NEW DEVELOPMENTS, INCLUDING NEW COMPOUNDS, NOVEL FORMULATIONS, OR NEW APPLICATION METHODS (cont.)

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ACARICIDE GROUP

THIOQUINOX* - A NEW SPECIFIC ACARICIDE OF THE QUINOXALINE GROUP

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Summary

Thioquinox is a new acaricide based on quinoxaline-2,3-diyl-trithiocarbonate. It has a low mammalian toxicity and a specific action which is primarily directed against Tetranychidae. In trials carried out here and abroad in 1959/61 applications of 1 - 2 lb per acre of thioquinox 50% wettable powder have given consistently good results against M. ulmi, including organophosphorus resistant strains. Thioquinox was also effective against powdery mildew on apples but when used more than six times at 0.1% has shown phytotoxicity. No adverse effect has been noticed following up to 3 post-blossom applications of thioquinox at concentrations up to 0.1%.

In laboratory and field trials, thioquinox proved to be effective against Glasshouse Red Spider mite (T. telarius) including organophosphorus resistant strains.

Introduction

Since Unterstenhöfer (1960a) reported its acaricidal properties, we have carried out, since 1959, a number of field trials with thioquinox in this country to assess its efficiency against Fruit Tree Red Spider mite (M. ulmi) under British conditions and to obtain information on phytotoxicity and residues. A small scale trial was also made against powdery mildew (Podosphaera leucotricha) on apples. In this paper we give the results of these trials, at the same time quoting results of trials work done on the Continent and in South Africa, made available to us through the Biological Institute of Farbenfabriken Bayer A.G., Leverkusen.

Chemical, physical and toxicological properties of thioquinox

Reference to the chemical, physical and toxicological properties of

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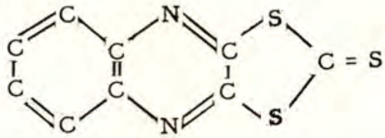
* Proposed common name for quinoxaline-2,3-diyl-trithiocarbonate

thioquinox is made by G. Unterstenhöfer (1960a) and K. Sasse (1960. Chemically, it is quinoxaline-2,3-diyl trithiocarbonate, a brownish odourless powder, insoluble in water and stable at temperatures up to 200° C. The chemical structure is:



Thioquinox was available as a 50% wettable powder formulation.

The toxicity of thioquinox was assessed by O. Klimmer (1960), the acute oral LD50 to rats being 3,400 mg/kg (± 447.1 mg/kg). The acute intraperitoneal LD50 on rats is given as 231.5 mg/kg. Doses up to 3000 mg/kg applied to the skin of rats caused no symptoms. According to A. Worden (1961) the oral LD50 to pheasants is approximately 2500 mg/kg.

Biological properties of thioquinox

Thioquinox is mainly an acaricide although it shows a slight aphicidal action under laboratory conditions. It has no effect on honey bees (*Apis mellifera*) and is classified as being harmless to bees by the German Federal Biological Institute. Ichneumonidae, Braconidae and Coccinelidae were found to be resistant to thioquinox (Unterstenhöfer, 1960). Reports from the U.S.A. suggest some effect on *Psylla pyricola*. The fungicidal action of thioquinox against powdery mildew on apples was noted by Sasse *et al*. (1960), and the Federal Biological Institute at Vienna has approved its use for the control of powdery mildew on grapes.

The effect of thioquinox on *Tetranychidae* is more pronounced than its effect on *Tarsonemidae* and *Eriophyidae*. In laboratory experiments Unterstenhöfer (1960b) found *M. ulmi* more susceptible to thioquinox than *T. telarius*, the lowest efficient concentrations being 0.005% and 0.008% respectively. He also established that thioquinox kills the summer eggs, the larval and nymphal stages as well as adults of *M. ulmi* and *T. telarius*; winter eggs of *M. ulmi* are affected to a lesser degree.

Thioquinox shows a considerable persistance, especially against larval stages which seem to be more susceptible than other stages. Its effect on *Tetranychidae* is slow and often a 100% kill of active stages can only be observed 5 - 7 days following application.

Laboratory work indicates that thioquinox is effective as a contact and stomach poison but nothing is known about its primary mode of action, i.e., which specific system if affects.

Field trials work against M. ulmi - 1959/61

In 1959 thioquinox and azinphos-methyl were included in a replicated trial at Rowhill Experimental Farm, Kent. Both materials were applied high volume on the variety Cox's Orange Pippin, James Grieve and Worcester Pearmain on the 28th May, 22nd June and 22nd July. The results expressed as mites per 30 leaves are given in Table 1.

Table 1. RED SPIDER TRIAL, ROWHILL FARM, 1959
Results (mites per 30 leaves) Trial 3 x replicated

Date of counts	Thioquinox (50% w.p.) 0.1%	Azinphos-methyl 0.2%	Control
4th June	1.3	0.6	241
18th June	3.6	7	301
2nd July	-	-	172
16th July	3.0	0.3	344
30th July	-	0.3	464
20th August	13	6	1,135
4th September	50	10	1,489

A similar trial was carried out at Rowhill in 1960 giving two applications instead of three. These were applied on the 2nd/3rd June and 26th/27th July. The results are given in Table 2.

Table 2. RED SPIDER TRIAL, ROWHILL FARM, 1960
Results (mites per 40 leaves) Trial 4 x replicated

Date of counts	Azinphos-ethyl		Thioquinox (50% w.p.)		Control
	0.05%	0.1%	0.05%	0.1%	
1st June	336	204	454	297	275
9th June	3	3	2	8	170
23rd June	4	1	10	3	320
7th July	9	5	12	5	568
21st July	9	5	31	22	298
4th August	2	3	5	2	678
25th August	5	5	13	9	837

A transformation of these results into percentage control (Henderson and Till) shows that the two thioquinox sprays resulted throughout the season in a degree of control which was never below 91.5% when applied at 0.1%, and 86.1% when applied at 0.5% of the formulated product.

