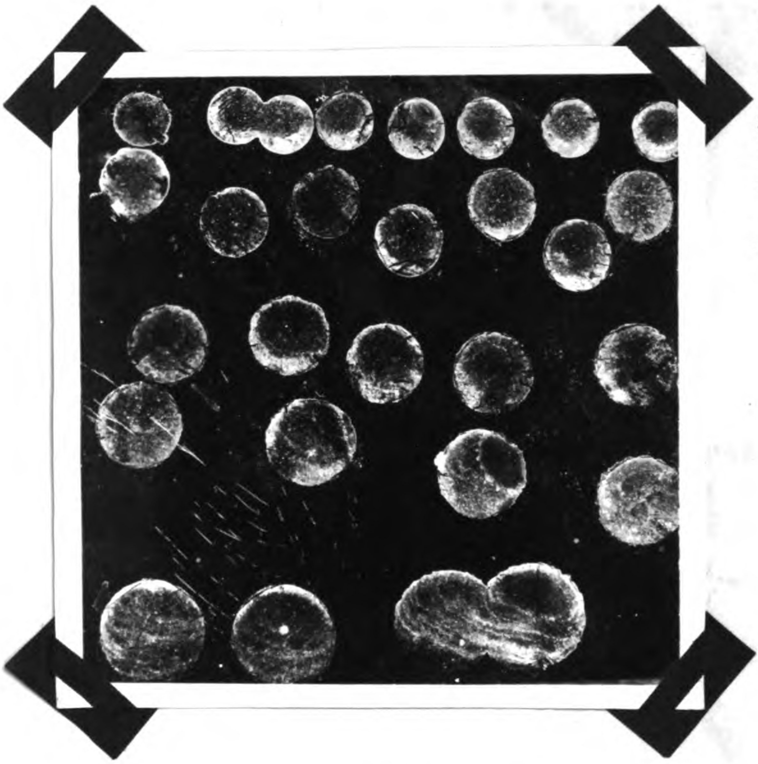
Tests were made with Bordeaux mixture (4-4-50) and with liquid lime sulfur (1-30).

No direct comparison is possible between the three tables given below (II, III, and IV) because different sized capillary tubes were used. But in each case a definite increase in area of spread is apparent as the striking velocity is increased.

<u>Table II</u> <u>Showing Relation Between Velocity and Spreading</u>

(Bordeaux Mixture on Glass)

Height of Fall (cm)	Area (sq. cm.)
Practically 0	.148
1	.451
4	.819
9	1.103
16	1.29



(Note- Drops at top of photograph have fallen from a height of ~~1~~0 cm.; those at bottom have fallen ~~25~~16 cm. Intermediate drops have fallen from heights of ~~4~~1 cm., ~~9~~4 cm., and ~~16~~9 cm., respectively.)

Photograph showing areas covered by drops which have fallen from heights indicated in Table II.

Table III (Lime sulfur, fairly large drops)

Height of fall (cm)	Area (sq. cm.)
1	.297
4	.393
9	.819
16	.98

Table IV (Lime sulfur, drops smaller, delivered from smaller tube).

Height of fall (cm)	Area (sq. cm)
1	.168
4	.226
9	.303
16	.393
25	.452
36	.477
49	.529
64	.555
81 (some spattering)	.574
100 (considerable spattering; areas too irregular to measure accurately)	

The reason for selecting the heights of fall shown above was to give striking velocities in an arithmetic progression. For example, if a large drop falls from a height of one inch, its striking velocity will be approximately half that of a drop which has fallen a height of four inches, and one-third that of a drop which has fallen nine inches, and so on. (This follows from the well known law of falling bodies,--Velocity (V) squared is equal to twice the product of the acceleration of gravity (g) and the height (h) $\therefore V = \sqrt{2gh}$ or V varies as h. Correction of this formula will be taken up under "Mathematical Aspect of Air Resistance").

The data shown in Tables III and IV were obtained by using lime sulfur (surface tension=110) on a perfectly clean glass plate. No spreader was used. Areas were calculated from diameters determined by use of a Filar Micrometer.

Tables V and VI indicate a different set of conditions. In both of these cases, drops were released from heights ranging from one to one hundred centimeters as before but the areas were found to be identical, regardless of the height of fall.

