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# A STUDY OF THE EFFECT OF ACCESSORY SUBSTANCES ON THE ADHERENCE OF LIME SULFUR SPRAY TO THE INTEGUMENTS OF INSECTS

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# A STUDY OF THE EFFECT OF ACCESSORY SUBSTANCES ON THE ADHERENCE OF LIME SULFUR SPRAY TO THE INTEGUMENTS OF INSECTS.

The importance of the physical properties of contact insecticides is fully recognized,and such forces as surface tension,interfacial tension,viscosity,absorption,adsorption,cohesion,adhesion,and others have been rather extensively investigated.Water alone and also many spray solutions do not spread or adhere well either to the waxy coating of leaves and fruits or to the bodies of insects. To overcome this,sundry materials have been added to spray solutions.The addition of such supplementary materials alters many of the physical forces,and may also increase or decrease the toxicity of the spray.These studies on the influence of spreaders and adherents on contact insecticides may be classified rather broadly under five heads;1-A study of the inherent physical forces of the spray solution;2-Influence of accessory materials on the chemical composition and reactions;3-The nature and quality of the film obtained on plant surfaces;4-A study of the spray solution in contact with the insects' body both as to external covering and internal penetration;5-The influence of the added materials on toxicity values.Most of the investigations are not confined to a single study,but in their natural scope may include several of these allied fields.

Altho contact insecticides and the use of accessory substances have received considerable attention from experimental workers, there still remain many unsolved problems in connection with their use. The reactions are so widespread and the varying factors so many, that the problem becomes an intricate one. The nature of the spray; it's chemical composition and concentration; the kind and amount of material used; the plant surface and the insect to be killed or controlled; and environmental factors such as seasonal growth, temperature, and humidity all have a part in determining the final results secured.

## Scope of This Investigation.

Very little experimental work has been undertaken concerning the actual amount of spray that adheres to treated surfaces, especially the integuments of insects. In this study the amount of sulfur residue has been determined quantitatively on the integuments of two different insects and on the surface of clean glass, using lime surfur spray with and without the addition of varying amounts of the several ingredients. It was not expected that such data as could be secured with this type of an experiment would solve the problem as to the advisability of using accessory substances with lime sulfur solution. This problem is too complicated to be so easily disposed of. A quantitative laboratory study such as has been undertaken should prove of value in showing the relative values of the various substances, and the importance of the amount used on the film obtained.Sprays when applied to insects leave residual amounts as external deposits, and often as internal penetrants.No attempt has been made to differentiate between surface film and penetrated spray,for the reason that with present analytical methods,it is impossible to determine accurately the one and not include the other. The data submitted are a measure of total spray residue left on the insects'body with the treatment given.

In order that a contact spray may kill it must at least be in close contact with the insect.This intimate relation between spray and insect is in turn dependent upon the operation of several physical and chemical factors. O'Kane and Conklin (8) have stated this relationship very aptly, "It is manifest that a liquid which is to kill an insect as a so-called contact spray,especially if it is to exhibit its efficiency in the liquid phase,must to some degree wet the insect to which it is applied.It is true,also, though not always fully recognized,that the ability of a contact insecticide to wet an insect is dependent in marked degree on its chemical and physical properties, especially as these properties relate to the chemical and physical nature of the integument of the insect,the lining of the tracheal tubes and such other parts as the material may reach.Quite apart from the intrinsic toxic qualities of a given spray,performance will be profoundly influenced by physical properties."

This work is concerned only with a measure of the spray adhering to the surfaces studied,and the conclusions will be based on these figures.However the author is not unmindfulof the worth of the many othere factors involved and the performance of liquids on solids,or of the probable effect of certain spreaders and adherences on the toxicity of the resultant solution.In a final evaluation of any spray solution all pertaining factors must be considered.It is considered that the film obtained and the amount of spray present on the insect is of importance,especially in those sprays that kill by contact,and that the magnitude of this coverage will be of value in determining the relative value of different spray combinations.

Consideration of the Literature.

A large number of references are found in the literature that pertain to solutions in general and also to particular spray solutions.A knowledge of the fundamental laws that govern the physical and chemical changes occurring,either in the spray solution before application or after it is applied,is necessary as a background for this work.Among the references available are numerous ones that relate to the spreading and adhering properties of various substances when used in different spray solutions.Many of these references have been read but no attempt will be made here to give an extended historical review of the subject.Moore(6) and more recently O'Kane and coworkers(7)have published extensive reviews and bibliographies, and for references on phases of the problem not covered here, these may be consulted. Only references to the literature actually quoted from are included in the bibliography attached to the end of this paper.

Terminology and Definitions.

The science and study of spray materials have developed a certain terminology. The terms spreaders, wetters, adherents, and even emulsifiers have been used in spray work to convey different meanings. Their reactions on spray materials are also not the same. The word, spreaders, has often been used to include any harmless substance added to a spray solution that improves the physical qualities of the solution, and results in the formation of a more continuous uniform film of poison on the surface to be covered. Under this term are often included certain materials, that are not in the strict sense of the word spreaders, but substances that may be of value in increasing the amount of spray retained on the sprayed surfaces. Woodman(12) has differentiated and defined a wetter as a substance causing the spray fluid to wet the surface sprayed so that it does not collect in drops; and a spreader as one causing the film to expand or extend over the part of the surface not directly hit by the spray. Moore(6) defined spreading as denoting the formation or the maintenance after being formed of a continuous film over the surface of the leaf; and adherence as applied to the resistance to the action of rain,dew,and wind,exhibited by the spray material after it dries.He defined wetting, as the slight chemical or physical affinity between the liquid and solid on which the spray is applied.O'Kane(7) gives the term,extension,to the spread of a liquid on a solid,and draws attention to the fact that the term, spreading,is not applicable in the same sense as when one liquid spreads on another liquid.

We are using the term,spreaders,here to indicate a group of substances that are usually considered or used for their ability to give improved film coverage; and adherents,to include those substances that are primarily valuable for adhesive properties.No attempt is made to classify the materials used either before they are used, or on the basis of the results secured.The terms,spreader and adherents,are employed to indicate groups of substances,not as verbs indicating any particular action. If a spray is deposited or remains on the surface to be examined,and the amount quantitatively determined,this deposited spray is taken as the relative value of that spreader or adherent when combined with the insecticide used.

Experimental Data.

1-Spray Solutions,Spreaders,and Adherents.

Lime sulfur was selected as the contact spray because it is one of the most universally used materials,and one to which spreaders are added either to improve its adhesive and filmforming qualities,or to improve its compatibility with other spray ingredients.A high grade commercial brand of lime sulfur was selected,and this same material was employed in all the experiments.The original lime sulfur tested 33 degrees Baume.A standard stock solution was prepared by adding water to reduce the density to 31.5 degrees. Baume.This stock solution was then further diluted to a 1 to 10 solution in all combinations.This final dilution was prepared fresh for each test and used as soon as possible after preparation.

The number of substances that may be used as spreaders and adherents is very large.It is obvious that only a comparatively few could be selected for trial.The materials selected for trial are listed in Table 1,together with the amounts used,source of supply,and certain other pertinent data as regards their use or reactions.Most of the substances selected are commonly used,and have a certain known value.A few materials were tested because of specific requests from other departmental workers.The selected materials cover representatives of most of the classes of compounds usually used in spray solutions.More casein spreaders were tested than any other kind of substances,and this class of material is also more universally used than the others.Tests also were carried out with materials not usually used with lime sulfur because of certain physical disadvantages or chemical reaction.A few commercial spreaders were tested out.The aim of many of the commercial manufacturers in more recent years,has been to place on the market a material that combines spreading and adhesive properties. The material selected represents several types of commercial spreaders,both solids and liquids.

