THE FUNGICIDAL PROPERTIES OF CERTAIN SPRAY-FLUIDS. II.

By J. VARGAS EYRE, E. S. SALMON AND L. K. WORMALD.

(Research Department, South-eastern Agricultural College, Wye, Kent.)

INTRODUCTORY

IN a previous communication¹ we have adduced evidence to show that solutions of alkaline sulphides are probably of fungicidal value owing to the polysulphides which they contain.

This work has been continued along similar lines, and the following account gives the main results obtained during the past three years 1916-18. During the first two years a number of ammonium polysulphide solutions were made according to different methods, and the fungicidal value of each determined with a view of ascertaining whether a relationship existed between the polysulphide sulphur content and the fungicidal action of these solutions.

During this period evidence accumulated that the death-point of the mildew (*Sphaerotheca Humuli* (DC.) Burr.) varied according to its stage of development.

In 1918 by the selection of suitable material a method was adopted whereby any two solutions could be very strictly compared with regard to their fungicidal action. Thus it could be determined whether the nature of the polysulphide was of importance.

METHODS.

While the general methods used in our experiments in 1915, which have been described in detail², were adopted in our work in 1916-18, it was found necessary to pay closer attention to the stage of development of the mildew-patch sprayed. On this point we wrote in 1915: 'The plant used for spraying was carefully selected as bearing on a number of its leaves young and vigorously-growing patches of the mildew in its conidial stage. In order to make the experiments as strictly comparable as possible only those patches of mildew were used where the

¹ J. Vargas Eyre and E. S. Salmon, "The Fungicidal Properties of Certain Spray fluids," *Journ. Agric. Science*, 7, 473-507 (1916).

² J. Vargas Eyre and E. S. Salmon, *loc. cit.*, p. 477.

growth was so vigorous that the abundant conidiophores had produced masses of ripe, free conidia. This stage is denoted by the term "powdery" in the details of the experiments given below.

During the work in 1916 it became evident that the "powdery" patches on the older leaves of the plant were more easily killed than those on the younger leaves. In the experiments with the different solutions which are described in detail below, several instances will be found recorded where the powdery stage on a young leaf survived the application of a solution which killed the powdery stage on an older leaf,—sometimes even at the next node. In the later experiments in 1916, and in all those in 1917 and 1918, information is given in the Tables as to the relative age of the leaves on which the mildew occurred. In the experiments recorded below, just over 900 leaves, each usually bearing several "powdery" patches of mildew, have been sprayed and kept under close observation in the greenhouse.

Taking everything into consideration, the best standard to adopt for comparing the relative fungicidal powers of different solutions was found to be that based on the "death-point" of the young powdery conidial stage of the mildew found on the young, vigorous leaves of the hop-plants used in the experiments. It is by this standard that the fungicidal values of the solutions used have been fixed. In the experiments carried out in 1918 to compare the fungicidal action of two given solutions as closely as possible, the method was adopted of selecting mildew-patches at the same stage of development on opposite leaves at the same node,—the mildew-patches on leaves at the nodes above and below serving as controls.

SOME BIOLOGICAL FACTORS DETERMINING THE FUNGICIDAL ACTION OF THE SOLUTION.

In some of the experiments the behaviour of the solution towards the earliest stages of development of the mildew, i.e., those immediately following infection, has been noted. Very frequently, in the case of young and rapidly growing hop-leaves, the first sign of infection is the presence of a convex "blister" or "hump"; this is green at first, with no apparent sign of the mildew, then later (as observed under a pocket-lens) fine, branched hyphae appear straggling over its surface, which increase until the "hump" becomes covered over with the young, delicate vegetative mycelium. Conidiophores then quickly begin to appear, and after a few days a small, "powdery" patch results.

The early stages of development of the mildew antecedent to the

production of conidiophores have a much greater resistance to the fungicidal action of ammonium polysulphide solutions. The following tabulated results of three experiments in which three different solutions were used may be given here to illustrate this point.

Ref. No. of Experiment	Ammonium polysulphide solution, and its dilution	Mildew in the "powdery" conidial stage	Mildew in the early, non-powdery stages	Results
10/17	II; 1 : 50	(1) on 8 leaves, at 5th to 8th node from apex	(2) on 1 leaf at fifth node, among "powdery" patches	(1) all killed (2) unaffected
55	IV; 1 : 100	(1) on 6 leaves at 5th to 7th node	(2) on 1 leaf at 5th node	(1) all killed (2) checked
59	IV A; 1 : 100	(1) on 3 leaves at 5th node	(2) on 3 leaves at 4th node	(1) all killed (2) somewhat checked

In several of the experiments it was noticeable that a considerable variation occurred as regards the resistance shown to the solution even when the mildew-patches were all in the powdery conidial stage. The powdery patches on the young leaves resisted a concentration of the solution which was lethal to those on the older leaves of the same plant. Some of the more striking cases are tabulated below.

Ref. No. of Exper.	Solution	Position of leaves bearing the mildew-patches (in the powdery conidial stage) sprayed	Results
91	Ammonium polysulphide Solution II; 1 : 60	plant 1, 6th node (a) " 1, 5th " (b)	(a) some patches killed; others more or less checked (b) unaffected
79	A.p. S. III; 1 : 100	plant 1, 5th node (a) " 1, 4th " (b) " 2, 5th " (c) " 2, 4th " (d)	(a) killed (b) some patches killed, a few greatly checked, some slightly checked (c) killed (d) some patches killed, some greatly checked
65	A.p. S. IV A; 1 : 150	plant 1, 5th node (a) " 1, 4th " (b) " 2, 5th " (c) " 2, 4th " (d)	(a) (c) most patches killed; a very few just alive (b) (d) patches slightly checked or unaffected

The explanation of the fact that the powdery patches on the older leaves were easier to kill than those on the younger leaves may be that the former were all older, and that older patches are more vulnerable, or possibly that the vigour of the leaf directly affects the vigour and power of resistance of the powdery mildew.

It is clear from the cases mentioned above—and others will be found described below—that the mildew shows in its different stages of development very different powers of resistance to the same solution, being very hard to kill in the stages just following infection, and comparatively easy to kill when in its powdery conidial stage on the “older” leaves.