<u>Table V. Lime Sulfur</u> (1 - 30) <u>plus Sun Oil</u>
(Surface tension=53)

Drops of the above solution were permitted to fall on a clean *glass* plate from heights corresponding to those in Table IV. Result -- Areas were identical)

Table VI Lime sulfur (1 - 30)(Surface Tension=110)

(Drops of the above solution were permitted to fall on a paraffin plate from heights corresponding to those in Tables IV and V. Result--Areas were identical).

In the last two cases cited, the drop of spray material could be observed to flatten out at the instant of contact with the surface but on account of a lack of attraction between liquid and solid, the margin of the drop immediately receded toward the center of the area involved.

From the tests just described, one would infer that the application of spray drops with considerable velocity is desirable upon surfaces which do not permit of intimate contact between spray and surface. In this class, are included surfaces covered with hair-like projections, or other irregularities, and also those holding previously adsorbed materials which might be displaced sufficiently by a driving spray to permit the solution to reach the surface itself. Undoubtedly a driving spray is desirable on the rough bark of trees to penetrate the crevices but on the leaves and fruit, added velocity is very apt to cause injury of more consequence than any benefit to be derived from better covering. Such injury is probably due to abrasion or mechanical breaking of the tissue by the drop itself and by the particles of solids carried in suspension.

If we refer again to Tables V and VI, and consider them as illustrating two possible orchard situations with regard to spray material and surfaces to be covered, it becomes apparent that velocity cannot be depended upon to increase spreading of all materials on every type of surface.

Mathematical Aspect of the Problem of Air Resistance

The following table shows that large drops of a liquid are retarded less in their motion through the air than are small drops.

The first column gives the characteristic diameter of drops, and the second column gives the rate of fall under the pull of gravity, after falling from a sufficient height to attain a constant velocity. (Both values are in centimeters.)

Table VII (Humphrey, "Physics of the Air," 1920, page 268)

Popular Name	Diameter	Velocity
Fog	.001 cm	.3 cm/sec
Mist	.01	25
Drizzle	.02	75
Light Rain	.045	200
Moderate Rain	.1	400
Heavy Rain	.15	500
Excessive Rain	.21	600
Cloudburst	.3	700

This table was utilized to determine the true striking velocity of the drops involved in Table IV.

Instead of the formula $V = \sqrt{2\ gh}$, we have $V = \sqrt{2\ gh}\left[1 - \frac{c}{3}\sqrt{\frac{2h}{g}} + \frac{c2}{36}\left(\sqrt{\frac{2h}{g}}\right)^2 + \frac{11c^3}{540}\left(\sqrt{\frac{2h}{g}}\right)^3 \cdots\right]$ which is the true striking velocity, having eliminated the retarding effect of the air. The constant c varies for each size of drop, and is found by dividing the acceleration of gravity (g) by the velocity given in the table above. Thus, for excessive rain, $c = \frac{980}{600} = 1.63$

Applying the formula to this size drop, falling from heights of 4, 25, and 81 cm respectively we found that the striking velocities as computed by the formula $V = \sqrt{2\ gh}$ are off by 7%, 11% and 21%, respectively. These corrections were then applied to the data given in Table IV to see if there were a constant increase in area as the velocity is increased. In other words, does doubling the velocity double the area? It was found in this case (lime sulfur on glass), that the increase is far short of that amount. And since this represented only a special case, both as regards liquid and surface, the proportionality factor would have no significance, and is therefore omitted from this report.

It is quite evident from the foregoing discussion that, in the case of drops within the size range ordinarily applied, the actual striking velocity would not be such as to have any appreciable influence on the tendency to spread, for it should be borne in mind that the smaller drops suffer greater retardation than the larger ones.

3. Relation of SIZE of DROP to Spreading

More time was devoted to this portion of the investigation than to either of the preceding studies, first, because of the extreme difficulty in the technique involved, second, because of the large number of measurements necessary to make the data conclusive, and third, because the "size factor" gave greater promise of throwing light upon the problems of spraying, since it is subject to the greatest variation of any of the physical factors and at the same time is quite largely under the control of the man who operates the sprayer.