The amount of the various spreaders to use is important. The author consulted the literature and recommendations put out by other men and the commercial manufacturers.In most of the commercial material the recommendations given by the manufacturers have been followed.As the work progressed the importance of the proper strength of each spreader under test was very strikingly brought out.It would have been very desirable to extend the list so that several concentrations of each spreader might have been tested.The dilutions selected for study are the ones the author considered best for the particular conditions of the experiment.He is aware that certain of these may be open to criticism.The aim has been to keep the amount of the various accessory substances used,as uniform as possible.

The non-homogeneous mixture obtained with the oils and lime sulfur was a decided drawback in their use.In a large container with high agitation better mixtures probably could be obtained,but with the small lots used in the laboratory they could not be satisfactorily handled without first emulsifying.For making these emulsions 0.05% Kayso

Table I-Spreaders and Adherents Used in Experimental Work.

| Material | Dilutions | Source of Supply | Remarks |
|---|---|---|---|
| Calcium Caseinate | 0.5-0.1 & 0.05% | Prepared from (Tech.grade) Casein and hydrated lime in a ratio of 4 to 1 | |
| Dried Skim Milk | 0.1% | Lab.supply | Original source unknown |
| Skim Milk | 1.0% | Fresh local supply | 0.05% hydrated lime used with it. |
| Blood Albumin | 0.5-0.1 & 0.05% | Lab.Reagent | Tech.grade |
| Dextrin, white | 1.0 & 0.5% | " " | " " |
| Soluble Starch | 1.0 & 0.5% | " " | " " |
| Gelatine | 0.5% | " " | " " |
| Saponin | 0.5 & 0.05% | " " | C.P. " |
| Hard Wheat Flour | 1.0-0.5% | Commercial product | - |
| Kaolin(acid washed) | 1.0% | Lab.Reagent | |
| Pipe Clay | 1.0% | " " | A finely divided pottery clay. |
| Sodium Silicate | 1.0% | " " | Tech.grade |
| Ferric Hydroxide | 0.2% | Freshly prepared from NaOH and $FeCL3.6H_2O$ | |
| Sulfite Residue | 1.0% | Residue from waste sulfite liquid obtained from Paper Mill. Acid reaction-lime water used in mixing. | |
| Cottonseed Oil | 1.0% | Lab.Reagent | Used with 0.05% Kayso |
| Linseed Oil, Raw | 1.0% | Commercial product | " " " " |
| Fish Oil | 1.0% | Blumauer-Frank Co. | " " " " (Supply on hand and used in spraying by Ent.Dept.) |
| Resin-Fish Oil Spreader | 0.5% | U.S.Bureau Plant Path., Corvallis | 4pts.Resin, 1pt.fish oil, 1pt.water and 1pt.KOH. |
| Kayso Spreader | 0.5 & 0.05% | Unopened pkg.of 1931 stock | A commercial spreader of Golden States Company Ltd. |
| Leffingwell's XXX | 0.5% | Supply on hand | Mfg. by Leffingwell Rancho Co. |
| Penetrol | 0.5% | Furnished by Co. | " " Kay Laboratories. |
| Fluxit-Ore.#1 | 0.1% | " " " | " " Colloidal Products Corp. |
| Fluxit-Ore.#2 | 0.1% | " " " | " " " " ". |
| Fluxit-Formula #1871 | 0.1% | Unopened pkg.1931 stock | " " " " " |

Table 1

was used.These emulsions were not very permanent,but were sufficiently so to make a workable mixture of the combination.

II- The Amount of Lime Sulfur Found Adhering to Pine Leaf Scales.

Chionaspis pinifolioe(Fitch)was selected for these tests instead of either the common oyster shell scale or San Jose scale.These insects are not only larger,but their location on the needles of coniferous trees permitted them to be handled and removed from the needles without extraneous adhering bark.A supply of fresh scales was also available at the time of year when the tests were made(late fall and early winter).Metcalf(5)has studied the nature of shells of several scale insects.He reported that the pine leaf scale covering contained 40% of wax,while that of the oyster shell scale contained 35% of wax.The wax of both was a mixture of several ingredients.It is therefore evident that there is considerable similarity in the coverings of the two scale insects.

Scale infested branches of sugar or yellow pine were brought to the laboratory and needles carrying an excess of fifty scales were tied at one end into loose bundles.Attempts were made to use only full grown live scales,without having to spend an unreasonable amount of time in making the examinations.The various spray solutions were freshly prepared in 100cc lots and a medium sized test tube nearly filled with the solution.The tied bundles of needles were then immersed in the liquid,immediately removed and hung on a rack to drain and dry.Fifty scales were then removed singly and cleanly from the needles and brushed into the container used for the chemical determinations.

The amount of sulfur adhering to fifty scales was too minute to determine accurately gravimetricly.So a microchemical or colormetric method was resorted to.The original method came from the laboratory of the National Canners' Assoc.and was one D.E.Bullis of the Agricultural Chemistry Dept.of this Station,had modified and used to determine the residual sulfur left on fruits that were to be canned (unpublished data).It was further modified by the author to adopt it to this work with insects and as finally used was as follows:

The fifty treated scales were brushed into a 100cc test tube and 10cc of 2cc caustic soda solution added.The tubes were placed in a water bath and held at boiling temperature for a half hour or longer.The solution was cooled and 40cc hydrochloric acid(1 part conc.acid to 4 parts water)added. This was followed by approximately 2 grams of sulfur free granulated zinc,and the tube immediately connected up by means of suitable stoppers with a modified Gutzeit tube and acid catch tube(the whole setup being similar to that used in determining small amounts of arsenic).The upper tube was of 1/8 inch bore and in it was placed a strip pf hardened filter paper sensitized with 5% lead acetate solution.The reaction was allowed to proceed at room temperature for a time,and to finish it,the tubes were placed in a hot water bath.Several hours or over night was allowed for complete evolution of hydrogen sulfide.

The reactions in the above determinations are that first, the sulfur compounds are brought into solution with the caustic.This sulfur in solution is then reduced by the nascent hydrogen evolved in the reaction between the zinc and acid,and the hydrogen sulfide gas produced reacts with the lead acetate in the paper to produce a characteristic black stain of lead sulfide.Standard stains were prepared using known amounts of sodium thiosulphate.Blank determinations were run on the reagents and fifty scales.Waste sulfite residue and the Penetrol both contained sulfur and special blank determinations were necessary on these.At the start of this experiment rather erratic results were secured,but as the work progressed a better understanding of the underlying causes of these inconsistancies resulted in very acceptable check determinations being finally secured.Some of the determinations had to be rejected because of uneven stain.Spray solutions containing the oils proved difficult to work with.It was hard to remove the insects and not rub off the oil deposit,and the duplicate determinations do not check any too well.In a majority of the tests,the duplicate determinations were made on two or more different days.All tests were made in an upstairs laboratory and both temperature and humidity varied within a narrow range.Records were kept of these,but as no correlation appeared to exist between variations and results they are not reported here.

The results of the tests on fifty leaf scales are reported in Table II.The average for each solution is corrected for blank and these figures both as to length of stains and milligrams of sulfur are diagrammaticly presented in Chart I.Thirty-four separate tests were made using various combinations and including all the substances listed in Table I.With over half of these only one strength combination was tried out.On five,two concentrations were tried;while on two,namely,calcium caseinate and blood albumin,three solutions using varying percentages of spreaders were tested.A study of the table and graphs show that eighteen of these combinations gave more residual sulfur on the fifty scale insects than lime sulfur alone.Seven gave approximately the same amounts and eight gave less.The oils and sodium silicate combinations gave the highest deposits of sulfur on those materials where only one strength was tested.Marked differences were secured with the same spreader lime-sulfur combinations by varying the concentration of the accessory material.For example calcium caseinate at 0.5% gave less residual sulfur than lime sulfur alone, but at 0.1% it gave more, and when the amount used was further reduced to 0.05% the deposited sulfur was still higher. The last dilution gave a 57.5% increase in deposited sulfur over and above that obtained by using 0.5% calcium caseinate. Blood albumin used in the same amounts as the calcium caseinate did not show such extreme variations. However 0.5% proved too much to use to get a maximum deposit, and while 0.05% gave more sulfur residue than the higher strength it gave less than the 0.1% combination. Other combinations tested, where more than one strength of the material was used, further indicate the importance of the amount used. This is especially shown with Kayso, where reducing the amount of spreader 10% or from 0.5 grams to 0.05 grams per 100cc increased the deposit approximately 100%; and with saponin, where a 64% increase was obtained. Small increases were also obtained by reducing the amount of dextrin and soluble starch.