By the selection of only those patches of mildew in the same stage of development and on young, vigorously-growing leaves it is possible to keep a sufficiently fixed standard by which to measure satisfactorily the fungicidal value of different solutions. Where, however, two solutions have to be compared under as strictly similar biological conditions as possible, it is necessary to use mildew-patches in the same stage of development on leaves at the same node. It is much to be hoped that in future work dealing with the “powdery mildews” and their fungicides exact indication will be given both of the stage of development of the mildew-patches used and of the position of the leaves bearing the mildew.

MATERIALS USED.

Distilled water has been used in the preparation of the various solutions, and with the exception of a few instances which are referred to, soft soap was added to ensure the proper wetting of the mildew.

Soap. In nearly all cases where soap has been used alone or in conjunction with other substances, the kind known commercially as “Chiswick Soft Soap” has been employed. The sample was a moderately firm type of soft soap practically neutral in character. The total alkali was found to be equal to 12.8 % KOH (or 9.1 % NaOH).

In the other cases where soap was used it was that known commercially as “Cook’s Soap,” a rather fluid type of soft soap which exhibited a neutral or slightly acid character. The total alkali was found to be equal to 11.6 % KOH (or 8.36 % NaOH).

Saponin. The material used was the ordinary white powder sold commercially.

Ammonium hydrosulphide. This was prepared by saturating a 4 % solution of ammonia in water with sulphuretted hydrogen gas. The

amount of sulphide sulphur present in the solution was found to be 6.24 %.

Yellow ammonium sulphides. Eleven different solutions containing ammonium polysulphide were used during the course of this work. The analyses of these solutions are given on p. 306. Briefly described their mode of preparation was as follows¹.

Solution I. This solution was made by saturating 200 c.c. of a 10 % solution of ammonia in water at 17° C. with sulphuretted hydrogen gas and then adding 400 c.c. of 10 % ammonia solution and 1000 c.c. of water. To this mixture 24 grms. of flowers-of-sulphur were added and when this was completely dissolved the clear solution formed the Stock Solution No. I. The specific gravity of this stock solution was 1.001 at 15° C.

Solution II. This was prepared by saturating 1.5 litres of 30 % aqueous ammonia with hydrogen sulphide gas until the specific gravity of the liquid rose to 0.955. To this solution 3 litres of 30 % ammonia were added and 567 grms. of flowers-of-sulphur. This gave a dark brown fluid which had sp. gr. 0.950 and showed a tendency to deposit sulphur when largely diluted with water.

Solution III. This was prepared from Solution II by passing more sulphuretted hydrogen gas through the liquid until the specific gravity reached 1.05. This Stock Solution III was more stable when diluted with water than Solution No. II from which it was prepared.

Solution IV. To 500 c.c. of Stock Solution No. II, 55 grms. of flowers-of-sulphur were added and a current of sulphuretted hydrogen gas passed through the liquid until all the sulphur was dissolved. The resulting liquid had a sp. gr. 1.036 and was very dark in colour. When diluted largely with water a considerable deposition of sulphur occurred after about ten hours.

Solution IV A. This solution was prepared from Solution IV by allowing a current of sulphuretted hydrogen gas to pass through the solution until its specific gravity became 1.087. Solution No. IV A proved to be less liable to deposit sulphur when diluted with water and allowed to stand.

Solution V. A solution of ammonia in water (sp. gr. 0.987 at 15° C.) was saturated with sulphuretted hydrogen gas and an aqueous solution of ammonia was added until on testing with copper sulphate

¹ Several of the solutions used were made according to the details given by Bloxam. Vide "The Sulphides and Polysulphides of Ammonium," *Trans. Chem. Soc.*, **67**, 1895, pp. 277-309.

288 *Fungicidal Properties of Certain Spray-fluids*

solution¹, it was found that (S) and (NH₄) were present in the necessary proportions to form (NH₄)₂S. In one litre of this solution, 12 grms. of flowers-of-sulphur were dissolved, giving a pale yellow liquid referred to as Stock Solution No. V.

Solution VI. To 300 c.c. of the solution of (NH₄)₂S referred to in the preparation of Solution V, 30 grms. of flowers-of-sulphur were added and the liquid kept in a warm place for some time. After about 24 hours the clear, red liquid was decanted from the excess of sulphur, and it formed the stock solution. This stock solution did not allow of being diluted with water without depositing large quantities of sulphur, nor could it be kept for long unchanged.

Solution VII. A current of sulphuretted hydrogen gas was passed through a litre of aqueous ammonia (sp. gr. 0.987 at 15° C.) until the solution was practically saturated. The solution was then mixed with a litre of aqueous ammonia of the same sp. gr. as that used in the first instance. To this mixture 200 grms. of flowers-of-sulphur were added and a further quantity of hydrogen sulphide gas passed through the liquid until the clear liquid had sp. gr. 1.034 at 15° C. This clear liquid formed the Stock Solution No. VII.

Solution VIII. To 400 c.c. of strong aqueous ammonia (sp. gr. 0.880) an equal volume of distilled water was added and whilst a current of sulphuretted hydrogen gas was passing through the liquid, flowers-of-sulphur were added in excess from time to time. After several hours, when no more sulphur would dissolve and the temperature of the liquid decreased, the deep red clear liquor which resulted was decanted from the undissolved sulphur into a stoppered vessel. After standing for several days, this decanted liquid deposited crystals which on analysis were found to contain 18.33 % NH₄ and 81.2 % S, therefore agreeing with the composition (NH₄)₂S₅. To a weighed quantity (8.2354 grms.) of these crystals in a stoppered bottle, cold recently boiled water was added, resulting in the deposition of sulphur and the formation of a golden yellow solution. The water was run in until the addition of a small quantity produced no further precipitation of sulphur, the volume of water necessary in this case being 200 c.c. After remaining for two days in the closed vessel, the golden yellow solution was separated from the deposited sulphur and this formed the Stock Solution No. VIII.

Solution IX. This solution was prepared in the same way as Solution VIII, i.e. by decomposing crystals of (NH₄)₂S₅ by adding water

¹ The method used was that given by Bloxam. *Vide Trans. Chem. Soc.*, 1895, p. 289.

to them and taking the golden yellow solution formed. The results of analysing Solutions VIII and IX showed them to consist practically entirely of ammonium trisulphide $(\text{NH}_4)_2\text{S}_3$ in solution.