Whenever an attempt is made to break a liquid into small drops by forcing it thru a capillary tube, a limiting size is very soon reached. This is to be expected from the very nature of the orifice. If the tube is of large diameter the curvature of the sides is slight, but as tubes of smaller diameter are used, the curvature increases with a resultant increase in the effect of surface tension in maintaining rigidity in the issuing column of liquid. (For the same reason, a drop of small diameter is more stable than one of large diameter). Very small tubes, then, emit a continuous stream or a series of drops at such frequent intervals that they are difficult to manage, since we must confine our measurements to areas over which the individual drops spread.

The device shown in Figure 2 was found suitable for fairly large drops, that is, drops down to approximately .008 of a cubic centimeter. Such a drop has a diameter of about .25 cm.

Briefly the method of using this apparatus was as follows:--The burette was filled, and the drops allowed to fall into a beaker while a count was being taken. The telescope was adjusted, and at the instant that the surface of the column reached a given graduation on the burette, a helper gave the signal. Drops were then counted until a second signal denoted that one cc of liquid had flowed thru the tube. Usually three checks were made of the number of drops and these seldom varied by more than one or two drops per cc. Then, with drops falling at the same rate as when the count was made and with the tip of the capillary tube very near the glass plate, individual drop areas were produced by moving the plate horizontally on the table. When a sufficient number of these had been obtained the spray material was removed from the burette, the tube was cleaned and the tip broken off to secure an opening of different diameter. The tip of the tube was paraffined as before and the counting and plating process repeated. In each case the same distance between tip of capillary tube and glass plate was maintained to eliminate the velocity factor.

Table VIII gives the results of three such drop measurements. Mention should be made of the fact that in all of these area determinations only circular areas were considered. If a drop showed a tendency to spread more in one direction than another it was assumed that that part of the surface was not perfectly clean. In every case, the area shown in the table is an average of at least twenty individual drop areas.

Table VIII (Showing Relation Between Size of Drop and Area of Spread.) Drops were formed by use of capillary tube.

No. of Drops per cc	Average Diameter of Drops (cm)	Area (in cm2)covered by 1cc of solution
84	.283	77.28
111	.258	79.92
120	.251	81.12

It will be observed from this table that there is an increase in area covered by a given volume, if the material is applied in smaller drops.

Previous mention has been made of the impossibility of duplicating the finer spray drops with a capillary tube. Those just described are of the magnitude of excessive rain. For finer particles of spray materials an entirely different method of transfer was necessary. Figure 3 shows the tools used in producing smaller individual drops.