These results are with a certain peculiar surface, but also one that is significant, as lime sulfur is widely used in the control of scale insects. The exposed surface of a scale insect is not a hard surface to wet with lime sulfur as it has a certain undetermined absorptive or adsorptive power. The physical forces were not measured, but observation would indicate that where the leaves were immersed and the scales drenched with the solution, there was no creeping of the spray away from the margin of the insect

Table II-Results of Sulfur Determination on Fifty Pine Leaf Scales Using Various Spray Solutions.

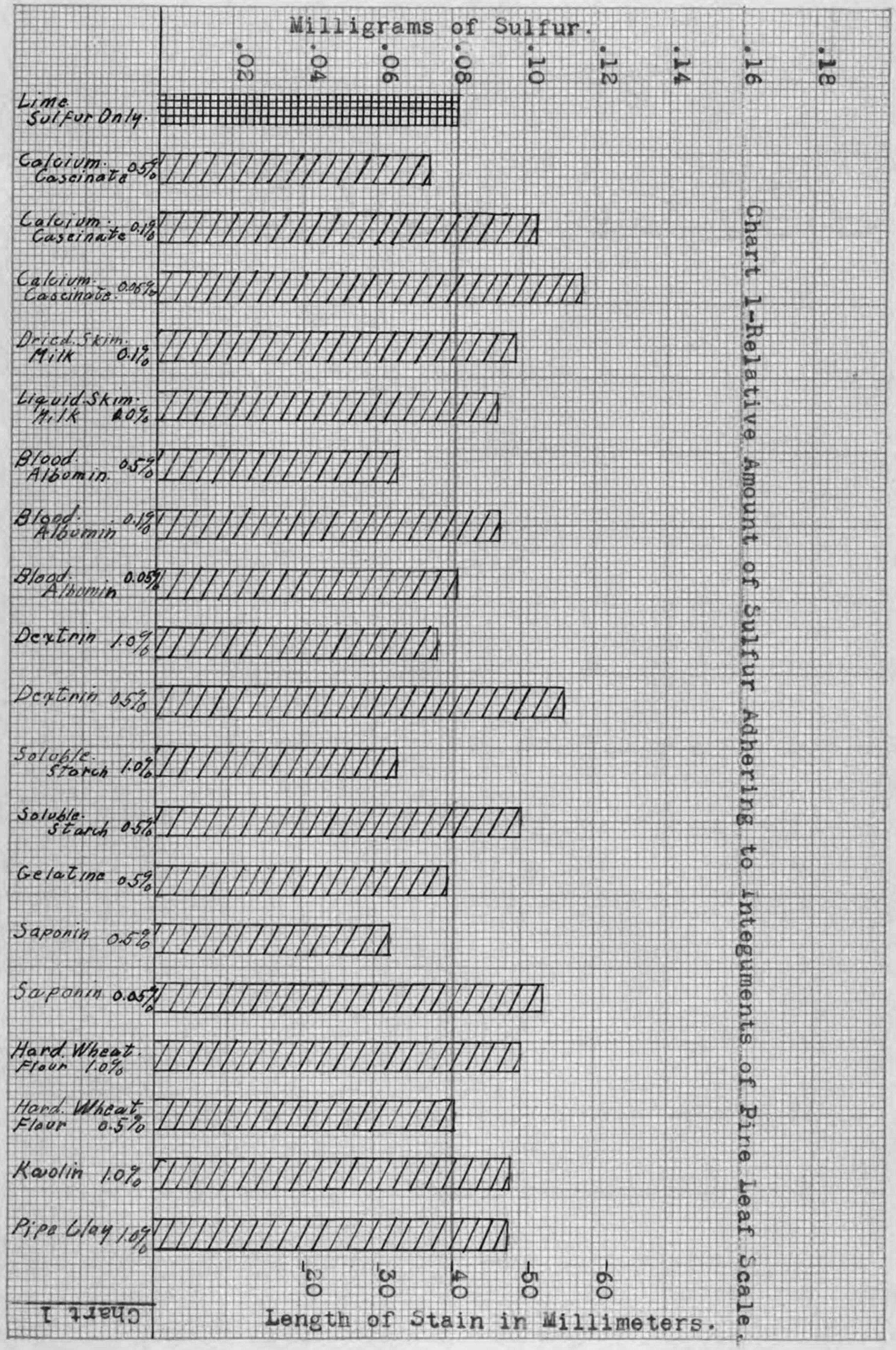
| Spreaders or Adherents Used With 1. to 10 Lime Sulfur | A'mt used | Duplicate Determination length of stain in mm. | | | | Ave. Stain in mm. | Stain corrected for blank | A'mt sulfur in mgs. |
|---|---|---|---|---|---|---|---|---|
| | | 38.5 | | | | | | |
| Lime sulfur only | | 45.0 | 38.5 | 48.0 | 37.0 | 41.4 | 40.1 | .082 |
| Blank on reagents plus scales | | 1.1 | 1.6 | 2.0 | 1.4 | 1.3 | | .00266 |
| Lab.prepared Calcium Caseinate | 0.5% | 41.0 | 38.0 | 33.0 | | 37.3 | 36.0 | .0793 |
| " " " " | 0.1% | 52.0 | 51.5 | | | 51.7 | 50.4 | .1035 |
| " " " " | 0.05% | 48.0 | 70.0 | 56.0 | | 58.0 | 56.7 | .1164 |
| Dried Skim Milk | 0.1% | 45.0 | 50.0 | 52.0 | | 49.0 | 47.7 | .0979 |
| Fresh Skim Milk | 1.0% | 42.5 | 40.0 | 57.0 | | 46.5 | 45.2 | .0926 |
| Blood Albumin | 0.5% | 38.5 | 27.5 | 33.0 | | 33.0 | 31.7 | .065 |
| " " | 0.1% | 43.0 | 55.0 | 44.0 | | 47.3 | 46.0 | .0945 |
| " " | 0.05% | 38.0 | 44.5 | | | 41.3 | 40.0 | .082 |
| White Dextrin | 1.0% | 39.0 | 36.5 | | | 38.7 | 37.4 | .0768 |
| " " | 0.5% | 57.0 | 55.0 | | | 56.0 | 54.7 | .1122 |
| Soluble Starch | 1.0% | 36.0 | 37.5 | 26.5 | | 33.3 | 32.0 | .0656 |
| " " | 0.5% | 53.5 | 59.5 | 35.8 | | 49.6 | 48.3 | .099 |
| Gelatine | 0.5% | 43.0 | 37.0 | 39.5 | | 39.8 | 38.5 | .079 |
| Saponin | 0.5% | 34.0 | 28.0 | 35.0 | | 32.3 | 31.0 | .0636 |
| " | 0.05% | 38.7 | 51.5 | 68.5 | | 52.9 | 51.6 | .1058 |
| Hard Wheat Flour | 1.0% | 48.0 | 50.0 | 40.5 | | 49.5 | 48.2 | .099 |
| " " " | 0.5% | 41.0 | 41.5 | | | 41.3 | 40.0 | .082 |
| Kaolin | 1.0% | 55.0 | 51.0 | 40.0 | | 48.7 | 47.4 | .0972 |
| Pipe Clay (potters) | 1.0% | 53.0 | 52.0 | 40.5 | | 48.5 | 47.2 | .0969 |
| Sodium Silicate | 1.0% | 78.5 | 79.5 | 59.0 | | 72.3 | 71.0 | .1455 |
| 'Ferric Hydroxide (freshly prepared). | 0.2% | 50.0 | 41.0 | 40.0 | | 43.7 | 42.4 | .087 |
| #Waste Sulfite Liquor Residue | 1.0% | 26.0 | 25.8 | 41.5 | | 31.1 | 27.1 | .0555 |