Solution X. A current of sulphuretted hydrogen gas was passed through a litre of a solution of ammonia in water (sp. gr. 0.980 at 15° C.) until it was practically saturated. An aqueous ammonia solution of the same strength was then added until by testing with copper sulphate solution it was found that (NH_4) and (S) were in the proportions required to form $(\text{NH}_4)_2\text{S}$. An excess of flowers-of-sulphur was then added and the liquid was warmed by placing the flask containing it in a water bath, the temperature of which was not allowed to rise above 80° C. When no more sulphur seemed to dissolve, the deep red liquid which resulted was poured off from the undissolved sulphur and put in a well stoppered bottle. This liquid formed the Stock Solution No. X. When kept in a stoppered bottle, this solution remained clear but on dilution with water it became cloudy in a few minutes owing to the deposition of sulphur.

Solution XI. During the preparation of Solution VIII, crystals of $(\text{NH}_4)_2\text{S}_5$ were formed and these were separated from the mother-liquor. Solution XI was made from that mother-liquor by mixing 250 c.c. with 250 c.c. of an aqueous ammonia solution (sp. gr. = 0.926 at 11° C.). The specific gravity of Solution XI at 15° C. was 1.075.

Lime sulphur. In the course of these experiments, the following two solutions of lime sulphur were used.

Solution XII. A mixture of 55 grms. of calcium oxide, 110 grms. of flowers-of-sulphur, and 400 c.c. of distilled water was boiled under a reflux condenser for $1\frac{1}{2}$ hours. This was left to stand for about 12 hours when the clear dark red liquid was decanted from the insoluble residue into a well stoppered bottle. After standing for two weeks, a few small crystals were observed to have separated. The clear liquid was separated from these and formed the stock solution for the spray-fluids. The specific gravity of this stock solution was 1.221 at 10° C.

Solution XIII. This was a commercial sample of lime sulphur.

The results of the analysis of both the above solutions are given on p. 306.

In preparing the actual spray-fluids from the stock solutions, distilled water was invariably used. The stock solution was diluted to such a volume that the concentration was double that finally required in the actual spray-fluid and this solution was mixed with an equal volume of a 2 % solution of soft soap. For instance, where a wash containing

290 *Fungicidal Properties of Certain Spray-fluids*

2 % of Solution No. IX and 1 % soft soap was used, this was prepared by diluting 8 c.c. of stock solution to 200 c.c. with distilled water and then adding 200 c.c. of a 2 % solution of soft soap in distilled water.

DETAILS OF BIOLOGICAL OBSERVATIONS.

Ammonium polysulphide Solution I.

This stock solution diluted 1:50 and upwards is not fungicidal, although at 1:50 it is nearly fungicidal, killing some patches and severely checking the others.

As with our experiments in 1915, it was found that the solution diluted 1:20 and containing 0.5 % or 1 % soft soap, is fungicidal for the "powdery" conidial stage. At this strength it did not kill the young non-powdery stage of the mildew in two experiments, but in a third experiment, where the host plant was *H. Lupulus* var. *cordifolius*, the effect was fungicidal and very striking.

The solution, diluted 1:20, was found to lose much of its potency if allowed to stand, after dilution, for four days, and had no fungicidal value after six days.

Ammonium polysulphide Solution II (with 1 % soap).

Although in two experiments this solution diluted 1:160 killed the patches of mildew, there is reason to believe that this happens only when the patches are on old leaves and therefore with a comparatively slight power of resistance. In three later experiments (with 14 leaves), where a record exists as to the comparative age of the sprayed leaves, it was found that the solution at this strength has no fungicidal power over the powdery conidial stage on the younger leaves. The solution at 1:100 has considerable fungicidal power, but in no case did it kill all the patches on all the leaves sprayed in the experiment. At 1:50 it was fungicidal for the powdery conidial stage in two out of four experiments. At 1:30 it was fungicidal in two experiments (with 12 leaves). At this strength the solution may injure the leaves.

In some of the experiments it became obvious that the death-point of the "powdery" mildew-patch varied according to the age of the leaf on which it resided. Thus in Experiment 31, with the solution at 1:160, two leaves were sprayed on one plant; the "upper" leaf bore eight powdery patches, and the "lower" many powdery patches. On the fifth day after spraying, the patches on the lower leaf were "much checked or even semi-obliterated," while on the upper leaf all the

patches had begun to produce fresh conidiophores. By the ninth day it was evident that some of the patches on the lower leaf were dead, and from the remaining patches only a few weak conidiophores had been produced; on the upper leaf all the eight patches had densely clustered conidiophores and were again powdery.

Again, in Experiment 91, with the solution at the same strength, the powdery patches on the two leaves of one plant, at the sixth and fifth nodes from the apex, showed different powers of resistance. On the fifth day after spraying, the patches on the lower leaf were sterile or partly obliterated, while the control leaf was densely powdery; the patches on the upper leaf had regrown conidiophores and were now almost as powdery as those of the "control" leaf. By the tenth day some of the patches on the lower leaf were dead, but a few patches had revived and produced conidiophores and were now sub-powdery; on the upper leaf all the original patches were now densely powdery like those of the "control" leaf.

Ammonium polysulphide Solution III (with 1 % soap).

This solution diluted 1:100 has considerable fungicidal powers. At 1:50 it was completely fungicidal in one experiment, and very nearly fungicidal in two experiments. It was fungicidal at 1:30 in the one experiment at this strength, and caused slight but distinct injury to six of the eight leaves sprayed.

In Experiment 79, with the solution diluted 1:100, there was clear evidence showing that the reaction of the mildew to the solution varied according to the different stages of growth reached by the fungus. On one of the plants used three leaves were sprayed; leaf (a) at the fifth node from the apex bore numerous powdery patches, leaf (b) at the fourth node also bore numerous powdery patches, while leaf (c) at the third node bore very young mycelial patches without conidiophores. On the eleventh day after spraying, the patches on leaf (a) were dead, while the control leaf bore powdery patches; on leaf (b) a few patches were dead, some patches had newly produced a few scattered conidiophores either at the centre of the patch or at its periphery, but most patches had produced clustered conidiophores again over most of their surface and were again powdery or sub-powdery—the mildew-patches on the control being only slightly more vigorous; on leaf c there were numerous very powdery patches,—the solution not having stopped the development of the young stage, there was no difference between the sprayed leaf and the control leaf.

Ammonium polysulphide Solution IV (Table 1).