Owing to a very slight infestation of M. ulmi on apples at Rowhill in 1961 it was decided to compare the effect of one application of thioquinox and azinphos-methyl on Myrobalan plums which were heavily infested. A high volume application was made on 11th July. The results expressed as percentage control (Henderson and Till) are given in Table 3.

Table 3. RED SPIDER TRIAL, ROWHILL, 1961 ON MYROBALAN PLUMS
Results as percentage control (Henderson & Till)

Treatment	Date of assessment 13th July	24th July	1st August
Azinphos-methyl (20% emulsion) 0.2%	91	69	85
Thioquinox (50% w.p.) 0.075%	80	99	80

The three trials described were carried out on Fruit Tree Red Spider mites known to be susceptible to organophosphorus compounds. To obtain information on the effect of thioquinox against resistant strains of Fruit Tree Red Spider mites, a field trial was laid down in 1961 in an orchard in Essex, where previously organophosphorus compounds had given poor control. Here thioquinox was applied once on 25th May at a rate of 1 and $1\frac{1}{2}$ lb of a 50% wettable powder per acre in 250 gallons of water on the variety Cox's Orange Pippin. The results in Table 4 are expressed as the number of mites per 105 leaves.

Table 4

Date	Thioquinox (50% w.p.) 1 lb/acre	$1\frac{1}{2}$ lb/acre
Pre-spraying count 25th May	3199	3390
Post-spraying counts		
1st June	16	21
8th June	6	2
19th June	5	5
3rd July	6	17
17th July	123	33
31st July	56	134

Further information of the effect of thioquinox on organophosphorus resistant Fruit Tree Red Spider mite is available from trials carried out by the Biological Institute of Farbenfabriken Bayer A.G. in the Rhineland in 1960. Table 5 gives the results (average of 7 trials) as percentage control at several intervals following one treatment with thioquinox, azinphos-methyl and demeton-S-methyl.

Table 5. TRIALS AGAINST OP-RESISTANT RED SPIDER MITE (M. ULMI) IN THE RHINELAND, 1960

Results expressed as percentage control (mean of 7 trials)

Treatment (Beginning of June)	Concentr. (a. i.)	Number of days after treatment 2-5	6-10	11-20	>20
Thioquinox	0.05%	100	94	96	95
Thioquinox	0.025%	84	97	93	95
Thioquinox	0.0125%	85	89	82	84
Azinphos-ethyl	0.04%	79	94	96	91
Demeton-S-methyl	0.025%	74	82	49	45

Effect of thioquinox on T. telarius (L.)

The results of two trials were made available to us by the Biological Institute of Farbenfabriken Bayer A. G. Table 6 gives the results of a laboratory trial against T. telarius on beans. The figures refer to the percentage control at different intervals after application following artificial reinfestation.

Table 6. LABORATORY TESTS AGAINST T. TELARIUS ON BEANS

	Percentage kill after days 1	3	10	17
Thioquinox 0.0125%	15	50	100	100
Thioquinox 0.025%	25	60	100	100
Thioquinox 0.05%	75	100	100	100

The effect of thioquinox, demeton-methyl and azinphos-methyl against organophosphorus resistant T. telarius has been assessed in a replicated field trial carried out in 1959 by the Technical Staff of Agro-Chem in South Africa. The results expressed as number of active stages per 120 leaves are given in Table 7.

Table 7. TRIAL AGAINST OP-RESISTANT RED SPIDER MITE (T. telarius) on apples (Var. "Cape Province") South Africa, 1959 (6 x replicated) Results (active stages/120 leaves.

Treatment	Pre-treatment	Post-treatment		
	23.3.59	28.3.59	6.4.59	16.4.59
Demeton-methyl (50% emulsion) 0.1%	1,814	428	575	650
Azinphos-methyl (25% w.p.) 0.15%	2,372	444	258	197
Thioquinox (50% w.p.) 0.1%	3,353	149	16	14
Control	2,703	2,244	1,180	812

W.H Read stated (personal communication) that thioquinox applied at 0.1% has given good results against organophosphorus resistant Glasshouse Red Spider mite in this country.

Effect of thioquinox against Powdery Mildew on apples

Thioquinox was included in a replicated trial at Rowhill Farm in 1960 on the variety Cox's Orange Pippin. Six high volume applications were given using a rate of 0.1% of the formulated product. Counts of secondary infections were made in August, 1960, the leaves being graded according to the severity of infection from 0 - 5. The figures in Table 8, expressing the results, were obtained by multiplying the number of leaves in each category by the category value and summing. Colloidal sulphur 40% is included as a comparison.

Table 8. MILDEW TRIAL, ROWHILL, 1960 Secondary infection counts August, 1960 Results (number of leaves in category (0-5) x category value)

Treatment	Block I	Block II	Block III	Mean
40% Coll. sulphur (0.5%)	24	37	27	29
Thioquinox (50% w.p.) (0.1%)	29	40	30	33
Control	65	94	82	80

Spraying Dates: 28.4 / 11.5 / 25.5 / 10.6 / 21.6 / 20.7

This assessment was followed up by flower truss counts in spring 1961, the results of which are given in Table 9 as percentage of mildewed clusters.

