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MAKING AND USING CONCENTRATED LIME-SULPHUR WASH.

SUMMARIZED BY F. H. HALL

FROM BULLETINS BY

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P. J. PARROTT AND W. J. SCHOENE.

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POPULAR EDITION*

OF

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MAKING AND USING CONCENTRATED LIME-SUL-PHUR WASH

F. H. HALL

Lime-sulphur to washes most supopular.

Probably no one topic is more actively discussed to-day by New York orchardists than the limesulphur wash. Spraying as a regular orchard practice is the custom with ten fruit-growers now where it was with one ten years ago; and

now where it was with one ten years ago; and the lime-sulphur wash seems likely to be more used by these orchardists than any other mixture. Not only has it been proven the best remedy for San José scale, blister-mite and similar insects, but it seems almost a specific for peach leaf-curl and a convenient and effective medium for early treatment for apple scab; while recent developments indicate that many apple-growers in western New York will use it for summer spraying to prevent later infections of scab and other fungi, and will combine with it some arsenical to control codling moth and leaf-eating insects.

Serious spray injury to apples in recent years, ascribed to bordeaux mixture, has caused the popularity of that fungicide to wane, and lime-sulphur washes promise to take its place; since

Names of those who so desire will be placed on the Station mailing list to

receive future bulletins, popular or complete, as issued.

^{*} This is a brief review of Bulletin No. 329 of this Station on Chemical Investigation of Best Conditions for Making the Lime-Sulphur Wash, by L. L. Van Slyke, A. W. Bosworth and C. C. Hedges, and of Bulletin 330 on Experiments with Home-Made Concentrated Lime-Sulphur Mixtures, by P. J. Parrott and W. J. Schoene. Anyone interested in the detailed account of the investigations will be furnished, on application, with copies of the complete bulletins, so long as these are available.

these preparations, properly made and applied at the right strength, give good control of apple diseases, with less russeting and deformation of fruit than result when bordeaux is used.

Economy well worth consideration. Since lime-sulphur preparations are to be so widely used, it is of great importance that fruit-growers should be able to make, regularly and economically, washes of this nature whose strength they can control as closely as they can that of bordeaux mixture. Considerable economy

and increased certainty in making and diluting these washes were secured by Station work during 1909; but the further work of 1910 has provided a formula, method of making and table of dilutions which secure almost perfect utilization of the lime and sulphur, moderate concentration, minimum quantities of sediment or unsprayable material, little or no deterioration on standing and very close agreement with standards after diluting. These results have been secured by the Chemical Department; while tests of the washes have been made in the field by the Entomological Department, both in Station work and in co-operative experiments supervised by the Entomologist, in which the feasibility, economy and ease of making concentrates at home have been shown, as well as the reliability of the diluted mixtures in controlling various insects and diseases.

Chemical studies.

When lime and sulphur are boiled together for some time, the sulphur and the calcium of the lime unite to form new compounds. If the lime and sulphur are not used in proper proportions,

however, some of one or the other will not combine but will remain behind as sediment to be lost so far as spraying value goes and to interfere with good work with the outfit. If enough water is not used some of both sulphur and lime may remain undissolved. Even if sulphur and lime all combine, the resulting solution may not be the most effective possible for spraying purposes, since sulphur and calcium form different compounds which are of unequal insecticidal values. Also, in boiling, some of the sul-

phur and lime always unite with oxygen to form calcium thiosulphate. This is a soluble compound and probably of value as an insect destroyer; but if the boiling is carried too far, or if the solution is exposed too freely to the air, the thiosulphate changes to calcium sulphite, an insoluble compound, helping to make sediment. Since it is difficult to secure the various calcium sulphides in pure form and keep them unchanged, the value of each of them as an insecticide has never been determined by actual tests; but the weight of evidence seems to show that the pentasulphide, in which four parts by weight of sulphur combine with one of lime, is most efficient.

Based on this chemical knowledge, much of it obtained from the studies of last year, work in the laboratory was designed to secure several things in one wash: (1) Perfect union of lime and sulphur so that no sediment should be formed or material wasted; (2) formation of as much as possible of the pentasulphide; (3) avoidance of thiosulphate that would easily oxidize to sulphite and be lost in the sediment; (4) sufficient concentration so that time and labor could be saved in making the concentrate rather than making the old-style wash; and (5) permanency to allow storage of the material for some time without great change.

To secure the desired result many mixtures were made and boiled and the washes analyzed. While it was found impossible to unite perfection in all the points mentioned, a very satisfactory compromise was secured, by which the orchardist may feel confident of producing at home, at much lower cost, a lime-sulphur wash as reliable, and almost as uniform as the commercial mixtures, though not quite so concentrated.

Proper proportions of materials.