This solution diluted 1 : 300 has considerable fungicidal power, which varies according to the age of the leaf on which the "powdery" conidial patch resides (see Table 1). At 1 : 100 it is fungicidal for all powdery patches on both old and young leaves, and it checks the development of the young non-powdery stages. At 1 : 75 the check to the young stages is more marked, and at 1 : 50 the mildew in its very earliest stages of development is almost or quite killed. Some details of three experiments in which the solution was used at 1 : 100, 1 : 75 and 1 : 50 may be noted here, as they give clear evidence that the mildew in different stages of development has different powers of resistance to the solution.

In Experiment 55 (1 : 100) one of the leaves sprayed (c) had 20 "humps," showing the early stages of development of the mildew. On the eighth day after spraying three tiny tufts of clustered conidiophores occurred arising from three "humps," while on 17 of the "humps," where the mildew had existed in its earliest mycelial growth, the fungus was killed. On the tenth day, the sprayed leaf bore three small, more or less powdery patches, while the control leaf bore 20 powdery patches. Where, on the six other sprayed leaves, the mildew had been in the form of vigorous powdery patches, it was killed.

In Experiment 73 (1 : 75) seven leaves were sprayed. On four leaves (a, c, d, f) the mildew was in the powdery conidial stage; on one leaf (b) the only sign of the presence of the mildew was the occurrence of numerous "humps," indicating where infection had taken place, although no mycelium was visible (under a lens) on the surface of the "hump"; on one leaf (e) the patches were at that stage of development when mycelium has been produced but as yet no conidiophores; on one leaf (g) there were a few powdery patches, one very young sterile patch and several "humps" bearing a few sterile mycelial hyphae radiating from their centres. By the fifth day after spraying the patches on the four leaves (a, c, d, f) were all sterile and either dead or dying—some being semi-obiterated; while the patches on the control leaves were as powdery as before; on leaf (b) only two of the numerous "humps" bore a few weak conidiophores, while the control leaf bore very numerous powdery patches. It was clear that the solution had dealt summarily for the most part with the young stages of the mildew. On the seventh day the sprayed leaf bore four tiny groups of clustered conidiophores arising from four "humps," while the control leaf was almost continuously

TABLE 1. *Ammonium polysulphide Solution IV and 1 % soap.*

Ref. no. of Exper.	Dilution	No. of leaves sprayed	Position of leaf and stage of mildew	Effect of solution on "powdery" stage	Effect of solution on young stage
22	1 : 300	6	"Lower" and "upper" leaves* powdery patch	Killed on "lower" leaves; more or less checked on "upper" leaves	—
23	1 : 300	6	"Lower," "middle" and "upper" leaves* "	Severely checked on "lower" leaves; slightly checked or unaffected on "middle" and "upper" leaves	—
24	1 : 200	7	— "	Some patches killed; some severely checked; a few slightly checked	—
55	1 : 100	7	Plant 1 (a) 7th node " 1 (b) 6th " " 1 (c) 5th " " 2 (d) 6th " " 2 (e) 5th " " 3 (f) 7th " " 3 (g) 6th " "	Killed on (a), (b), (d), (e), (f), (g)	Checked on (c)
49/17	1 : 100	10	At 3rd to 7th nodes on three plants "	Killed on all leaves	—
73	1 : 75	7	Plant 1 (a) 5th node " 1 (b) 4th " " 2 (c) 5th " " 2 (d) 4th " " 2 (e) 3rd " " 3 (f) 4th " " 3 (g) 3rd " "	Killed on (a), (c), (d), (e), (f)	Greatly checked on (b), (g)
72	1 : 50	7	Plant 1 (a) 5th node " 1 (b) 4th " " 1 (c) 3rd " " 2 (d) 4th " " 2 (e) 3rd " " 3 (f) 4th " " 3 (g) 3rd " "	Killed on (a), (d), (f), (g)	Killed on (b), (e) Very nearly killed on (c)

* Indicates the relative position at successive nodes.

294 *Fungicidal Properties of Certain Spray-fluids*

covered over with densely powdery patches; on the tenth day there were seven very small powdery patches. On leaf (e) there was no sign of any living mildew on the fifth day, while the control leaf bore very numerous powdery patches. On leaf (g) on the fifth day the only sign of life was one small group of clustered conidiophores from one "hump," the mildew in the other stages of development having been killed; the control leaf was almost continuously covered with powdery patches. By the tenth day four tiny tufts of conidiophores were observed coming from the "humps."

In Experiment 72 (1 : 50), on leaf (b) the mildew had reached the stages of development characterised either by the presence of a minute sterile patch of mycelium or by the presence only of scarcely observable young mycelial hyphae radiating over the surface of the "hump"; on leaf (c) there was no visible sign of infection beyond the presence of green "humps"; on leaf (e) the mildew occurred either in the form of tiny sterile mycelial patches or as "humps," while on leaf (g) only the former stage was present. The solution proved fungicidal for all stages of the mildew except the very earliest ones on leaf (c). On this leaf by the fifth day there were a very few weak conidiophores from one infection spot, while the control leaf bore numerous small powdery patches. On the seventh day conidiophores to the number of 12 existed on the sprayed leaf, and no further development had taken place by the tenth day.

Ammonium polysulphide Solution IV A (with 1 % soap).

This solution diluted 1 : 150 exerted strong fungicidal powers. At 1 : 100 it was fungicidal for all "powdery" patches in one experiment, and very nearly so in the second experiment. At 1 : 75 all "powdery" patches were promptly killed, in many cases being almost completely obliterated by the fifth day after spraying. At 1 : 50 the solution proved, in two experiments, fungicidal for even the youngest stages of development.

Comparison of Ammonium polysulphide Solutions VIII and XI (Table 2).

These solutions tested¹ at four strengths gave practically identical results.

With 0.010 % polysulphide sulphur the solutions were entirely

¹ In these experiments, as in all the following ones in which two solutions were compared with each other, the leaves sprayed with the two solutions were always at the same node.