Table 9. MILDEW TRIAL, ROWHILL, 1960
Flower Truss Counts, Spring, 1961
Results (percentage mildewed clusters)

Treatment	Block I	Block II	Block III	Mean
40% Coll. sulphur (0.5%)	7.0	1.8	1.4	3.4
Thioquinox (50% w.p.) (0.1%)	9.8	4.8	6.7	7.1
Control	15.3	16.4	13.4	15.0

It must be pointed out that, in this trial, the plots treated with colloidal sulphur had already received a series of sulphur sprays in 1959 when this mildew trial was started, whereas thioquinox was used on previously unsprayed trees. Hence the initial mildew infection in the thioquinox plots was higher in the spring of 1960.

In an unreplicated field trial against powdery mildew on apples carried out in Essex in 1961, plot 1 received 6 sulphur and 3 thiram sprays during the season. In plot 2 thioquinox was used twice post-blossom, primarily for Red Spider control and on these occasions the sulphur spray was omitted and replaced by thiram. 200 leaves per plot were sampled in August and graded 0 - 5 in order to assess the incidence and severity of secondary mildew infections. By multiplying the category value by the number of leaves in each category and obtaining a total, an index figure was arrived at which was 336 in plot 1 and 287 in plot 2, indicating that the applications of thioquinox have helped to maintain mildew control.

In Holland (Wäckers, 1960) replicated trials on the variety Jonathan were carried out to assess the effect of thioquinox on secondary infections of Powdery Mildew when used in combination with thiram and another organic fungicide referred to as "Product X". 10 spray applications were given from the 21st April to the 13th July. An assessment of mildew was made on 500 leaves per treatment and the results, expressed as the percentage infection, are given in Table 10.

Table 10.

Thioquinox 0.05% + Product X	11.2%
Thioquinox 0.05% + thiram	7.2%
Thioquinox 0.1% + Product X	11.2%
Thioquinox 0.1% + thiram	4.4%
Fungicide X	83%

Effect of thioquinox on plants

Observations on the effect of thioquinox on plants were made at Rowhill Farm from 1959 to 1961. Under the conditions of these trials up to 3 applications of thioquinox (50% wettable powder) at concentrations up to 0.1% did not lead to an increased russetting on apples of the varieties Cox's Orange Pippin, James Grieve, Laxton's Superb, Bramley's Seedling, Worcester Pearmain and Tydeman's Early Worcester, nor was there any phytotoxic effect on the leaves. Where thioquinox was applied six times in a season at a concentration of 0.1% on the variety Cox, a higher degree of russetting was noticed compared with the control and the plots treated with colloidal sulphur 40% at 0.5%. The leaves, in comparison to the control, were harsher, of a lighter colour and brittle in texture. Similar observations were made in Holland (Wackers, 1960) where 7 - 10 applications of thioquinox at concentrations of 0.1% caused leaf damage whilst 3 sprays at a concentration of 0.1% and 7 sprays at 0.05% had no adverse effect. In these trials a brown discolouration of petals was noticed when thioquinox was sprayed on apple trees in full blossom. In trials carried out in the Rhineland, the effect of thioquinox on 45 apple varieties was studied. 2 - 3 sprays high volume at rates between 1 and 2 lb of the 50% wettable powder per acre caused yellowing of the leaves on two varieties only, namely James Grieve and Berlepch whilst the other varieties were unaffected.

In two trials leaf damage on beans (Phaseolus vulgaris) was noticed following the application of thioquinox at 0.1%. Hops seem to be very sensitive to thioquinox and its use on this crop cannot be recommended. In the United States no damage was noticed on 150 varieties of roses following the application of thioquinox.

Thioquinox Residues

Residues on plant material can be assessed using the method described by Tietz, Osman, Frehse and Niessen (1960).

At the time of writing, the full results of this year's residue tests on apples and plums treated in this country are not available. On apples of the variety Golden Delicious, treated in South Africa with thioquinox at 0.1% a residue of 1.3 p.p.m. was found on the day of the spray treatment which decreased to 0.88 p.p.m. within a fortnight.

Discussion of the results

Thioquinox has, under trials conditions, given consistently good results against Fruit Tree Red Spider mite on apples and Myrobalan plums in this country and in trials on the Continent. A concentration of 0.1% of the 50% wettable powder formulation was slightly more effective than the concentration of 0.05% but the differences may not be significant. It is difficult to judge the true residual effect of acaricides from field trials but all our observations, as well as those from workers in other countries, indicate that thioquinox has a fairly long persistence, especially against the larval stages. In years not favourable to the development of Fruit

Tree Red Spider mite one spray application after completion of winter egg hatch would probably be sufficient to maintain good red spider control throughout the season. In "red spider years" a second application 3 - 4 weeks after the first application might become necessary. As thioquinox affects summer eggs as well as all active stages, the larvae being more susceptible than the adults, timing is thought to be less critical than with acaricides whose action is limited to certain development stages only. Trials evidence and observations from here and abroad show that thioquinox is equally effective against "normal" and "resistant" strains of M. ulmi. This property and the chemical structure of thioquinox indicates an entirely new mode of action. This development appears to be a step in the direction indicated by Collyer and Kirby (1959).

Thioquinox would seem to be particularly suitable for use in areas where resistance to acaricides in current use has already occurred and also where growers wish to adopt a "rotation" in the use of acaricides in order to prevent or delay the development of resistance. Its low mammalian toxicity, its harmlessness to bees and probably to other beneficial insects and its specific action are noteworthy advantages. More detailed studies on the effect of thioquinox on important predators in this country are, however, desirable.