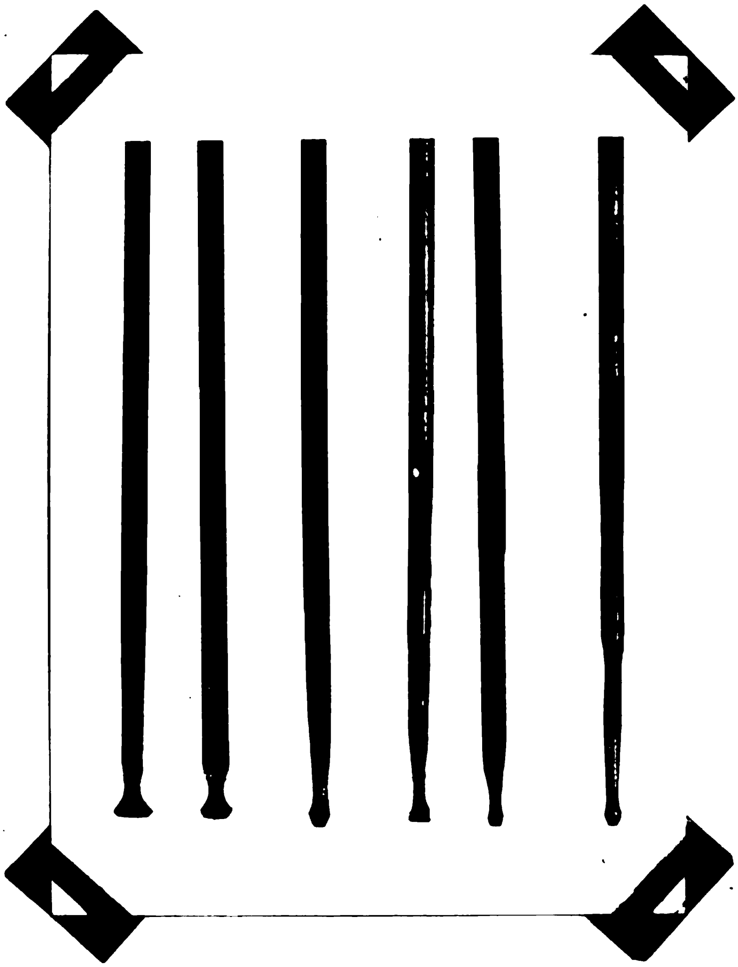


Fig. 3 Tips of Knitting Needles were ground differently, thus giving each a different liquid-holding capacity.

By means of the knitting needles shown in Figure 3, transfer of droplets of varying size was made possible. Microscope slides of the best glass obtainable were used. These were cleaned thoroughly as in previous tests and the spray material plated as follows. A small amount of the lime sulfur solution was poured out on a clean glass plate and the tip of one of the needles inserted. Upon lifting the needle, a certain amount of the material clung to the tip in a drop. The slide was touched lightly, thus releasing part of the material and the operation repeated. As many areas were placed on one slide as possible, without overlapping. Three such slides were prepared with each needle in order to eliminate error in determining the average drop area.

Figure 4 shows a series of six slides. The one at the extreme right contains 500 drop areas and was made by using the needle in the extreme right of Figure 3. The average area covered by these individual drops was .0048 square centimeters.