(Table continued)

Table II-(continued)

| Spreaders or Adherents Used With 1 to 10 Lime Sulfur | A'mt used | Duplicate Determination length of stain in mm. | | | | Ave. Stain in mm. | Stain corrected for blank | A'mt sulfur in mgs. |
|---|---|---|---|---|---|---|---|---|
| Cottonseed Oil plus .05%Kayso | 1.0% | 53.5 | 57.0 | | | 55.3 | 54.0 | .1108 |
| Linseed Oil plus .05% Kayso | 1.0% | 61.5 | 82.0 | 74.0 | 44.0 | 65.4 | 64.1 | .1315 |
| Fish Oil " " " | 1.0% | 42.0 | 39.5 | 75.5 | 75.0 | 58.0 | 56.7 | .1162 |
| "Fish Oil Resin Spreader | 0.5% | 28.5 | 24.0 | 32.0 | | 28.2 | 26.9 | .0552 |
| Commercial Spreaders | | | | | | | | |
| Kayso | 0.50% | 31.5 | 30.5 | | | 31.0 | 29.7 | .0609 |
| " | 0.05% | 61.0 | 70.5 | 59.3 | | 63.6 | 62.3 | .1277 |
| Leffingwell XXX, Liquid Spreader | 0.5% | 23.0 | 33.5 | 48.5 | | 31.3 | 30.0 | .0615 |
| +Penetrol | 0.5% | 54.5 | 59.5 | 47.5 | | 53.5 | 51.0 | .1046 |
| Fluxit Ore.#1 | 0.1% | 33.0 | 35.0 | | | 34.0 | 32.7 | .0671 |
| " " #2 | 0.1% | 35.0 | 42.0 | 39.5 | | 38.9 | 37.6 | .0771 |
| " Formula 1871 | 0.1% | 54.0 | 52.0 | | | 53.0 | 51.7 | .106 |

"A chemical reaction between spreader and lime sulfur.
+Blank for this was 2.5 mm.
\# " " " " 4.0 mm.


Milligrams of Sulfur.
.02
.04
.06
.08
.10
.12
.14
.16
.18
Lime Sulfur Only.
Calcium Caseinate 0.5%
Calcium Caseinate 0.1%
Calcium Caseinate 0.05%
Dried Skim Milk 0.1%
Liquid Skim Milk 2.0%
Blood Albumin 0.5%
Blood Albumin 0.1%
Blood Albumin 0.05%
Dextrin 1.0%
Dextrin 0.5%
Soluble Starch 1.0%
Soluble Starch 0.5%
Gelatine 0.5%
Saponin 0.5%
Saponin 0.05%
Hard Wheat Flour 1.0%
Hard Wheat Flour 0.5%
Kaolin 1.0%
Pipe Clay 1.0%
20
30
40
50
60
Length of Stain in Millimeters.
Chart 1
Chart 1-Relative Amount of Sulfur Adhering to Integuments of Pire Leaf Scale.

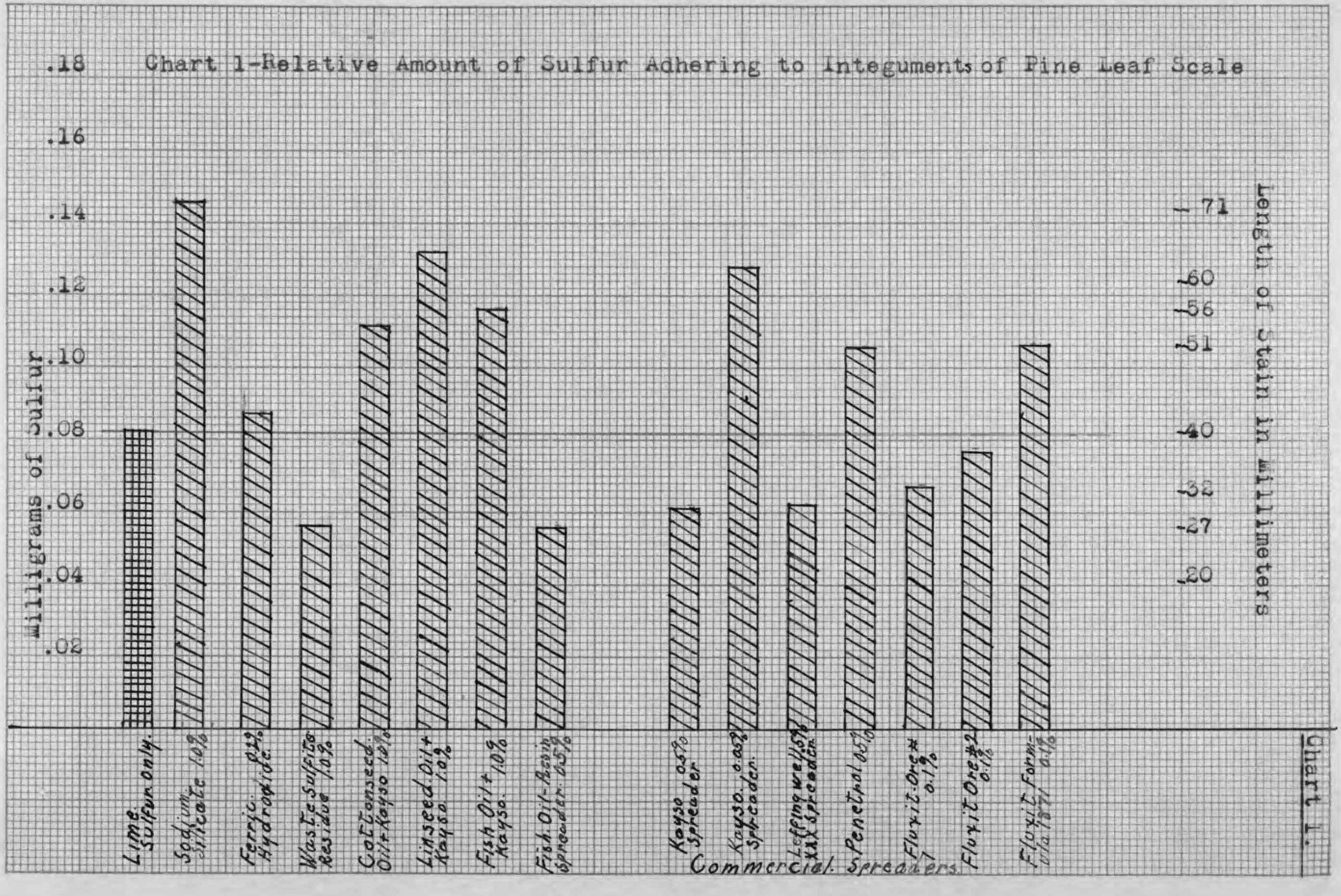


Chart 1-Relative Amount of Sulfur Adhering to Integuments of Pine Leaf Scale
Milligrams of Sulfur
.18
.16
.14
.12
.10
.08
.06
.04
.02
Length of Stain in millimeters
71
60
56
51
40
32
27
20
Lime. Sulfur only.
Sodium Silicate 1.0%
Ferric Hydroxide
Waste Sulfite Residue 1.0%
Cottonseed Oil+Kayso 1.0%
Linseed Oil+ Kayso 1.0%
Fish Oil+ Kayso. 1.0%
Fish Oil-Rosin Spreader 0.5%
Kayso 0.5% Spreader
Kayso. 0.05% Spreader.
Leffingwell XXX Spreader
Penetrol 0.5%
Fluxit Ore #1 0.1%
Fluxit Ore #2 0.1%
Fluxit Form- 0.1%
Commercial. Spreaders.
Chart 1.

covering as reported by O'Kane and Conklin(8) in their single drop studies on the angle of contact. Individual scales seemed to vary in adsorptive or retentive power. On the same twig some would show the lime sulfur over all the scale covering,while in others none could be detected. This phase of spray coverage was not followed up,and the above phenomena are simply presented because of their possible bearing on the subject.