There is evidence that where thioquinox is used against red spider in the apple spray programme, the addition of a specific mildew fungicide is not necessary, although further proof on this point should be obtained. Because of injury to apple trees of six or more applications of thioquinox at a concentration of 0.1%, a full mildew programme at this concentration must be ruled out. Further work using lower concentrations will, however, be carried out. Meanwhile we are satisfied that up to three post-blossom applications of thioquinox (50% wettable powder) at 0.1% will not cause any damage to apples or plums. On crops other than fruit there are indications that thioquinox could be useful against T. telarius, particularly organophosphorus resistant strains.

Acknowledgements

We gratefully acknowledge the help given to us by fruit growers in this country in making plots for trials work available. Thanks are also due to Mr. M. D. Austin who supervised part of the field trials work in 1961.

References

COLLYER, E. and KIRBY, A. H. M. (1959). Annual Report East Malling Research Station for 1958, p. 131.

KLIMMER, O. R. (1960). Unpublished report on toxicity of Ss 1451. 25th June, 1960.

SASSE, K., (1960). Höfchen-Briefe, 13, 197.

SASSE, K., WEGLER, R., UNTERSTENHÖFER, and GREWE, F. (1960). Angew. Chemie, 72, 973.

TIETZ, H., OSMAN, M. F., FREHSE, H. and NIESSEN, H. (1960). Unpublished report, January, 1960.

UNTERSTENHÖFER, G. (1960a). Höfchen-Briefe, 13, 207.

UNTERSTENHÖFER, G. (1960b). Paper given at the German Crop Protection Congress, Freiburg 1960.

WÄCKERS, R. (1960). Paper given at Plantenziekemtagen IPO. Wageningen, 1960.

WORDEN, A. N. (1961). Internal report dated 26th June, 1961.

2,4,5,4'-TETRACHLORO-DIPHENYL SULPHIDE, AN ACARICIDE WITH OVO-LARVICIDAL PROPERTIES*

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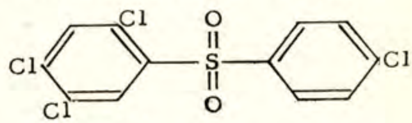
Introduction

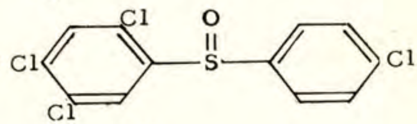
In 1952 2,4,5,4'-tetrachloro-diphenyl sulphone (tetradifon) was shown to possess extremely high acaricidal properties (Meltzer, 1955). As field trials and practical experience have proved this substance useful for mite control (Flik, 1957), a large group of related compounds have been examined (Huisman, et al., 1958).

In this paper the acaricidal properties of the sulphide homologue of tetradifon are compared with tetradifon and its sulphoxide homologue.

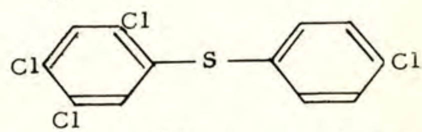
2,4,5,4'-tetrachloro-diphenyl sulphone



2,4,5,4'-tetrachloro-diphenyl sulphoxide



2,4,5,4'-tetrachloro-diphenyl sulphide



To examine the direct ovicidal action, beanplants (Phaseolus vulgaris) bearing eggs of Tetranychus telarius** were dipped in emulsions or suspensions of the compounds concerned. Larvicidal action following the hatch of the surviving eggs completes the acaricidal action. To examine the residual action of the compounds, dipped beanplants were infested with female mites after the deposit had dried. A detailed description of the methods used was given by Meltzer (1955).

It appeared that leaf penetration contributes much to the acarcidal action in this type of compound, and experiments were carried out to examine this property. In these experiments the upperside only of the leaves

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* Communication no 63 of the Agrobiological Laboratory "Boekesteyn", 's-Graveland, The Netherlands.

** The species of the telarius complex used are T. urticae, T. hydrangeae and T. cinnabarinus.

was treated with an emulsion, applied by means of an Agla micro-syringe and distributed over the whole surface with a glass rod. By using eggs on the underside of the leaves only, laid before and after application of the substances, the results give an indication of the penetration, and even of the relative speed of penetration of the compounds concerned.

In conclusion experiments were made with the fruit tree red spider mite, and, in particular, the action on wintereggs was studied.

Initial and residual ovo-larvicidal activity

With respect to the initial activity it will be seen from Table 1, that the sulphone possesses the highest strictly ovicidal activity. The inferior contact action of the two other compounds, however, is largely compensated by larvicidal action. It is known, from other experiments, that the mortality of larvae and nymphs at the lower concentrations is maindly due to oral intoxication (Meltzer, 1957a). So it may be assumed, that this compensation is due to a relatively strong penetration of both the sulphoxide and the sulphide into the leaf.

Table 1. Initial ovo-larvicidal activity of 2,4,5,4'-tetrachloro-diphenyl sulphone, -sulphoxide, and -sulphide on *Tetranychus telarius*. Mean percentage mortality of at least six experiments.
E = percentage egg mortality; T = total kill (eggs and larvae together).

Concentration in p.p.m.	Sulphone		Sulphoxide		Sulphide	
	E	T	E	T	E	T
30	98	100	90	100	60	100
10	95	100	63	98	52	98
3	74	98	48	96	23	88
1	32	90	15	60	15	60

The residual activities, i.e. the activity of the dry deposit on the leaf of the three compounds are similar (Table 2), though the strictly ovicidal activity of the sulphone is superior to both the other compounds. As has been shown in earlier work (Meltzer, 1957b) egg kill is mainly due to oral uptake of the deposit from the leaf by the female mites. In the experiments of Table 2, the period of three days between treatment and deposit of the lastly laid eggs enabled the compounds to penetrate and the ovicidal action is sharply increased with relation to the initial effect.