TABLE 2. *Comparison of Ammonium polysulphide Solutions VIII and XI (both solutions with 1 % soap).*

Ref. No. of Exper. 1918	Solution	% of polysulphide sulphur	No. of leaves sprayed	Position of leaf*	VIII } XI }	Effect of solution on mildew
15	VIII	.010	12	3 ¹ , 4 ¹ , 5 ³ , 6 ³ , 7 ³ , 8 ¹	VIII } XI }	unaffected
14	XI	.010				
13	VIII	.032	12	4 ³ , 5 ⁴ , 6 ² , 7 ² , 8 ¹	VIII } XI }	unaffected on two leaves at the 4th and 5th nodes; on other leaves some patches killed, rest more or less checked
12	XI	.032				
10	VIII	.053	11	4 ¹ , 5 ³ , 6 ³ , 7 ³ , 8 ³	VIII } XI }	nearly all the patches killed; a very few patches with a few, usually scattered, conidiophores
11	XI	.052				
9	VIII	.077	10	4 ¹ , 5 ¹ , 6 ³ , 7 ³ , 8 ³	VIII } XI }	nearly all the patches killed; a few patches with clustered conidiophores at the edges (on five leaves action apparently slightly less fungicidal than VIII)
8	XI	.078				

* The numeral in larger type indicates the node (counting from the apex), and the numeral in smaller type the number of leaves sprayed at that node.

296 *Fungicidal Properties of Certain Spray-fluids*

without fungicidal effect; on the fifth day after spraying all the patches were as powdery as before.

With 0.032 % polysulphide sulphur the fungicidal action was quite evident, and the identity of action of the two solutions was well seen. On the two leaves, each at the fourth and fifth nodes, the two solutions did not prevent most of the powdery patches from reforming clustered conidiophores by the fifth day; with regard to the other leaves there were a few dead patches on each leaf, and clustered conidiophores regrowing from the edge of most patches—the amount of growth of the mildew being the same for the two solutions.

With 0.053 % polysulphide sulphur Solution VIII proved very slightly more potent than Solution XI with 0.052 % polysulphide sulphur; the difference, however, was so slight (considering the variable biological factors concerned) that it cannot be held to impugn the identity in fungicidal action of the two solutions.

With 0.077 % and 0.078 % polysulphide sulphur the action was fungicidal; from the third day onward the sprayed patches remained white and persistently sterile until they died.

Comparison of Ammonium polysulphide Solutions XI and IX (both solutions with 1 % soap).

There was strong similarity in the action of these two solutions. Solution XI with 0.031 % polysulphide sulphur was apparently slightly stronger in fungicidal action than Solution IX with 0.029 %. With 0.039 % and 0.036 % respectively, Solutions XI and IX proved to be identical in action. In Experiments 3 and 4, Solution XI, with 0.052 % was very slightly stronger in fungicidal action than Solution IX with 0.048 %. With 0.078 % and 0.072 % respectively, Solutions XI and IX both proved fungicidal.

Comparison of Ammonium polysulphide Solutions V and VII (both solutions with 1 % soap).

At the only strength, viz., containing 0.077 % polysulphide sulphur, at which these solutions were compared, they proved identical in fungicidal action, as the following details show.

	Sol. V No. of leaf	Sol. VII No. of leaf*
Fungicidal	4, 5, 6, 7, 8, 10, 11, 12	4, 5, 6, 7, 10, 11, 12
Very nearly fungicidal ...	1, 2	1, 2
Not quite fungicidal ...	9	9

* leaf 8 died.

Comparison of Ammonium polysulphide Solutions VII and XI
(both solutions with 1 % soap).

The solutions proved similar in action at the only strength at which they were compared. Solution VII was used with 0.077 % polysulphide sulphur and Solution XI with 0.078 %. Ten leaves were sprayed. With Solution VII all the patches were killed on two leaves; many patches were killed on the remaining eight leaves, but some patches on each leaf regrew scattered or clustered conidiophores from their edges. With Solution XI many patches were killed on all the ten leaves, but it was not fungicidal for any leaf. The effect of the two solutions on the leaves at the same nodes are tabulated below:

	Sol. VII No. of leaf	Sol. XI No. of leaf
Fungicidal	1, 2	—
Very nearly fungicidal ...	5, 6, 8, 9, 10	1, 5, 6, 8, 10
Not quite fungicidal ...	3, 4, 7	2, 3, 4, 7, 9

Comparison of Ammonium polysulphide Solutions VIII and XI
(both solutions with 1 % saponin).

There was similarity in the action of these two solutions. In Experiments 28, 29, Solution VIII contained 0.077 % polysulphide sulphur and Solution XI 0.078 %. If we classify the results under the three headings "fungicidal," "not quite fungicidal," and "non-fungicidal," we have the table:

	Sol. XI No. of leaf	Sol. VIII No. of leaf
Fungicidal	2, 4, 5	2, 4, 7
Not quite fungicidal ...	3, 7, 8	1, 3, 5, 8
Non-fungicidal	1, 6	6

In Experiments 35, 36¹, where both solutions contained 0.157 % polysulphide sulphur, if we tabulate under four headings, we have

	Sol. XI No. of leaf	Sol. VIII No. of leaf
Fungicidal	1, 7, 9, 10, 12	4, 7, 9, 10, 12, 13
Very nearly fungicidal ...	3, 4, 5, 13	3
Not quite fungicidal ...	2, 6, 8	1, 2, 5, 6
Non-fungicidal	11	8, 11

The absence of complete fungicidal action with 0.157 % polysulphide sulphur is probably to be attributed to the inferior wetting powers of saponin as compared with soap.

¹ Sufficient force was used in this experiment practically to drench the leaves.

298 *Fungicidal Properties of Certain Spray-fluids*

Ammonium hydrosulphide (containing 3.12 % sulphide sulphur) compared with Ammonium polysulphide Solution XI (diluted to contain 0.038 % sulphide sulphur and 0.113 % polysulphide sulphur) (both solutions with 1 % soap).

With ammonium hydrosulphide there was at first a severe checking action, so that on the fifth day after spraying seven of the leaves were still sterile, and on the three remaining leaves only a very few conidiophores had been produced at the edges of the patches. By the ninth day it was clear that that ammonium hydrosulphide was non-fungicidal for at least some leaves; while Solution XI was everywhere fungicidal¹. The material on the whole was rather poor, which makes the non-fungicidal action of the ammonium hydrosulphide the more remarkable. On the 14th day the leaves were classified as follows:

	Ammonium hydrosulphide No. of leaf	Solution XI No. of leaf
Fungicidal	—	1-10
Non-fungicidal (several "powdery" patches)	2, 3, 7, 8, 9, 11, 14	—
Checked; clustered conidiophores from several patches	1, 6, 10	—
Severely checked; a very few conidiophores from a few patches (poor material) ...	4, 5	—
Leaves discarded (injury)	12, 13	—

Solution XI (ammonium polysulphide) compared with Solution XII (lime-sulphur)—both with 1 % saponin (Table 3).

These solutions behaved very similarly.