III- The Amount of Lime Sulfur Found Adhering to the Integument of the Box Elder Bug.

The common box elder bug,Leptocoris trivittatus (Say) (Lygaeus),was the second insect to be used in this investigation.This insect is a flat elongated species from 10 to 13 mm.long.The wings are held closely to the body and cover the abdomen.Both wing covers and exposed part of the body are well chitenized,shiny,and viterous.The insects were available in numbers at the time of year when the work was being done.They proved excellent specimens to work with as the dorsel surface proved difficult to wet and consequently contrasts between good and poor spreading solutions were more manifest.In solutions with poor adherence the triangular area on the notum at base of wings was the only portion to retain the liquid.Improvement in the physical properties of the spray resulted in the wing covers and other portions of the dorsel surface holding films of the solutions.As spreading qualities were improved,the area covered was increased by first,the liquid adhering on mid dorsel line where wing covers meet, and this followed by adherence to the membraneous portion of the wing.The thickened basal part of the wings was generally the hardest to wet.

Preliminary trials were made to determine the best way to handle the insects.Trial was made by immersing the insect,either with legs and antennae clipped,or without removing appendages.The procedure finally selected was to use five uniform insects,anesthetize them with ether to render them insensible and motionless.With a pair of forceps,the insects were grasped by the legs and gently placed on their backs upon the surface of the liquid under test and allowed to float undisturbed for 30 seconds. If any of the appendages came in contact with the fluid,they were clipped off.This method of handling proved very acceptable and uniform results were secured with different lots of insects.This was not true however where the insects were completely wet as it was found that the legs and antennae retained varying size drops which invalidated the results.Solutions that showed tendencies to settle or separate were well stirred before each insect was floated.

The above method of handling the insects worked very well with all the combinations tested except the one containing Penetrol.In this one the insects would not stay on their backs,but turned either on their sides or ventral surfaces, and submerged immediately.Evidently the surface tension of this combination was so completely modified that the liquid immediately crept over the entire surface.With this mixture all legs and antennae were clipped.The results secured are probably higher than warranted,as they represent spray deposition over a greater area than with the other combinations,and for this reason are not strictly comparable with the rest.

By using five insects for each test, a weighable amount of $Ba\ SO_4$ was obtained, and the gravimetric determination of the sulfur residue was resorted to. The five insects after floating were placed into 30cc of a 2 1/2% caustic soda solution and boiled for a few minutes to bring the sulfur into solution.The insects were then filtered out,and to each solution was added 8cc of oxidizing solution(10cc liquid bromine,20 gr.KBr.and 200cc water) and 5cc Of conc. nitric acid.The covered beakers were then set in a warm place over night.They were evaporated to dryness,then about 20cc of water and 5cc of hydrochloric acid were added and the solution again brought to dryness,and finally baked over a free flame to remove the last trace of nitrates. The residue was brought into solution with 50cc of water and few cc HCl,filtered,and the sulfur precipitated and weighed as barium sulfate following the usual accepted procedure. Blank determinations were made on the reagents and five insects.Also separate blanks were run on the Penetrol and waste sulfite residue-combinations.These insects were found to contain appreciable amounts of sulfur,and the blanks were subtracted from the results obtained.The data are reported in Table III,and after correcting for the blank are diagrammaticly presented in Chart II.

Not all the spreaders and adherents listed in Table I were tested with these insects,as work with the scale insects had shown the inadvisability of further consideration of some.As was to be expected with an insect more difficult to wet,more of the tested materials gave an increase in lime sulfur coverage than they did with scale insects.Of the 21 combinations tested all but five gave a marked improvement.

The importance of using the proper amount of a substance with the spray solution is again demonstrated with these insects.The differences in the two surfaces treated,namely, the integument of scale insects and box elder bugs,and their influence on the amount of a spreader necessary to show improved coverage are shown by making a comparison of the results secured with blood albumin.With the scale insects 0.5% gave less deposit than the 0.05%;but on the box elder bug,an insect more difficult to cover,the 0.5% strength gave the best film.The oils,sodium silicate, and certain of the commercial spreader combinations all gave very

Table 3-Results of Sulfur Determinations on Five Box Elder Bugs Using Various Spray Solutions.

| Spreader or Adherent used with 1 to 10 lime sulfur | A'mt material used % | Duplicate Determination Mgs. of Sulfur | | | Ave. Results in Mgs. of S. | Corrected for Blank. |
|---|---|---|---|---|---|---|
| Lime Sulfur only | | 0.673 | 0.742 | 0.673 | 0.696 | 0.394 |
| Blank on Reagents & 5 insects | | 0.330 | 0.343 | 0.234 | 0.302 | |
| Calcium Caseinate } lab. prepared | 0.5% | 0.618 | 0.563 | 0.632 | 0.604 | 0.302 |
| " " | 0.05% | 1.443 | 1.51 | | 1.477 | 1.175 |
| Dried Skim Milk | 0.1% | 1.03 | 1.136 | | 1.083 | 0.781 |
| Fresh Liquid Skim Milk | 1.0% | 0.934 | 0.989 | | 0.961 | 0.669 |
| Blood Albumin | 0.5% | 1.25 | 1.278 | | 1.264 | 0.962 |
| " " | 0.05% | 0.700 | 0.645 | 0.632 | 0.692 | 0.390 |
| White Dextrin | 0.5% | 1.11 | 1.11 | | 1.11 | 0.808 |
| Soluble Starch | 0.5% | 0.714 | 0.783 | | 0.748 | 0.446 |
| Gelatine | 0.5% | 0.535 | 0.576 | | 0.555 | 0.253 |
| Saponin | 0.5% | 1.043 | 1.167 | | 1.105 | 0.803 |
| Hard Wheat Flour | 0.5% | 0.851 | 0.947 | | 0.899 | 0.597 |
| Kaolin | 1.00% | 1.098 | 0.824 | 0.920 | 0.947 | 0.645 |
| Sodium Silicate | 1.00% | 1.415 | 1.305 | | 1.360 | 1.058 |
| #Waste Sulfite Residue | 1.00% | 0.947 | 1.03 | | 0.988 | 0.562 |
| Cottonseed Oil - .05% Kayso | 1.00% | 1.758 | 1.675 | | 1.716 | 1.414 |
| Linseed Oil - .05% Kayso | 1.00% | 2.265 | 2.390 | | 2.377 | 2.075 |
| Fish Oil - .05% Kayso | 1.00% | 1.84 | 1.785 | | 1.812 | 1.510 |
| Kayso Spreader | 0.05% | 1.126 | 1.1208 | | 1.167 | 0.865 |
| Leffingwell XXX Spreader | 0.5% | 1.552 | 1.648 | | 1.60 | 1.218 |
| /-2 Penetrol | 0.5% | 1.799 | 1.896 | | 1.848 | 1.491 |
| Fluxit Spreader Formula #1871 | 0.10% | 1.387 | 1.442 | | 1.414 | 1.112 |

# Blank on this including insects was 0.426 mg. S.

/ " " " " " " 0.357 mg. S.