Table 2. Residual ovo-larvicidal activity of 2,4,5,4'-tetrachloro-diphenyl sulphone, -sulphoxide and -sulphide on *Tetranychus telarius*. Mean percentages mortality of at least six experiments.
E = percentage egg mortality; T = total kill.

Concentration in p.p.m.	Sulphone		Sulphoxide		Sulphide	
	E	T	E	T	E	T
30	100	100	93	100	88	98
10	100	100	89	97	83	99
3	92	100	85	98	71	96
1	24	69	55	62	32	66

The duration of the residual action of the three compounds, however, is different, as can be seen from Table 3. The sulphone- deposit shows the most lasting action; the sulphide the least, whereas the sulphoxide takes an intermediate position.

The higher initial egg killing activity of the sulphone, and particularly the longer residual action led to the choice of the sulphone (tetradifon) for spider mite control during summer.

Table 3. Residual action of miscible oil preparations of 2,4,5,4'-tetrachloro-diphenyl sulphone, -sulphoxide, and -sulphide. E = percentage egg mortality; T = percentage total mortality.

Infestation after	Conc. (p.p.m.)	Sulphone		Sulphoxide		Sulphide	
		E	T	E	T	E	T
0 days	300			100	100	100	100
	100	100	100	100	100	99	100
	30	100	100	97	100	100	100
	10	93	98	88	95	97	100
	3	91	97	31	83	95	99
7 days	300			98	100	97	100
	100	93	99	87	99	85	99
	30	86	99	74	97	79	98
	10	81	96	41	55	67	77
	3	39	83	9	12	5	6
14 days	300			77	100	82	99
	100	97	99	81	100	80	95
	30	95	99	30	73	34	58
	10	83	97	28	43	22	26
	3	49	69	9	11	6	9
21 days	300					61	78
	100	80	100	41	83	43	46
	30	78	94	11	31	23	27
	10	63	97	3	3	0	0
	3	24	55	5	5	0	0

Leaf Penetration

The different leaf penetrating properties of the three compounds concerned have been reported earlier (Meltzer and Dietvorst, 1957). The results may be briefly summarized here, because leaf penetration and duration of action, and leaf penetration and action on winter eggs seem to be correlated.

The treatment of the upperside of bean leaves of about 30 cm^2 with 0.1 ml of an emulsion of the compounds concerned will cause mortality of eggs and larvae on the underside of the leaves. In the experiments recorded in Table 4, the sulphide gave the best results.

On leaves treated after the mite eggs have been laid, only the sulphide is capable of killing a certain number of them. The eggs that aged three days, and which were just about to hatch at the time of application, were not killed. So this substance is not only able to penetrate into the leaf, but also into the eggs. On leaves treated before the eggs are laid on the opposite side, all compounds exerted ovicidal action, though again the sulphide appears to be superior in relation to leaf penetration properties.

Table 4. Leaf penetration of 2,4,5,4'-tetrachloro-diphenyl sulphone, -sulphoxide, and -sulphide. Only the upperside of the leaf is treated. Eggs of *Tetranychus telarius* at the underside only, 0 - 3 days old.
E = percentage egg mortality; T = percentage total mortality.

Compound	Dosage ug/leaf	Eggs laid before treatment		Eggs laid after treatment	
		E	T	E	T
	100	1	100	79	100
Sulphone	10	1	100	41	100
	1	2	30	22	53
	100	9	94	95	100
Sulphoxide	10	2	100	56	99
	1	3	23	9	57
	100	68	100	100	100
Sulphide	10	3	100	95	100
	1	1	82	26	98

Activity on Metatetranychus ulmi Koch

In earlier work the summer eggs of the fruit tree red spider mite was found more susceptible to the sulphone (tetradifon) than were the eggs of *Tetranychus telarius* (Meltzer, 1957c). It appeared, that the summer eggs of Metatetranychus are also more susceptible to the sulphide than the eggs of Tetranychus.

The differing leaf penetration properties of the three compounds led us to compare their effects on the wintereggs of Metatetranychus ulmi (Meltzer, in the press). The results demonstrate that the sulphide, which shows the best leaf penetration also possesses the highest activity on the wintereggs (Table 5).

Table 5. Activity of 2, 4, 5, 4'-tetrachloro-diphenyl sulphone, -sulphoxide, and -sulphide, as compared with fenson on winter eggs of Metatetranychus ulmi. Mean percentage reduction of hatch after dipping egg-bearing apple twigs in emulsions (three experiments).

Concentration in p.p.m.	Sulphone	Sulphoxide	Sulphide	Fenson
500	7	7	100	71
250	10	14	90	61
125	5	0	87	29

In later experiments with emulsifiable concentrates and wettable powders of the sulphide at lower concentrations, no difference in activity was found between the two types of formulation. (Table 6).

Table 6. Percentage reduction of hatch of winter eggs of Metatetranychus ulmi, after treatment with emulsifiable concentrate and wettable powder of the sulphide.

Concentrations act. mat. (p.p.m.)	Emulsifiable concentrate (6 expts.)	Wettable powder (3 expts.)
300	100	100
100	97	99
30	96	97

Field experiments with the sulphide

Field experiments on wintereggs of the fruit tree red spider were carried out at two application dates, viz. at the green tip stage, and at the time that hatching of wintereggs is beginning. The first date is the time for the application of the DNC/mineral oil winter wash; the latter the optimal time for application of fenson.

Table 7 summarizes some results obtained with preparations of the sulphide as compared with the standard DNC/mineral oil and fenson for the two dates of application.

Table 7. Mite counts of field experiments on winter eggs of Metatetranychus ulmi. Mean counts of samples of four replicates of 100 leaves each.
Time of application: Golden Delicious I March 23; II April 24.
Cox's Orange Pippin I March 20; II April 29.