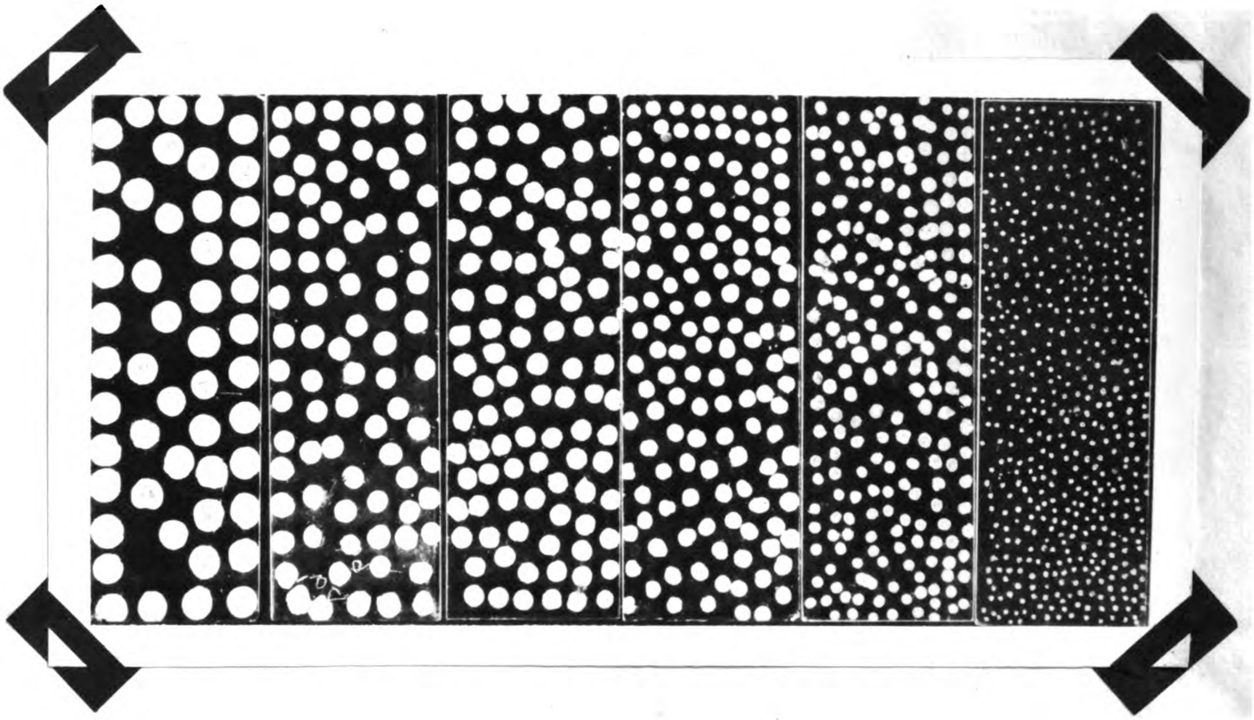


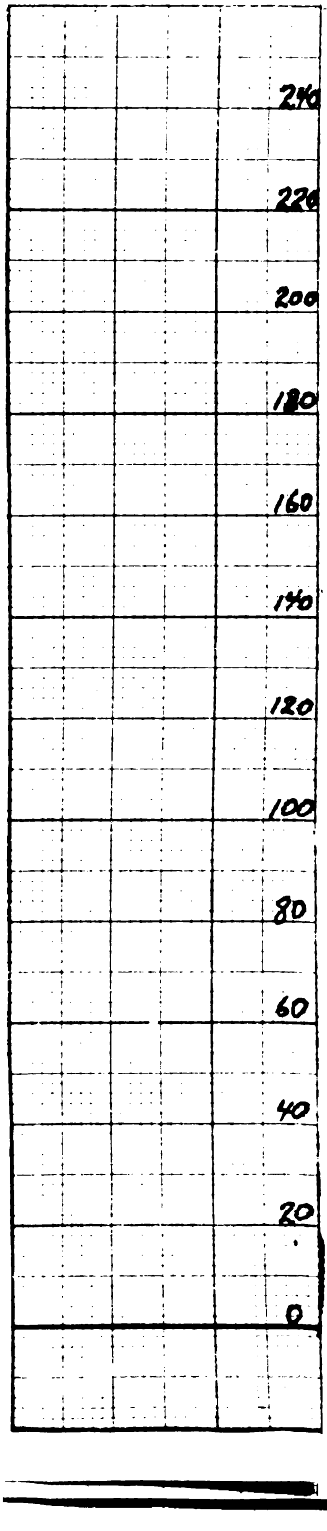
Figure 4. Slides showing Drops Transferred by Needles Pictured in Figure 3.

The task of determining the number of drops per cc in the tests just mentioned involved very careful weighing. The slide was weighed empty, and again after the drops had dried thoroughly. This difference divided by the number of drops on the slide gave the dry weight of one drop of material. (An average weight was taken from the three slides) Then by carefully measuring, drying and weighing one cc of the solution, and dividing this weight by the dry weight of one drop, the number of drops per cc was determined.

Table IX (Showing Relation Between Size of Drop and Area of Spread). Drops were formed by use of knitting needles.

No. of Drops per cc.	Average Diameter of Drop Areas (cm)	Area (in cm^2) covered by 1cc of solution
550	.451	87.9
710	.416	96.6
1015	.394	123.8 ✓
1220	.340	100.7
1535	.306	113. ✓
2060	.269	107.6
2230	.250	109.5
3300	.231	138.3 ✓
6600	.156	126.2
47100	.078	228.

In the curve, accompanying this table, the values obtained from three of the above



fluence of velocity and size of drop is of tests were omitted (viz. 3rd, 5th, and 8th). Even though every precaution was taken to eliminate chances of error, it appears that there must have been some slip in those three values, since the others follow in progression as indicated by the curve.

From these data it is evident that the total area over which a given volume of liquid spreads varies inversely with the size of the drops into which it is broken. This relation of total spread to size of drop is such that the increase in area gradually diminishes as we continue to decrease the size of drops. In other words, if 1 cc of a liquid is broken up into 500 drops, another cc into 1,000 drops and a third cc into 2,000 drops, allowed to fall on uniform surfaces and total area in each case measured, a greater increase will be noted between the first and second cases than between the second and third.

Any attempt to correlate the influence of velocity and size of drop is of little avail because of the extreme variation in surfaces and the multiplicity of factors involved. In fact, such a correlation is impossible except for one particular set of conditions, and for that reason impracticable in its relation to the problems of spraying.