2-See text for behavior of this solution.

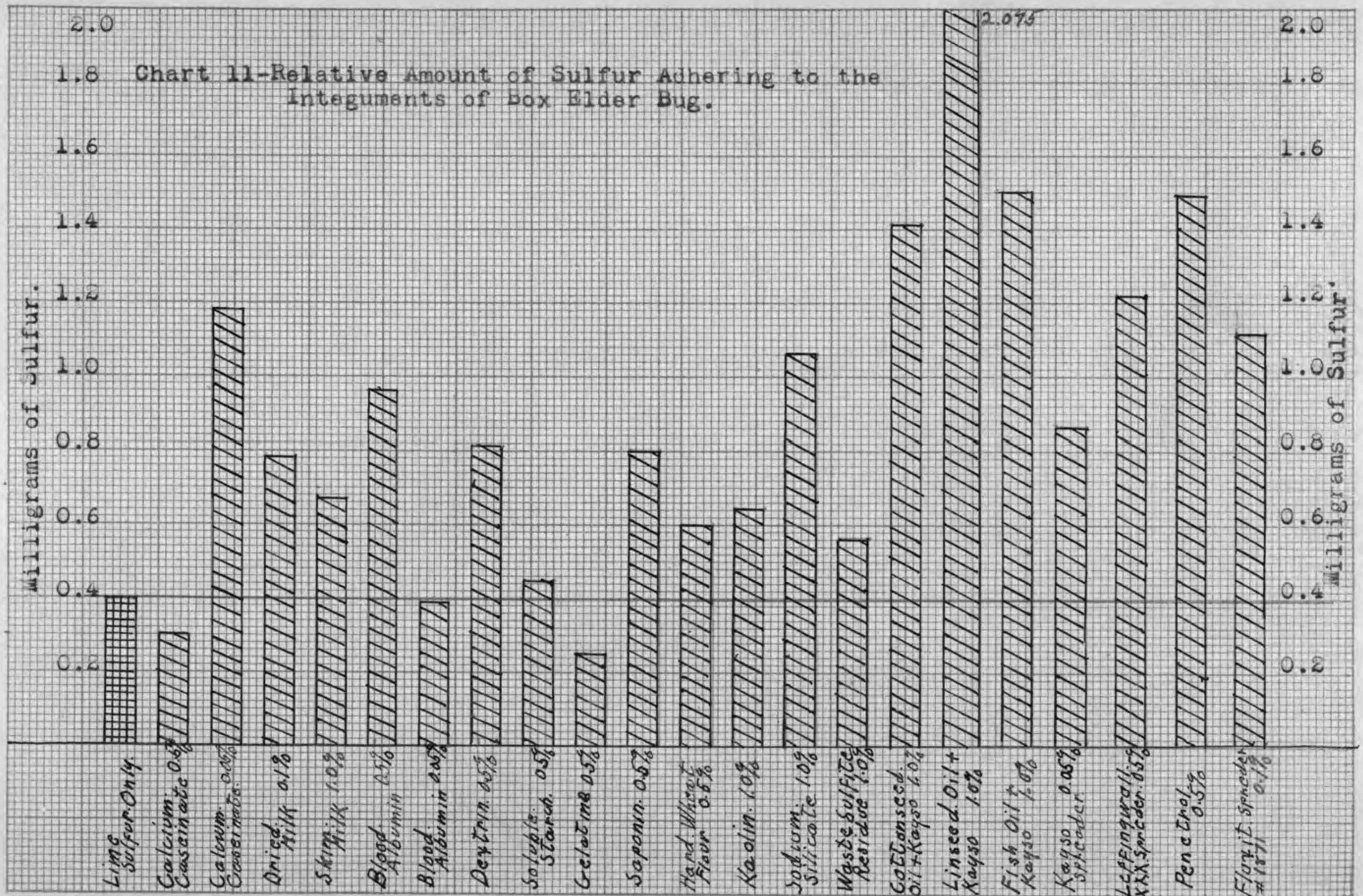



Chart 11-Relative Amount of Sulfur Adhering to the Integuments of Box Elder Bug.

high spray coverage.

IV-The Amount of Lime Sulfur Found Adhering to a Clean Glass Surface.

It has been pointed out by Robinson(9)and also others, the kind of surface to be covered is important in any attempt to evaluate spreaders.The use of clean glass microscopic slides would be another surface.In using such a uniform area and surface,a determination could be made of the residual sulfur without the introduction of the several variable constants that are unavoidable when insects are used.Even with careful selection,insects will vary as to size,age,placement of body parts,motion within the body, variation in composition and surface contour of the integument,etc.None of these variations would be encountered in the use of a glass surface.

The use of a glass surface has been resorted to by others in their studies with spray solutions-O'Kane(8),Hamilton(3), and Woodman(12)all used a glass surface in studying interfacial tension,angle of contact,and other physical forces. Woodman presented data to show by means of a comparison of surface tension and angle of contact measurement,obtained with the Searles Torsion Balance,that the magnitude of such measurements on chemically clean glass was on the average nearly the same as that secured on heavily waxed leaves of the cherry-laural.

In this experiment shellaced glass slides were first tried,but were unsatisfactory due to the difficulty of getting a uniform coating;and what proved more objectionable was the trouble of removing the sulfur spray from the coated slides without dissolving off certain portions of the coating.Coated slides were therefore discarded in favor of the clean glass surface.The procedure used was to clean microscopic slides(75.5 x 25.5 x 1mm)and then keep them in a strong chromate solution until desired for use.They were then removed with forceps,held under the tap and washed free from the cleaning solution,and then submerged in a beaker of distilled water.The various spray solutions were then prepared the same as was done in the previous experiments,and two containers(100cc cylinders cut-off) were filled.The slide was then plunged into the first receptacle to wash off adhering water,and finally into the second using a slow in and out immersion.The slide was then suspended by the forceps,(grasping the slide at extreme corner) to drain at an angle with the lowest corner touching the side of a beaker,and allowed to drain for 10 minutes.It was then boiled up with 30cc of 2.5% caustic soda solution to bring the sulfur compounds into solution,finally removed and scrubbed with a policeman,if necessary,and washed.The liquid was transferred to a 250cc beaker,and from here on the method followed in determining the sulfur as barium sulfate was the same as used in the preceding experiment.

Table IV-Results of Sulfur Residue Adhering to a Clean Glass Surface.
(Glass microscopic slides 75.5 by 25.5 by 1 mm were used.)

| Spreaders & Adherents Used With 1 to 10 Lime Sulfur | Am't Used | Mgs. of Sulfur Duplicate Determination. | | Ave. Am't of Sulfur in Mgs. |
|---|---|---|---|---|
| Lime Sulfur only 1 to 10 solution | | 2.24 | 2.335 | 2.237 mg |
| Calcium Caseinate (Lab. prepared) | 0.5% | 2.33 | 2.36 | 2.345 |
| Skim Milk plus $Ca(OH)_2$ | 1.0% | 2.17 | 2.225 | 2.20 |
| Blood Albumin | 0.5% | 2.84 | 2.75 | 2.805 |
| White Dextrin | 0.5% | 2.32 | 2.29 | 2.30 |
| Soluble Starch | 0.5% | 2.02 | 2.10 | 2.06 |
| Gelatine | 0.5% | 2.36 | 2.36 | 2.36 |
| Saponin | 0.5% | 2.94 | 2.97 | 2.955 |
| Hard Wheat Flour | 0.5% | 2.40 | 2.49 | 2.445 |
| Kaolin | 1.0% | 2.50 | 2.486 | 2.493 |
| Sodium Silicate | 1.0% | 2.95 | 3.06 | 3.005 |
| #Waste Sulfite Residue | 1.0% | 3.03 | 2.97 | 2.643 |
| Cottonseed Oil plus 0.05gr Kayso | 1.0% | 2.57 | 2.55 | 2.56 |
| Fish Oil plus 0.05gr Kayso | 1.0% | 3.38 | 3.27 | 3.325 |
| Linseed Oil plus 0.05gr Kayso | 1.0% | 2.855 | 2.87 | 2.862 |
| Kayso Spreader | 0.05% | 2.06 | 2.14 | 2.10 |

#Blank contained 0.357 milligrams of sulfur-subtracted from average.