With 0.078 % polysulphide sulphur the two mixtures appeared to be identical in action. This was shown by the fact that the four leaves on which the patches were all killed by each solution were at the same nodes on the same plants, as was also the case with the six leaves on which many patches produced more or less clustered conidiophores round their edges.

With 0.113 % polysulphide sulphur the action of the two solutions, although very similar, was slightly more fungicidal in the case of the ammonium sulphide, as the following details show. On leaf 1 the action of the two solutions was identical; on leaves 2, 3, 4, 5 the ammonium sulphide solution proved almost fungicidal (i.e., most of the

¹ Four leaves, Nos. 11-14, opposite to those sprayed with the ammonium hydrosulphide, were left unsprayed as "controls." On the fifth day only on one leaf, No. 14, were the patches powdery, on the remaining three leaves the mildew appeared to be dying away.

TABLE 3. *Solution XI (Ammonium polysulphide) compared with Solution XII (Lime-sulphur)*
(both solutions with 1 % saponin).

Ref. No. of Exper.	Solution	% of polysulphide sulphur	No. of leaves sprayed	Position of leaf	Effect of solution on mildew
20	XI	.078	10	4 ³ , 5 ⁴ , 6 ³ , 7 ¹	XI } all patches killed on four leaves; on six leaves some XII } patches killed, but many only more or less checked
21	XII	.078			
24	XI	.113	10	4 ¹ , 5 ³ , 6 ² , 7 ³ , 8 ²	XI almost fungicidal on four leaves; patches severely checked on four leaves, slightly checked on two leaves XII patches severely checked on five leaves, slightly checked on five leaves
25	XII	.113			

TABLE 4. *Ammonium polysulphide Solution XI compared with this solution after precipitation of sulphur*
(both solutions with 1 % soap).

Ref. No. of Exper.	Solution	No. of leaves sprayed	Position of leaf	Effect of solution on mildew
39	XI	13	3 ² , 4 ⁴ , 5 ³ , 6 ³ , 7 ¹	XI Fungicidal (no injury) Precipitated sulphur. Fungicidal, with occasional injury
40	Precipitated sulphur			
42	Ammonium chloride	14	3 ⁵ , 4 ⁵ , 5 ¹ , 7 ³	<i>Ammon. chloride</i> . On two leaves patches ultimately unaffected; on four leaves patches slightly checked; on three leaves patches greatly checked, and nearly killed (remaining leaves unsatis- factory). Occasional injury
44	Precipitated sulphur	7	3 ² , 4 ³ , 5 ¹ , 7 ² (opposite leaves 8-14 of Experiment 42)	<i>Precipitated sulphur</i> . Fungicidal; with occasional injury
43	Soap (1 %)	7	3 ² , 4 ³ , 7 ¹ (opposite leaves 1-7 of Experiment 42)	<i>Soap</i> . On four leaves patches unaffected; on two leaves patches checked (one leaf unsatisfactory)

300 *Fungicidal Properties of Certain Spray-fluids*

patches were killed, but a few on each leaf produced a very few conidiophores at the edges), while on these leaves sprayed with the lime-sulphur solution although some of the patches were killed, most regrew some clustered conidiophores. On leaves 7, 8, 9, the ammonium sulphide solution had the same effect as that described above for the leaves 2-5 sprayed with lime-sulphur, while the lime-sulphur solution on leaves 7, 8, 9 was decidedly less effective, most of the patches regrowing densely clustered conidiophores. On leaves 6 and 10 both solutions had this same almost non-fungicidal effect.

As has been mentioned, at neither strength were the solutions completely fungicidal. Since the action was less marked at the higher concentration of the solution, it seems clear that some new factor was operative, perhaps that of a reduced spreading power.

Comparison of Lime-sulphur Solutions XII and XIII (both with 1 % saponin).

In Experiment 41 Solution XII, with 0.17 % polysulphide sulphur, was fungicidal for nine out of the eleven leaves. The two leaves on which the mildew lived and produced powdery patches of conidiophores were mildewed over practically their whole surface at the time of spraying. It is possible that under such conditions the inferior spreading powers of saponin did not ensure contact everywhere with the solution. In Experiment 45 the solution, at the same concentration, was fungicidal for seven leaves; on three leaves a few of the patches regrew a few scattered conidiophores, and on one leaf (at the third node) some patches regrew clustered conidiophores.

With 0.23 % polysulphide sulphur both solutions proved completely fungicidal. Used at this strength with 1 % saponin both these lime-sulphur solutions leave no visible deposit on the sprayed parts,—a point of considerable economic importance when such fruits as gooseberries are sprayed.

At the present time lime-sulphur solutions are invariably used in this country as a "summer spray" (without the addition of saponin or any other spreading agent) at a dilution of 1 in 30, the concentrated solution having the specific gravity of 1.30. With such a commercial brand as that used in the above experiments, such a dilution gives 0.77 % of polysulphide sulphur.

If the result obtained in the above experiments (where a concentration of 0.23 % polysulphide sulphur proved fungicidal) holds good when mildews on plants growing in the open are sprayed, it is obvious that

such commercial brands of lime-sulphur can safely be used at a much greater dilution than at present, in which case no disfigurement of the sprayed parts due to the dried deposit (such as is found at stronger concentrations) would occur.

Comparison of Ammonium polysulphide Solutions X and XI
(both solutions with 1 % soap).

Each solution was diluted to contain 0.078 % of polysulphide sulphur.

In Experiments 18, 19, the two solutions behaved identically on the leaves at the same nodes on the same plants, killing all the patches on six leaves, and very nearly killing all the patches on the other six leaves, the patches remaining alive producing only a few scattered or clustered conidiophores at their edges.

In Experiments 26, 27, practically the same results were obtained, the mildew on each pair of leaves at the same node being affected in precisely the same manner.

It is obvious from these experiments (with 22 leaves, each bearing numerous "powdery" patches) that both these solutions, with 0.078 % polysulphide sulphur, were very nearly at fungicidal strength.

Ammonium polysulphide Solution XI compared with this solution after precipitation of sulphur (both solutions with 1% soap) (Table 4).

In the first experiment (39, 40) with 13 leaves Solution XI, before and after precipitation of sulphur, proved fungicidal; in the latter case severe scorching injury resulted to the edges or tips of three leaves.