Some of the drops used in this piece of work were larger than what we consider as making up a mist, although the smallest size would approximate mist particles. But there may be as many as several hundred thousand mist particles in a single cc of solution and the total area covered under such conditions would undoubtedly be in excess of the areas here determined. However, if mist particles are to be applied, the velocity which may be imparted to them is quite limited. We cannot therefore, control both the size of a drop and its velocity. So we must be content with some sort of a compromise.

Furthermore, the drops delivered by any nozzle will vary in size. It might even be said that no two drops are likely to be of exactly the same size. Drops in the center of the "cone" are generally larger than those around the outside. The effect of atmospheric resistance will therefore be felt more by some than by others. This is the reason for some of the material falling within a few inches of the nozzle, while other particles may travel twenty or thirty feet, even though the velocity at the orifice is identical. For the reasons just mentioned we can never hope to control both size of drop and velocity because if we apply drops of the most desirable size their velocity can have little or no effect upon their tendency to spread.

Discussion

What is the application of the foregoing to orchard practice? Four points stand out quite clearly in the data presented.

First, spreading of any given spray material depends upon its composition, because composition determines the extent to which it is adsorbed by the surface. And without adsorption neither wetting nor spreading will occur. Incidentally a so-called "spreader" must be specific in its action, and its use will prove beneficial to spreading on one particular type of surface to the extent that it is adsorbed by that surface. The matter of composition is a problem for the manufacturer rather than for the grower.

Second, velocity of spray drops is something which should be considered from the standpoint of distributing the material through the tree top rather than increasing its spread over the surface of the leaf. It is obvious that the velocity at any appreciable distance from the nozzle must depend more upon the size of the drop than upon the initial velocity imparted by the spray outfit, unless the actual carrying of the material is accomplished by a draft of air.

Third, the drops must be large enough so that their initial velocity will carry them throughout the range to be covered in the tree, while from the standpoint of maximum area to be covered, they should be as small as possible. In orchard practice this means a compromise. The spray gun offers such a compromise since it can be instantly adjusted to throw fairly uniform drops first of one size for close range spraying, and then of a larger size for the higher parts of the tree. Theoretically, the ideal outfit from the standpoint of thorough covering, is one which delivers a mist-like spray, always releasing it near the surface to be covered so as to secure suitable working velocity. The long spray rod with a fine nozzle is an attempt to attain the ideal in that regard.

Fourth, the principal advantage to be gained from using a high pressure, power outfit lies in its greater capacity or its ability to deliver into the tree in the proper form more gallons of material per minute. If such an outfit is utilized to deliver larger drops, at the same velocity, coverage per unit of spray material is decreased, and if larger drops are delivered at higher velocity, spray injury results. On the other hand, if the material is broken into extremely small drops poorer distribution through the tree tops is likely to occur. The principal advantage, then, lies in its capacity in terms of gallons per minute. And unless this advantage is capitalized by properly organizing the spraying operation, the investment is not netting the greatest possible return.

Summary

1. In general, a spray solution having a low surface tension will be more likely to spread than one whose surface tension is high, for two reasons,--first because of its greater tendency to flatten out and second, because such a solution can be more easily broken up into small drops. But the surface tension of a liquid is not a measure of the spreading tendency of that liquid on all surfaces. Rather, it is one of the factors and is probably less influential than the interfacial tension.

2. Of greater importance to the orchardist, than the factors mentioned above, is that the spray material be adsorbed by the surface. Adsorption is apparently strongest between substances of like constitution. If then, we can secure a solution, similar in its chemical make-up to that of the surface upon which it is to be applied, spreading should be greatly enchanced.

3. Velocity seems to exert an influence on spreading if the surface is one for which the spray material has an attraction. In other words, if the material is adsorbed by the surface, an added velocity will enhance spreading by aiding it in penetrating the surface layer which consists of a film of air or certain impurities. This penetration probably brings about a more intimate contact between liquid and solid, thus partially replacing the previously adsorbed material. Adsorption, then, is apparently a factor of greater fundamental importance than is velocity. It is doubtful if greater velocities are desirable in the orchard except as pointed out in the previous discussion.

4. The area covered by a given volume of spray material varies inversely with the size of the drops applied. The data pertaining to size of drops offers a strong argument in favor of a mist spray.

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