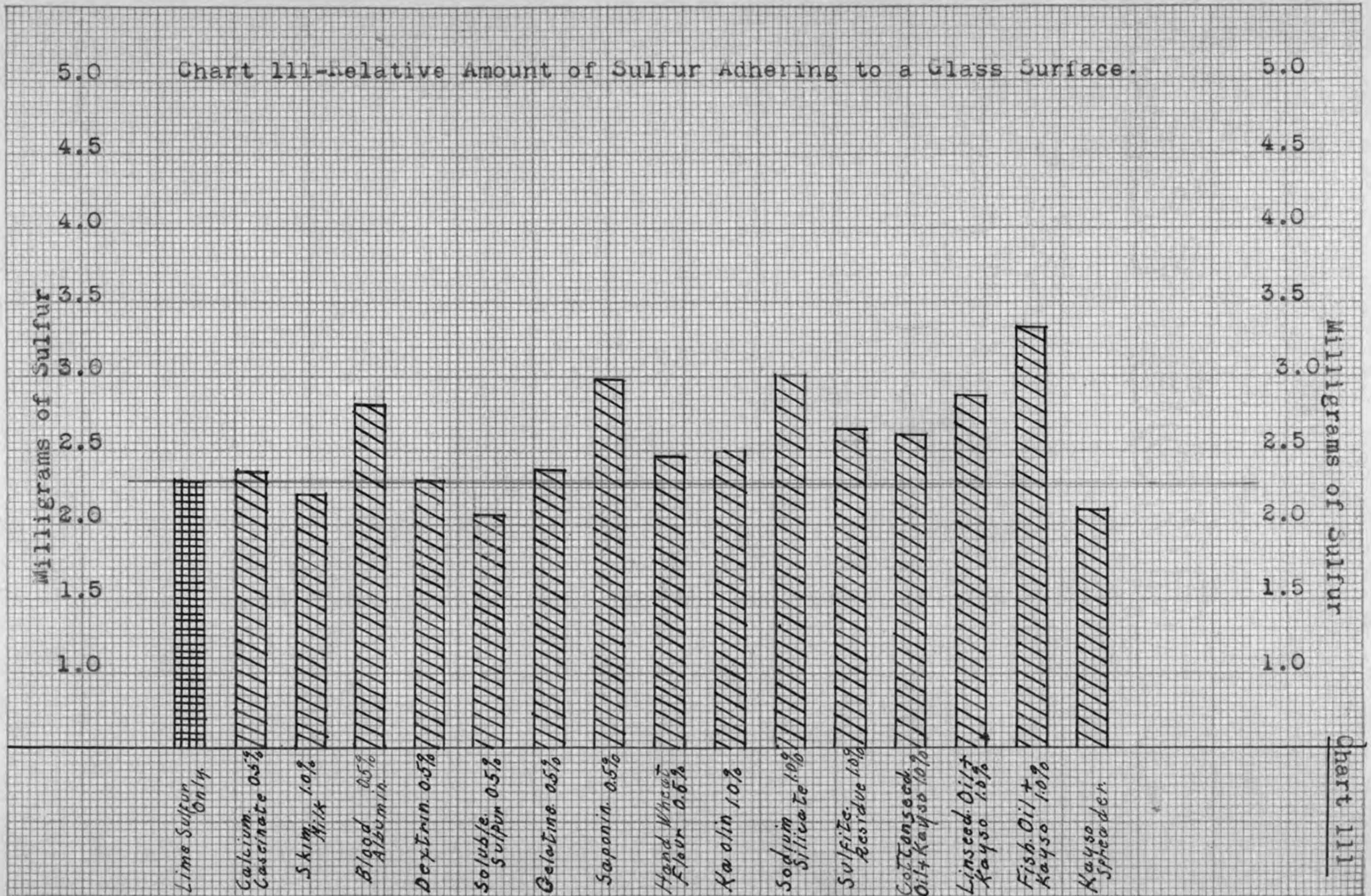


Chart 111-Relative Amount of Sulfur Adhering to a Glass Surface.
Milligrams of Sulfur
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Lime Sulfur Only.
Calcium Cascinate 0.5%
Skim Milk 1.0%
Blood Albumin 0.5%
Dextrin 0.5%
Soluble Sulpur 0.5%
Gelatine 0.5%
Saponin 0.5%
Hand Wheat Flour 0.5%
Kaolin 1.0%
Sodium Silicate 1.0%
Sulfite Residue 1.0%
Cottonseed Oil+Kayso 1.0%
Linseed Oil+ Kayso 1.0%
Fish Oil + Kayso 1.0%
Kayso Spreader
Chart 111

The results secured are presented in Table IV, and diagrammaticaly presented in Chart III. This surface was a much harder one to wet than the integuments of the two insects. It required more of several of the spreaders and adherents to get a good coverage on the glass surface. All but two of the fifteen materials tested gave more deposited sulfur than did the solution containing only lime sulfur. With the 0.5% calcium caseinate-lime sulfur combination on the two insects, less deposited spray was obtained than with lime sulfur alone, but here this combination gave a slight increase. This is no doubt due to a greater resistance of the glass to the liquid, conditioned by a high interfacial tension between the solid and liquid. The combination containing 0.5% Of saponin and blood albumin also gave a larger sulfur deposit on the glass slides, while dextrin, soluble starch and Kayso spreader combinations gave less. It is evident that on a surface difficult to wet, as represented by the glass, more spreader or adherent will be required than on a more easily covered surface, such as the scale insect integument.

General Discussion of Experimental Results.

Certain of the outstanding results of the three separate experiments have already been mentioned. It is apparent, however, that the accumulated data must be considered as a unit, and any deductions made must be based on an analysis of all the experimental evidence secured. There are three premises that are regarded as significant in these studies.None of the conclusions arrived at are original,but the accumulated data does more fully establish the importance of certain underlying factors upon which the spreading and adhering of spray solution combinations depend.

The major premise is that generalities as to the value of any spreader or adherent cannot be made unless due consideration is given to the surface to be covered,and to the amount of the substance that is used in the spray combinations.Some materials,of course,are of little or no value either as spreaders or adherents,no matter to what kind of a surface applied,or in what amounts.The performance of any accessory substance will vary in the several sprays,or they may be added to a spray solution for some other purpose than to improve the physical properties as these are related to spreading and adhering.In some cases chemical reactions may take place that may invalidate any other derived advantages.The conclusions arrived at here apply more strictly to reactions occurring in lime sulfur sprays,but the principles involved would probably be much the same with other spray solutions.

The first consideration of importance is that the surface to be covered will greatly influence the behavior of any spreader-spray combination.Cooper and Nuttal (9),Robinson(9),Moore(6),Woodman(12),and also other workers have all given attention to this subject.Much stress has been laid on the relationship between the surface tension of the solid and the liquid and the magnitude of these forces. Moore says,"It appears that spreading can be obtained only by lowering the surface tension of the liquid or the surface tension of the liquid solid interface,since the surface tension of the solid cannot be increased".More attention has been paid to these forces than to the influence of the surface on their modifications.Robinson(9)has called attention to the importance of a consideration of surfaces in his work with spreaders.In a discussion of the requirement of spreaders he says,"The difficulty in selecting a spreader with these requirements is increased by the fact that the plant may have several different kinds of surfaces. For example,the apple tree has the smooth upperleaf surface, hairy underleaf surface,and the waxy surface of the partially developed fruit,and in addition it may have the smooth bark and the wrinkled bark of spurs,and the young and old leaves may offer resistance in various ways to the spray." In an other place he says,"It has also been noticed that age and exposure of the leaf to the sun's-ray influences the degree of spreading." Robinson reported on work with spreaders applied to several fruit tree foliages and fruits and found considerable variation resulted from the various contacts.