In the second experiment 14 leaves were sprayed with 0.28 % ammonium chloride (which was the amount present in Solution XI after precipitation of its sulphur). Of the leaves opposite to these 14 leaves, seven (Nos. 1-7) were sprayed with 1 % Chiswick soap, in order to see whether this substance had any fungicidal effect¹ under the conditions obtaining at the time of spraying; the remaining seven leaves (Nos. 8-14) were sprayed with Solution XI after precipitation of its sulphur. Owing to the material being poor, several leaves had ultimately to be discarded.

¹ In an experiment on May 18, 1918, three leaves (at the 7, 8 and 9 nodes) bearing powdery patches were sprayed with 1 % Chiswick soft soap. On the next day only a few of the patches showed less than normal vigour, and by the third day all the patches were as powdery as before spraying.

302 *Fungicidal Properties of Certain Spray-fluids*

If we compare first the seven leaves sprayed with ammonium chloride with the seven leaves sprayed with the soap solution, we find that the condition of the mildew on the eleventh day was as follows:

	Soap No. of leaf	Ammon. chloride No. of leaf
Patches unaffected	3, 4, 5, 6	1*, 4*, 6*
Checked, but some patches with clustered conidiophores	1, 2	2, 3, 5*
Leaf discarded (mildew apparently dying away naturally)	7	7

* Tip of leaf showing "scorching" injury.

The seven leaves sprayed with ammonium chloride compared with the opposite leaves at the same node sprayed with Solution XI after precipitation of sulphur (and containing 0.28 % ammonium chloride) were classified on the eleventh day as follows:

	Sol. XI after precipita- tion of sulphur No. of leaf	Ammonium chloride No. of leaf
Fungicidal	8*, 10*, 11*, 12	—
Discarded as too poor material	9*, 13, 14	9*, 13, 14
Almost fungicidal (a very few scattered conidiophores from a few patches)	—	8*, 10*, 12
A few patches sterile; most patches with fresh clustered conidiophores	—	11*

* Tip of leaf showing "scorching" injury

There is, therefore, some evidence that the precipitated sulphur exerted a fungicidal action, although owing to the poor material used, this evidence cannot be considered as conclusive.

THEORETICAL CONSIDERATIONS.

In our previous communication we brought forward evidence showing that the fungicidal value of alkaline sulphide solutions is not to be ascribed to the total amount of sulphur such solutions contain, nor to the proportion of sulphur which is present in the form known as sulphide sulphur. We were led to conclude that the soluble polysulphides present were mainly responsible for their fungicidal behaviour.

During the seasons 1916-17 further evidence was gained in support of this view. On reference to the analyses of the solutions used in the course of this work which are given on page 306 it will be seen that Solution III contained approximately ten times the amount of sulphide sulphur present in Solution II, and eleven times that contained in Solution I. Also Solution III has three times the amount of total sulphur

present in Solution II, and eight times that contained in Solution I. By contrasting the behaviour of these it has been found that they all have apparently the same fungicidal value. Again, Solution IV contains less than half the sulphide sulphur contained in Solution III, and less total sulphur, yet Solution IV behaves more powerfully as a fungicide. The fact that this solution contains three times as much polysulphide sulphur as is present in Solution III supports our earlier conclusion that the proportion of polysulphide sulphur present is the important factor determining the value of a sulphide spray fluid.

Further experiments have been made with colourless ammonium hydrosulphide and these again point to the inefficacy of the sulphide form of sulphur. For example, a colourless ammonium hydrosulphide solution, when diluted so as to contain 3.12 % of sulphide sulphur, was sprayed upon mildewed leaves and, on similarly mildewed leaves at the same nodes, a diluted yellow ammonium sulphide solution was sprayed which contained only 0.038 % sulphide sulphur. The latter solution, however, proved to be fungicidal, whereas the colourless ammonium hydrosulphide solution, containing rather more than eighty times more sulphide sulphur, although severely checking the fungus for a time, was not fungicidal.

As experience was gained it became possible to make very close comparisons of the behaviour of these spray fluids and in 1918 attempts were made to determine whether there exists a relationship between the percentage of polysulphide sulphur present and the fungicidal action of such solutions. For this purpose solutions as widely different as possible were needed, and on reference to Table 5, it will be seen that from this point of view a comparison of Solution VIII with Solution XI was desirable. These solutions were therefore diluted so that each contained the same amount of polysulphide sulphur in solution and both these diluted fluids were sprayed upon mildewed leaves at the same nodes. These solutions were used in this way at four different dilutions, and in every case the fungicidal action was closely similar or identical (see Table 2). In precisely the same way Solutions IX and XI were used and in each case these two solutions behaved similarly when compared on a polysulphide basis. Two other solutions, Nos. V and VII, were diluted until each contained 0.077 % polysulphide sulphur and the fungicidal actions of the diluted liquids were observed to be similar. Solution XI was then diluted so as to contain 0.078 % polysulphide sulphur and then compared at the same node with a diluted solution of No. VII containing 0.077 % polysulphide sulphur.

304 *Fungicidal Properties of Certain Spray-fluids*

The two solutions, diluted in this way, exhibited very similar fungicidal behaviour.

In all the experiments just described the spray fluid contained 1 % of soft soap, added to ensure uniform spreading. In view of the possibility that this addition of soap exercised some disturbing influence, saponin was substituted for soap and a fresh comparison made between Solutions VIII and XI. On reference to p. 297 it will be seen that under these circumstances the fungicidal action of these two fluids was similar when they contained equal amounts of polysulphide sulphur.

These results seem to indicate a parallelism between the fungicidal action and the polysulphide sulphur content of these solutions. It seems that ammonium polysulphide solutions containing equal amounts of polysulphide sulphur behave in exactly the same way fungicidally.

From the foregoing results it was thought possible that ammonium polysulphide solutions and lime-sulphur solutions, having the same polysulphide content, would have the same fungicidal action. To ascertain whether this were the case, a lime-sulphur solution, made in the laboratory, and containing 17.02 % polysulphide sulphur, was diluted until the polysulphide sulphur content was 0.078 % when it was sprayed on mildewed leaves; the opposite and similarly mildewed leaves at the same nodes being sprayed with an ammonium polysulphide solution (XI), also containing 0.078 % of polysulphide sulphur. The results given in Table 3 show how very similar these two solutions were in their fungicidal action. In both these solutions saponin was used instead of soap so as to secure a fair comparison. These two solutions were again used at a different strength, each having a polysulphide sulphur content of 0.113 %, and again similar action was observed.