The chemical work was done with pure lime and pure sulphur and the proportions of these and of the water were taken by weight. The formula which gave the best results, all things considered, was pure lime (calcium oxide) 36 pounds, sulphur 80 pounds and water 50 gallons. With

washes made from this formula 96 per ct. of the sulphur used and 97.5 per ct. of the lime were dissolved, leaving only 7

pounds of sediment in 50 gallons. A little less sediment was left when the sulphur was decreased to 71½ pounds, but only one-fourth as much of the sulphur was in the desired pentasulphide form in the last formula as in the first. Less than one-fifth of the sulphur used in these formulas went into the thiosulphate form. The density of the solutions approximated 24½° or 25° Beaumé, and a sample of one of them stood for a month or more in a closed jar without perceptible change.

The lime and sulphur in this formula are in the approximate ratio of one to two and one-fourth, and their combined weight is to the weight of water as one to three and one-half. When less sulphur was used, so that the ratio became one to two, the sediment was slightly decreased, as mentioned above; but when more was used, making the ratio one to three, the sediment was increased to more than thirty pounds. In other experiments the proportion of water was reduced, by successive decreases, from about one to four to one to one and one-half and with each decrease there was an increase of the amount of sediment in the resultant wash. That is, high concentration of lime-sulphur washes should not be sought by using large quantities of lime and sulphur to start with; but after the materials have completely combined, by an hour's boiling, concentration may easily be secured by further boiling. In doing this, however, much of the thiosulphate of the original mixture will change to calcium sulphite, crystallize out and go into the sediment. The other sulphides are not appreciably affected by the concentration. It is probably not economical, unless the wash is to be permanently barreled and shipped or transported long distances, to concentrate the solution, since this process costs fuel and time and causes some loss of previously soluble material. The wash must be again diluted before use, in any case, and the extra expense for barrels for storing the less concentrated solution is but slight.

It is also essential that the volume of the boiling mixture be kept practically constant, since failure to do this really decreases the proportion of water to solids and leads to an increase in the amount of sediment just as though less water had been used at first. The water needed should be added in small quantities at short intervals so as to interfere as little as possible with the boiling.

Change in table of dilutions.

Before using these concentrated mixtures they must be greatly diluted both as a matter of economy and to avoid injury to the trees. The hydrometer reading has hitherto been considered a reliable index for use in diluting; and the

hydrometer does show correctly the density of the solution. is indispensable in finding the strength of the concentrate. But chemical study of solutions of different density, as shown by Beaumé hydrometer readings, proves that a difference of one degree Beaumé does not quite correspond to equal quantities of sulphur in solutions of low density and in those of high density. For example, of sixty-two samples of known composition that were tested, practically all of those reading below 25° Beaumé contained from 0.60 to 0.70 per ct. of sulphur in solution for each degree B., those testing 25° to 30° B. from 0.70 to 0.75 per ct. for a degree, and those testing 30° to 36° from 0.75 to 0.78 per ct. for a degree. In other words, solutions of high density contain somewhat more sulphur for each degree than those of low density. All the evidence seems to show that the sulphur content measures the spraying value of the wash; hence to secure uniform results the orchardist must apply equal quantities of sulphur in each gallon of diluted mixture, whether that mixture comes from a concentrate testing 25° B. or 33° B. diluting, as recommended in the past, this result has not always been secured, as shown by actual analyses. The table below gives the results from diluting each of two solutions, one of low density and one of high density, by the old method and by using the new table of dilutions (given on page 12).

TABLE I. - COMPARISON OF RESULTS BY DIFFERENT METHODS OF DILUTION.

Density of original solution	Amount of dilution	Density of diluted solution	Sulphur in diluted solution	Sulphur in diluted solution per gallon	Amount of dilution	Sulphur in diluted solution	Sulphur in diluted solution per gallon	
Standard of strength for spraying.								
		Deg. B. 4.5		Ozs. 4.75		Per ct. 3.45	Ozs. 4.75	
		Result	s by old m	nethod	Results by	new met	hod .	
Deg. B. 21.6 33.6	$Sol'n:Water\ Gals. \ 1:4rac{1}{1}:8rac{1}{2}$	Deg. B. 4.5 4.5	Per ct. 3.03 3.44	Ozs. 4.17 4.69	Sol'n : Water Gals. 1 : 33 1 : 81	Per ct. 3.50 3.50	Ozs. 4.82 4.82	

These results show that in case of the weaker solution, dilution to $4\frac{1}{2}^{\circ}$ B. gives too weak a spraying mixture, containing only 3.03 per ct. of sulphur, instead of 3.45, and 4.17 ounces of sulphur per gallon instead of 4.75, while dilution by the new method gives a solution of strength slightly higher than required (3.5 per ct. of sulphur or 4.82 ounces per gallon). In case of the concentrated solution, dilution by either method gives nearly the same results. It would appear, therefore, that in case of homemade mixtures, the old method of diluting to a density of $4\frac{1}{2}^{\circ}$ B. is apt to give too weak solutions.