But little work has been done on the spreading and adherence of spray solution on the integuments of insects, and that which has been reported was either in connection with studies on tracheal or wax penetration,or studies of certain physical factors.Wilcoxon & Hartzell(11)and O'Kane (7)report angle of contact studies using several insects. Lefroy(4)says in regard to the action of insecticides on the insect that there are three points to be considered- mere spreading over mechanically,wetting with spreading,and toxic action after wetting.However he was more interested in the relationship between wetting and spiracle penetration than in the other phases of the question.We have actually determined quantitatively the amount of spray residue left on two widely different insect integuments.Before any very definite conclusions are drawn,several other integuments should be studied,however we have at least shown that there is a difference in the ease of wetting the integuments of different insects,and furthermore there is also a difference in the wetting of the different portions of the same integument.It was found that the hard shiny chitinized integument of the box elder bug was harder to wet than the scale insect and that the body regions on the dorsel surface of the box elder bug varied greatly in their resistance to wetting.Considering the results secured with the insects and also on the more resistant glass surface, the necessity of a consideration of the surface to be covered is very clearly indicated.

These experiments have clearly shown that the amount ofa substance used in any given spray solution is very important.The results secured by varying the amount of calcium caseinate and blood albumin from 0,05%,to 0.1% to 0.5% have already been pointed out,as has also those secured with more than one strength of several other substances.,aterials chiefly valuable for their spreading properties will undoubtedly have more effect on a spray solution,when the amount used is varied,than those substances that are primarily adhesives.Woodman(12)has gone into this question of the influence of accessory substances in spray combinations rather extensively.He defines as the "critical surface tension",the point where the surface tension of the liquid has been reduced,and the maximum amount of a spray fluid is retained by the leaf. Failure to reach this point results in imperfect wetting, and after it is reached the surface tension ceases to be a dominating factor influencing the volume of liquid retained by a surface,and the important factor governing the increased retention is the viscosity of the liquid.

R.H.Smith(10)has shown the effect of certain spreaders on the film obtained and that certain materials so lower the surface tension that the resultant coating of spray solution is too thin.He calls attention to the desirability of combining suitable adhesive qualities along with spreading ability.Dorman(2)shows that some spreaders do not improve the insecticidal value of lead arsenate spray and less poison is actually left deposited by their use.He also says a film is necessary and spreaders that give this may result in an improvement even if some arsenic is lost,if this is not carried too far.

The results reported here show that there is a point, corresponding to the critical surface tension point of Woodman,where the amount of material used results in a maximum deposit of spray,and that if more spreader is used not only is no additional deposit secured,but the amount of deposited spray will actually be decreased and the surface will carry less spray solution than if none had been used at all.The use of the correct amount of any spreader gave a decided improvement in the amount of deposited spray.This work has also shown that this critical surface tension point will vary and will be dependent upon the surface to be covered. This is brought out by the fact that the blood albumin gave a maximum deposit on scale insects at 0.1%,concentration, while on box elder bugs the 0.5% concentration gave the best results.These same relationships were established when more than one strength of several other combinations were used. It is doubtful whether the point of maximum efficiency of any of the substances was actually reached as only a limited number of strengths were tested out,but this is not of great importance due to extreme variation in surfaces that will be encountered in actual spray practices.A secondary deduction of practical importance that might be made is, that in actual spraying operation,the use of too little spreader from the standpoint of maximum covering obtained would not be as serious a mistake as the addition of an excessive amount.

It hardly seems conceivable that the adherence obtained and the amount of residual spray left on the surfaces studied were entirely due to the surface tension phenomena.The influence of viscosity as mentioned by Woodman was not tested out.It was noticed that the parts of the integument of the box elder bug varied in their ability to retain the spray.This appeared to be due chiefly to irregularities in surface contour.If so adsorption would be a factor.With the oils and also possibly certain other materials tried,wetting as defined by Moore,or where there is a slight chemical union,would partly explain the increase in residual spray.Adsorption of the spray solution around particles of inert material in certain of the spray combinations,such as kaolin,deposited on the surface as a residue might also increase the coverage.The drops of oil appear to hold a certain amount of spray solution either by emulsion or adsorption,and these oil drops are in turn adhesive to the surfaces studies.

In the light of the significance of surface phenomena and the importance of the correct amount of spreader to use,and due to the fact that only three surfaces were used and in many cases only one dilution tried,it would not be fair to try to evaluate the various substances tested. Undoubtedly some of the materials that gave poor results at the percentages used,at a higher or lower concentration would have given more adherence.Certain results can be pointed out but these must not be considered as final or absolute.

In general the several casein spreaders when used in correct amounts gave good spray adherence.These included the laboratory prepared calcium caseinate,the commercial product,Kayso,and both liquid and dried skim milk. The dried skim milk at 0.1% gave approximately the same results as 1.0% of liquid skim milk.Blood albumin did not appear to be equal to calcium caseinate at the same concentration. Dextrin,soluble starch,hard wheat flour,and Kaolin occupy rather an intermediate place.When used in proper amount they possess a fair spreading and adhering value.Saponin also gave a good film on pine leaf scales when only .05% was used,but not so good at 0.5%.Gelatine,the waste sulfite liquor,the fish oil resin spreader,and ferric hydroxide did not prove of much value at the concentrations tested out.The last two gave a chemical reaction with lime sulfur and for that reason are not practical solutions to use. Sodium silicate and the oils gave the highest average amounts of residual sulfur.With the oils,the drying linseed oil ranked above the semi-drying fish oil and the non-drying cottonseed oil in the average deposit obtained.The fish oil proved better than cottonseed oil.Most of the commercial spreaders gave satisfactory results in the limited number of tests made.

Conclusions.

Twenty four accessory substances were tested out with lime sulfur spray on the pine leaf scale for their effect in increasing or decreasing the amount of spray retained by the integuments of the insects.A portion of these were also applied to the common box elder bug and a clean glass surface.Several of the substances were used in two and three different dilutions.

The method used in estimating the relative value of the various combinations was to determine quantitatively the residual sulfur left adhering to the integuments of the insects and to glass slides.

The results secured emphasize three points:

(1) Generalities as to the value of a spreader or adherent cannot be made without due consideration being given to the amount of substance used in the spray solution and to the surface to be covered.Such other factors as the kind of spray,concentration,chemical reaction,etc.that were not tested out here would also have to be considered.

(2) The surface to be covered has a direct and impor-

tant bearing on the effectiveness of any spray solution. Surfaces more difficult to wet will require more spreader or adherent than those easily covered.Insect integuments vary in their ability to retain the spray fluid both as found on different species and also as to different body portions of the same integument.

(3) The quantity of the material used in any spray should be given serious consideration.Too much spreader proved to give less adhering spray than no spreader at all. This work shows that there is a point,corresponding to Woodman's critical surface tension point,where a maximum film on the surface studied was obtained.The correct amount of a substance to use to obtain maximum efficiency will vary with the surface,and the more difficult a surface is to cover the more accessory substance will be required.

The data secured are too limited in scope to permit any very definite conclusions being made as to the relative value of the various spreaders and adherents.A more extended study using more dilutions and surfaces would probably result in several changes occurring in the order of ranking the materials as to effectiveness.

The use of an excessive amount of certain accessory substances in the spray solution has been found to result in a reduction in the amount of deposited spray.From an economic control standpoint,it is evident that the use of an exhorbitant amount is a more serious error than the use of an insufficient quantity.

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