When the lime-sulphur solution previously referred to as having been made in the laboratory was diluted so that it contained 0.23 % of polysulphide sulphur it was found to be completely fungicidal. A commercial sample containing 23.21 % of polysulphide sulphur was likewise diluted until it also contained 0.23 % polysulphide sulphur, and this also was found to be completely fungicidal. Thus when working with lime-sulphur solutions as with ammonium sulphide solutions there seems to be this dependence upon polysulphides for fungicidal character. With the object of gaining information as to whether the higher polysulphides are more potent as fungicides than the lower polysulphides, special efforts were directed to prepare stock solutions of different chemical composition. For example, it was desired to make use of a solution for spraying purposes containing mostly low ammonium

polysulphides for comparison with one containing some of the higher ones. The analyses of the solutions prepared show that solutions Nos. VIII and IX were different from Solution XI with which they have been compared. In the preparation of these two solutions, that is VIII and IX, the attempt seems to have been successful in producing a solution of the lower polysulphides of ammonia; the analysis showing them to contain practically nothing else than the ammonium tri-sulphide $(\text{NH}_4)_2\text{S}_3$. On the other hand, Solution XI appears from the analysis to contain some high polysulphides. It is interesting, therefore, to find that solutions VIII and XI agree so completely when compared on a polysulphide basis, and this seems to indicate that equal amounts of polysulphide sulphur, whether the polysulphides present be high or low polysulphides, behave in precisely the same way fungicidally. In a previous attempt to discover whether the polysulphides are active as such in killing the fungus, or whether this property is due to the sulphur deposited when these compounds decompose, evidence was found favouring the former view. This was based upon some attempts to weigh directly the amount of sulphur deposited from solutions of colourless ammonium hydrosulphide and yellow ammonium sulphide. As was suggested then it was necessary to repeat and extend these experiments. Work along these lines has given very conflicting results and we are not inclined now to place as much reliance as formerly upon the evidence then at hand; unfortunately we have not been able to obtain concordant results. In this connection, however, the behaviour of some of the stock solutions, for example No. X, proves of interest. This solution was not stable when diluted with water and much sulphur was deposited. The fungicidal action of this solution, rendered opaque by the addition of water, was compared with that of Solution XI when both were diluted to contain 0.078 % polysulphide sulphur and 1 % soft soap. The fluid made from Solution XI was quite clear at the time of spraying while that from Solution X was yellow and opaque owing to the deposition of sulphur. Both liquids were found to have the same effect on the fungus. This comparison was repeated this time after the diluted Solution X had stood for two hours to secure as completely as possible the precipitation of sulphur. After agitation liquid No. X was contrasted with liquid No. XI and again the two solutions behaved similarly. This result seems to show that a high polysulphide solution may deposit some of its sulphur without losing any of its fungicidal power and suggests that the freshly precipitated sulphur may have some action on the fungus. In view of this result and a possible action

TABLE 5. *Analysis of solutions used.*

Solution	Grams per 100 c.c. solution					Excess of NH_4 over that required to form ($\text{NH}_4)_2\text{S}$	Sulphur in NH_4SH	Approximate fungicidal strength
	Total sulphur	Sulphide sulphur	Polysulphide sulphur	Total NH_4	Total CaO			
I	3.7	2.2	1.5	—	—	—	—	F. at 1:20. At 1:50 nearly f. (one exper.)
II	9.1	2.5	6.6	26.1	—	—	—	F. at 1:30. At 1:50 f. in two expts.; nearly f. in two expts.
III	29.1	24.6	4.5	19.4	—	—	14.06	F. at 1:30. At 1:50 f. in one exper.; v. nearly f. in two expts.
IV	24.2	10.6	13.6	20.3	—	8.62	—	F. at 1:100
V	3.8	2.6	1.23	3.13	—	0.10	—	At 1:16 nearly f. (like Sol. VII at 1:44)
VI	9.4	2.4	6.9	3.10	—	Nil	—	F. at 1:50 (not tried at other strengths)
VII	7.2	3.8	3.4	3.14	—	—	3.03	At 1:44 nearly f. (like Sol. V at 1:16)
VIII	1.72	0.56	1.16	0.60	—	—	—	F. at 1:15
IX	2.12	0.67	1.45	0.69	—	—	—	F. at 1:20
X	13.85	3.75	10.1	4.54	—	0.29	—	At 1:130 nearly f. (two expts.)
XI	20.9	5.23	15.7	13.13	—	7.0	—	F. at 1:200 in two out of five expts.*; f. at 1:139 in four expts.
XII	—	4.66	17.02	—	9.69	—	—	
XIII	—	6.68	23.21	—	13.1	—	—	

* The two experiments in which this solution was fungicidal were carried out on April 29 and May 11; the same dilution used on May 18, 24 and 28 proved to be not quite fungicidal.

of precipitated sulphur, a quantity of Solution XI was diluted with a known volume of water and the correct amount of weak hydrochloric acid added to neutralise the liquid and precipitate the polysulphide sulphur. This liquid was then made up to the same volume as that of the diluted unaltered Solution XI. The liquid containing the very finely precipitated sulphur was well shaken before being used and was sprayed on mildewed leaves at the same nodes as leaves sprayed with the clear No. XI solution. Both liquids were found to be equally fungicidal. This experiment was repeated and the same result was obtained. Although this suggests that the precipitated sulphur has some action on the fungus it does not afford satisfactory evidence that the precipitated sulphur alone was responsible for the fungicidal action because ammonium chloride was present in the liquid after precipitation. This amount of ammonium chloride, namely, 0.28 %, has been found to have a severe checking action on the fungus. (See Table 4.) Further work in this direction is in progress.

SUMMARY.

1. The resistance of the hop-mildew (*Sphaerotheca Humuli* (DC.) Burr.) to polysulphide solutions varies according to its stage of development. The earliest stages after infection and antecedent to the production of conidiophores are the most resistant, requiring approximately a solution of double the concentration lethal for the "powdery" conidial stage. The "powdery" conidial stage occurring on young leaves is more resistant than the same stage on older leaves.

2. Conclusive proof has been obtained that with polysulphide solutions neither the total sulphur content nor the sulphide sulphur content gives an index of their fungicidal value.

3. The percentage of polysulphide sulphur in polysulphide solutions appears to be the factor determining their fungicidal value.

4. The fungicidal value of such solutions does not depend upon the nature of the polysulphides present.

(Received March 6th, 1919.)