Tests of lime-sulphur washes made at the Station durhome-making ing 1910, complete success was attained in makof concentrates. ing a good sprayable wash. The sediment
varied from 3 pounds to 21 pounds in a barrel;
but in nearly all cases most of this undissolved material was so
finely divided that it passed readily through the spray nozzles. Both
old and new formulas were used, the old formula giving somewhat more concentrated mixtures, but also more sediment and
less perfect use of the materials employed. The densities ranged

from 22° to 31° B., averaging about 26½° B. There is undoubtedly some economy in using the new formula, though the lower density of the resultant wash makes it necessary to use more fuel and more time, or more kettles, to get the same amount of sulphur and lime into solution with the new than with the old formula. The uniformity of result and small amount of sediment by the new formula make its use advisable, without considering economy. In seventeen volunteer experiments, supervised in only a general way by the Station, all the makers but one secured very satisfactory results and will continue to make their own lime-sulphur mixture rather than to buy the commercial concentrates; and will make the concentrated rather than the ordinary boiled wash.

TABLE II.— Showing Results of Volunteer Experiments in Making Concentrated Lime-Sulphur Solution.

	Locality :	NAME	Form: la		Density	Vol- ume of	Cost per barrel		Kind of	
Nο.			Lime	Sulphur	Water	of clear solution	clear solu- tion*	Material	Labor	cooking outfit
3 4 4 5 6 7 8 8 9 10 11 12 13 14 15	Lockport Medina Carlton Albion Brockport Geneseo Shortsville Stanley Phelps	S. S. Hopkins. Asa Baldwin. A. H. Ernest. F. W. Paine A. J. Skinner. G. D. Simpson. Geo. B. La Mont. B. L. Perkins. L. R. Rogers. B. H. Henion. H. L. Bulkley M. E. Rose and Samuel Fraser. John Q. Wells. E. D. Palmer. F. A. Salisbury. Arthur E. Bell.	50 50 50 50 50 50 50 50 50 50 50 50 50 5	125 100 125 100 110 100 115 120 125 75 100 100 125 125 100 120 125 125 100 120 125 125 100 125 125 125 125 125 125 125 125 125 125	65 50 50 50 50	Degs. B. 28 22 26 31 31 26.5 to 29.5 29 to 32 28 30.7 \$30.7 \$30.7 \$30.7 \$29.5 \$26.7 \$29.5 \$26.5 \$26.3 \$32	90	2 50 2 50 2 25 2 18 2 13 2 71 2 76 2 .10 2 60 2 74 2 25	50 50 30 50 50 30 30 1 50 50 45 1 50 	Direct steam Steam Kettle Direct steam Kettle The steam Direct steam Direct steam Direct steam Direct steam Kettle

^{*}These figures were based on samples that were allowed to settle in glass jars. The actual amount of sediment by weight was not determined. While the volume of sediment in suspension appears large, the actual amount of dried material is usually only a small percentage of the total quantity of a mixture that is properly prepared.

Efficiency of home-made concentrates.

Home-made concentrates, made by various formulas, have been used by the Station for three years on its own orchards and adjacent ones under test and have given excellent results in controlling scale and blister-mite. Even in old

orchards of large trees, well infested with scale, this pest has not increased and fruits spotted with scale are rarely found. Blistermite has been as well controlled by these home-made washes as by the ordinary boiled wash or by commercial brands tested beside them. The Station has made no recent studies of the effect of lime-sulphur washes on scab and other fruit-tree fungi; but previous work on scab and the recent work of the Cornell Station promise much for the future of the wash along these lines.

In the volunteer experiments, ten out of eleven experimenters report satisfactory results against blister-mite and five out of seven against scale. The few failures are ascribed to other causes than defects in the lime-sulphur mixture. In all of the tests in which apple scab or peach leaf-curl were factors, excellent results were secured by the use of the sulphur wash for early treatments.

As an indication of the general impression produced by the use of these home-made concentrates, practically all of the experimenters intend to use these home-made mixtures during 1911, not only for spring treatment of dormant trees but also as summer sprays for fungi and with arsenicals, for codling moth.

Injuries from lime-sulphur washes. In some cases quite marked burning of leaves has followed the use of lime-sulphur sprays on foliage, and some fruit has been russeted by these mixtures, but except in rare instances the damage to leaves has soon been obscured by vig-

orous new growth of foliage; and in almost every case reported the damage both to fruit and to foliage is said to be less than the injury from bordeaux mixture under similar circumstances.

¹ Arsenate of lead is probably the best and safest arsenical for use with lime-sulphur solution.