Material and concentration	Time of spray	Mite Counts per 100 leaves Golden Delicious	Cox's Orange Pippin	
		May 19	May 14	May 25
Sulphide, 20% e.c., 0.2%	I	0.3	0.1	0.2
	II	0.0	0.1	0.05
Sulphide, 20% w.p., 0.2%	I	0.5	0.2	0.4
	II	0.05	0.2	0.3
DNC/mineral oil 6.0%	I	0.1	0.0	0.1
Fenson, 50% w.p., 0.1%	II	0.1	0.05	0.1
No treatment		4.7	0.9	4.2

Trials of concentrations below 0.2% are still going on. For the time being the concentration of 0.2% is recommended if hatching of the winter eggs occurs before or at the beginning of blooming; later 0.1% will suffice. The satisfactory results with 0.1% with later applications can be explained by the better action at increased temperature and the larger leaf surface present results in a greater amount of active material absorbed by the leaves, and as a consequence a high larvicidal effect.

Earlier it was found, that tetradifon effectively killed the first generation of the fruit tree red spider when applied after about 75% hatch of the winter eggs, and this is now readily understood, for this sulphone is not an effective ovicide but kills the larvae on the leaves. With the sulphide, however, the results are equal, whether there is a hatch of 20% or 60% or more at the time of application.

Many large scale field trials were carried out in Belgium and in the Netherlands during 1960 and 1961 on as many apple varieties as possible. The results of these trials confirmed those of the previous experiments, and, in most cases the mote control appeared to be so efficient that no further control measures were necessary during the whole season. In none of these trials have phytotoxic symptoms been observed.

The mammalian toxicity of the sulphide is low; the LD 50 for rats and mice, both oral and intraperitoneal exceeds 14700 mg/kg. Just as is the case with tetradifon, the sulphide appears to be a highly selective acaricide, safe for insect predators, bees, animals and human beings.

References

FLIK, H.M. (1957). Rept. XIVth Int. Horticult. Congr. Scheveningen 1955, 1, 837.

HUISMAN, H.O. UHLENBROEK, J.H. and MELTZER, J. (1958). Rec. trav. Chim. Pays-Bas, 77, 103.

MELTZER, J. (1955). Tijdschrift over Plantenz. 61, 130.

MELTZER, J. (1957a). Med. Landbouwhoegeschool. Opzoekingsstat. Gent 22, 457.

MELTZER, J. (1957b). Tijdschr. over Plantenz. 64, 104.

MELTZER, J. (1957c). Z. angew. Entomol. 41, 58.

MELTZER, J. (1958). Proc. 10th Int. Congr. Entomol. 1956, 3, 347.

MELTZER, J. (in the press) Nature Lond.

MELTZER, J. and DIETVORST, F.C. (1959). Proc. 4th Int. Congr. Crop Prot. Hamburg 1957, 1, 669.

INVESTIGATIONS OF A NEW SERIES OF NITROGENOUS ORGANOPHOSPHORUS COMPOUNDS. CHARACTERISTICS AND PROPERTIES.

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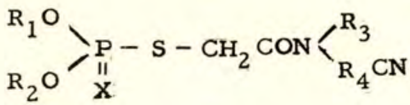
Summary

The series of nitrogenous organophosphorus compounds in question has the general formula:



where X stands for O or S, R_1 and R_2 stand for identical or different alkyl radicals, R_3 is H or an alkyl radical, and R_4 is an aliphatic hydrocarbon chain.

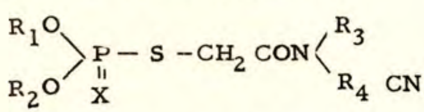
The insecticide and acaricide actions of these compounds were examined in correlation with their structure and properties.

From the laboratory and field tests described the compound $(C_2H_5O)_2$ PO. S. CH_2. CONH. $C(CH_3)_2CN$ was chosen for further tests.

1. Introduction

Research has proceeded for some time in our laboratories on organophosphorus compounds with insecticidal and acaricidal action (Fusco et al., 1959, 1960; Losco and Peri, 1959; Rossi, 1959) and has led to a new class of compounds (B. P. appl. 39743/60; IV. P. 625074; IV. P. appl. 17266/60). This class, and one of its members in particular, has been found to possess interesting properties in its action on crop pests.

These compounds have the general formula:



where: X is oxygen or sulphur; R_1 and R_2 are CH_3 and CH_3, or CH_3 and C_2H_5, or C_2H_5 and C_2H_5; R_3 is H or CH_3 or C_2H_5 and R_4 is CH_2 or $(CH_2)_2$ or $C(CH_3)_2$.

In the present paper we shall only consider those combinations of the above substituents on which screening values have been completely determined.

The compounds are of an oily nature, though in some cases, crystallisation occurs after prolonged storage.

These compounds conform to the rule (Rossi, 1959) that their solubility in water depends on the presence of the P=O linkage, for those with the P=S linkage are of low water solubility.

The insecticidal and acaricidal activity of the compounds of this class was determined by standard laboratory methods; in some cases field tests were also carried out.

In the laboratory, screening methods, which were standardised and therefore reproducable, were systematically applied to similarly formulated compounds; hence the results permitted the determination of the influence exerted by the various substituent groups on the insecticidal and acaricidal activity of the compounds.

In the field tests, commercial-type formulations of the chosen compounds were used and operations were carried out according to normal practice. Parameters and results of the experiments were recorded.

The toxicological findings of the screening, carried out on the usual laboratory animals, indicated fairly high acute toxicity values. These were, however, equal to or lower than those of many other substances already in commercial use. The values found for cumulative toxicity and for medium-term chronic toxicity of one of the field-tested compounds, viz. No. 21 (code number 1568), would indicate a rather rapid metabolism. The latter, it is presumed, does not permit accumulation in the organism and thus reduces the hazard. It is not yet possible to give more precise details, for the chronic toxicity tests are still in progress.