As with "bordeaux injury" many anomalous cases of lime-sulphur burning are reported; and various causes are assigned as influencing the occurrence or degree of injury. Undoubtedly young foliage, developing rapidly under circumstances that produce tenderness of tissue, will be somewhat burned by lime-sulphur though probably less than by bordeaux; but leaves whose skin has been broken by insect punctures, fungous spots, frost rupture, etc., will probably suffer more from lime-sulphur than they would from bordeaux.

As a whole, however, it is believed that much more good than harm will come from the use of well-made lime-sulphur concentrate, diluted as indicated by the table on page 12, if the scale blister-mite, apple scab, peach leaf-curl and codling moth threaten to be troublesome.

Making concentrated lime-sulphur wash. In making lime-sulphur wash, whatever the formula, only fresh, lump-lime should be used that is free from dust, grit, air-slaked material and magnesium oxide. It should not contain less than 90 per ct. pure calcium oxide. The

Station has a list, which will be sent on application, of those dealers who will furnish guaranteed lime of satisfactory quality. Local lime is sometimes satisfactory, but orchardists should be sure of the quality of the lime before attempting to make large quantities of the wash. The Station has devised a simple method for determining the approximate amount of impurity in lime, which is given in full in Bulletin 329. The description of this test has also been reprinted on a separate leaf which will be sent to all who desire it.

For sulphur, light and heavy sulphur flour, flowers of sulphur, "ground brimstone" or "commercial sulphur flour" if finely ground and bolted, will do equally well. Before adding to the mixtures the sulphur must be thoroughly moistened and made into an even, fluid paste without lumps.

In making, slake the lime in about 10 gallons of hot water, adding the lumps of lime gradually to avoid too violent boiling

and spilling over. Pour in the sulphur paste gradually during the slaking, stirring constantly to prevent the formation of lumps, and when the slaking has finished add the full amount of water and boil gently for one hour. If kettles and fire are used, more than the required amount of water may be used at first, to compensate for evaporation, or the volume may be kept constant by adding successive small quantities to hold the mixture at the original level as shown by a notch on a stick resting on the bottom of the kettle and marked when the mixture first begins to boil. When boiling with live steam the mixture will be more likely to increase in volume than to decrease, so that no water need be added.

Storing and diluting for use. This concentrate will keep with little change, unless the weather is below 5° F., if stored in filled, stoppered barrels. Even in open receptacles there will be no loss if the surface be covered by a layer of oil to prevent access of air.

Each boiling should be tested with a Beaumé hydrometer and its density marked on the barrels or other containers. These hydrometers, shown on the title page, with a convenient glass jar for holding the solution when testing, can be obtained from the Bausch and Lomb Optical Co., Rochester, N. Y., and probably from other wholesale dealers in druggist's supplies.

For use, it has been found that a solution containing 4¾ ounces of sulphur to the gallon is most efficient for San José scale, one containing about 3½ ounces for blister-mite and one containing a little more than ¾ of an ounce for application on foliage. The dilutions shown in the following table are based on these figures and will give very close to the required amount in every case, with the variation, if any, in favor of more rather than less, soluble sulphur. The figures given in this table have come from calculations based on the analysis of 62 lime-sulphur washes; and are believed to be thoroughly reliable.

Formula and table of dilutions.

The formula from which many of the concentrates were made in the field work discussed in this bulletin is: Lime 60 lbs., sulphur 120 lbs. and water 50 gallons; but the one now recommended by the Station is the following:

GENEVA	STATION	FORMULA	FOR	CONCENTRATED	LIME-SULPHUR	Solution.
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	22011011.
Lime { Pure CaO	36 lbs.
Lime { If 95 per ct. pure	38 lbs.
11 90 per ct. pure	40 lbs.
Sulphur, high grade, finely divided	80 lbs.
Water	50 gals.

Table III.—Dilutions for Dormant and Summer Spraying with Lime-Sulphur Mixtures.

Reading on hydrometer	Amount of dilution Number of gallons of water to one gallon of lime-sulphur solution				
reading on hydrometer	For San José scale	For blister- mite	For summer spraying of apples		
Degrees Beaumé	·				
35	9	12⅓	45		
34	81	12	431		
33	81	11½	411		
32	8	11	40		
31	7½	10⅓	37 3		
30	71	10	36 1		
29	63	91/2	341		
28	63	9	323		
27	6	81/2	31		
26	53	8	29 1		
25	51	7 1	27 3		
24	5	7	26		
23	41/2	6 1	241		
22	41	6	224		
21	3 1	5½	211		
20	31/2	5	193		
19	31	44	181		
18	3	41	17		
17	23	4	16		
16	21/2	34	15		
15	21	31/2	14		
14	2	3	124		

Note.—For convenience in reference, all figures needed in making and diluting lime-sulphur solution have been grouped on this page.