2. Evaluation by laboratory methods of insecticidal and acaricidal action.

A) Methods

The methods of screening used will now be described schematically. A sufficient number of repetitions was made for each test and the results obtained were then used for finding the LD50 and the LD 95 values.

I. Contact Aphicidal activity with Aphis fabae:

Small, 10cm-high broad bean plants (Fava di Siviglia variety), previously infested with parthenogenetic apterous A. fabae females, were dipped for 5" in aqueous dispersions of graded doses. The plants were then kept at a temperature at $26 \pm 1^{\circ}$ C and a relative humidity of $60 \pm 5\%$ and illuminated for 18 hours per day with fluorescent lamps (2,000 to 2,500 lux at leaf level). Insect mortality was recorded twenty-four hours after treatment.

II. Systemic aphicidal action through the roots on A. fabae:

The roots of the broad bean plants (variety and size as above) were dipped in an aqueous dispersion of the compound, and the leaves were infested with A. fabae females. The plants were then kept seven days under the environmental conditions of the contact test I and examined every day, the final mortality being recorded after seven days.

III. Contact acaricidal activity on Tetranychus telarius:

Bean plants (Borlotto lingua di fuoco "Flame-tongued" variety) with two cotyledonary leaves only were infested with T. telarius adults and treated with aqueous dispersions of the compounds under examination. Mortality was recorded after 24 hours, the plants meanwhile being held in the controlled environment of Test I.

IV. Activity on eggs of Tetranychus telarius:

Bean plants (variety and stage of development as under III.) on which female T. telarius eggs had been deposited during the previous 24 hours, were treated with aqueous dispersions of the compounds as in Test I and kept in the controlled environment for six days; the percentage of unhatched eggs was then determined.

V. Stomach poison action on Leptinotarsa decemlineata:

Larvae ten days old and weighing 70mg each were introduced, one per cell, into special cellular containers designed to avoid any possible contact action. Each larva had access to an area of 2cm of young potato leaves (Agnes variety), previously treated with 0.01 ml of aqueous dispersions of the compound under examination at graded concentrations. Tests were carried out in the controlled environment of Test I and mortality was recorded after twenty hours.

B) Results

Table 1 lists the compounds examined and Table 2 gives, for each compound in the same order as in Table 1, the LD50s found by the five methods described. The LD 95s were also determined, but are not given as they follow the same order as the LD50s.

It is evident from Table 2 that certain of the compounds show interesting properties both in intensity and in range of action. Compounds M1568, M1567 and M1506 were selected for field-testing.

It was also considered advisable to subject compounds M1553 and M1571 to field tests in case the field conditions, where factors differ from those in the laboratory, have an influence on the order of toxicity.

The acute LD50s of the field-tested compounds for white mice, both oral and by injection, are given in Table 3.

D) Field experiments

The field tests were carried out during the years 1960 and 1961. The pests examined were: Aphids: Hyalopterus pruni, Yezabura malifoliae, Aphis pomi; Acarids: Metatetranychus ulmi.

The compounds chosen were all used in an emulsifiable form containing 20% active ingredient in the case of Nos. 1506, 1553, 1568 and 1571, and 10% in the case of No. 1567.

In all the experiments OO-diethyl S-(N-isopropylcarbamoylmethyl) phosphorothiolothionate (FAC 20) was used as a reference, also in emulsifiable from containing 20% of active substance.

a) Tests on Hyalopterus pruni:

The specific purpose of the first test was to determine the action of the compounds on the aphid under field conditions, when the spray is applied mostly to the upper surface of the leaves of a heavily infested peach tree.

Spraying was carried out on 9th June, 1960, at Signa (Tuscany), using a hand-pump of 9 atmospheres pressure; the results of the test are given in Table 4.

In the second test, spraying was carried out on 23rd June, 1960, at San Benedetto Po (Lombardy) on a fine day, using a knapsack sprayer. Compounds M1568 and M1506 at a concentration of 600 p.p.m. and "F.A.C.20" at 300 p.p.m. of active substance, gave complete mortality of the aphids 24 hours after treatment, whereas the infestation of the control plant was unchanged.

In the third test, spraying was carried out on 26th June, 1960, at Cesena (Emilia), on a fine day with the temperature at 24 to 27° C, using a motor-pump at 30 atmospheres. Three peach-trees, distributed uniformly in two rows and all infested heavily were used. A complete control was obtained with M1568, M1506 and "F.A.C.20" at 250 p.p.m.

b) Test on Yezabura malifoliae

Treatment was carried out on 27th May, 1960, at Migliaro (Emilia), with a motor-pump at 20 atmospheres pressure, on apple-trees (Stark Delicious variety) ten years old and heavily infested. The results of the test are given in Table 5.

c) Tests on Aphis pomi:

The first group of tests consisted of four carried out in the months of June and July, 1960, in the following localities, all in Lombardy; Guidizzolo, Bondeno di Gonzaga, San Benedetto Po, and Pecorara di Pietra de' Giorgi.

The compounds were applied with a hand-sprayer and used at the following concentrations (p.p.m.):-

M1506:	600	-	500	-	300	-	250	-	-
M1553:	-	-	500	-	-	-	250	-	-
M1567:	-	-	-	-	-	-	250	-	125
M1568:	600	-	500	-	300	-	250	-	125
M1571:	-	-	500	-	-	-	250	-	-
"F.A.C.20"			:	-	300	-	250	-	-

The mortality of the aphids, determined 48 hours after treatment, was complete with all compounds.

Only one compound, M1568, was examined in the second group which consisted of five tests, carried out in Emilia and Lombardy in the months of May and June, 1961.

Complete mortality determined 48 hours after treatment was obtained with both No. 1568 and "F.A.C.20" at the 300 p.p.m. and the 200 p.p.m. levels. It appeared, as shown in Table 6 that No. 1568 was the faster acting of the two compounds.

d) Tests on Metatetranychus ulmi:

Many tests were carried out in 1960, in various regions of Italy and a few of the more important will be described here, including those carried out at San Bartolomeo in Bosco (Emilia) where, it was found that the mites were showing resistance to certain organophosphates. Motor-sprayers at pressures of 20 to 30 atmospheres were used for the application of the aqueous dispersions of test compounds. The results are given in Table 7 and 8.

The results of a third test, carried out on 1st July, 1960, at San Bartolomeo in Bosco (Emilia) are given in Table 9. Each plot consisted of three ten-year-old apple-trees (Stark Delicious variety). Infestation was extremely high. Before the tests, resistance to certain organophosphates had been noted.

Results of a fourth test, carried out on the 28th and 29th July, 1960, at San Bartolomeo in Bosco (Emilia) are given in Table 10.

A fifth test was carried out on 13th August, 1960, at Pegognaga (Lombardy) on rows of young apple-trees, Stark Delicious variety, of medium infestation. The determination of the infestation was made sixteen days after treatment by counting the live mites on forty leaves chosen from each tree of each treatment. The results are given in Table 11.

A sixth test was carried out on 5th July, 1961, at Guistella (Lombardy) each plot of two heavily infected apple trees. Both compounds M1567 and 1568, as well as the standard "F.A.C.20", at 300 p.p.m. eliminated the mites within two days.

It may be deduced from these results that, in general, all of the compounds under examination in the field are effective against Metatetranychus ulmi, though their efficiency was lower against organophosphate resistant mites except in the case of compound M1568.

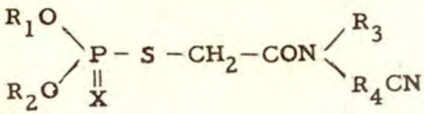
Discussion

Comparisons of the structures of the compounds (Table 1) with the results obtained in the laboratory (Table 2) reveals that the introduction of certain substituents is frequently accompanied by an improvement or alternatively a deterioration, in their toxicity. The substituents R_1 and R_2 = CH_3CH_3; R_3 = C_2H_5; R_4 = CH_2 are more frequent in the compounds whose LD50 is higher, whereas the substituents R_1 and R_2 = C_2H_5 and C_2H_5; R_3 = H; R_4 = $C(CH_3)_2$ are more frequent in those compounds whose LD50 is lower. Compare, for example, compound M1563, which has the highest LD50 (and thus the lowest level of action) in four of the five screenings, and, at the other end of the scale, M1568, whose LD50 is the lowest on A. fabae both by contact and systemically, and M1567 its sulphur analogue whose LD50 is the lowest on T. telarius, both adults and eggs.

The field tests carried out on the compounds under examination, although unfortunately cut down during 1961 for a number of reasons, have so far given good results against aphids and mites. In the case where the latter were resistant, a reduction in efficacy is apparent, but M1568, followed by M1567, proved on the whole to be the best of all the compounds examined, as in the screening tests.

In the field tests M1568 was also clearly superior to the reference substance "F.A.C. 20" whose practical value as an acaricide and aphicide is well known. In view of the results, M1568 is to be used on a wider scale during the coming season.

Table 1. Compounds tested
General formula of the class:



Compound	Substituent Groups				
Code	R_1	R_2	R_3	R_4	X
M1557	CH_3	CH_3	H	CH_2	S
M1668	CH_3	C_2H_5	H	CH_2	S
M1556	C_2H_5	C_2H_5	H	CH_2	S
M1507	CH_3	CH_3	CH_3	CH_2	S
M1506	C_2H_5	C_2H_5	CH_3	CH_2	S
M1563	CH_3	CH_3	C_2H_5	CH_2	S
M1669	CH_3	C_2H_5	C_2H_5	CH_2	S
M1553	C_2H_5	C_2H_5	C_2H_5	CH_2	S
M1565	CH_3	CH_3	CH_3	$(CH_2)_2$	S
M1670	CH_3	C_2H_5	CH_3	$(CH_2)_2$	S
M1560	C_2H_5	C_2H_5	CH_3	$(CH_2)_2$	S
M1571	CH_3	CH_3	H	$C(CH_3)_2$	S
M1671	CH_3	C_2H_5	H	$C(CH_3)_2$	S
M1567	C_2H_5	C_2H_5	H	$C(CH_3)_2$	S
M1626	CH_3	CH_3	CH_3	$C(CH_3)_2$	S
M1625	C_2H_5	C_2H_5	CH_3	$C(CH_3)_2$	S
M1555	C_2H_5	C_2H_5	H	CH_2	O
M1505	C_2H_5	C_2H_5	CH_3	CH_2	O
M1554	C_2H_5	C_2H_5	C_2H_5	CH_2	O
M1564	C_2H_5	C_2H_5	CH_3	$(CH_2)_2$	O
M1568	C_2H_5	C_2H_5	H	$C(CH_3)_2$	O
M1624	C_2H_5	C_2H_5	CH_3	$C(CH_3)_2$	O

Table 2. LD50 of the compounds in laboratory tests

Compound Code	On *A. fabae* contact p.p.m.	On *A. fabae* systemic p.p.m.	On *T. telarius* contact p.p.m.	On *T. telarius* (eggs) p.p.m.	On *L. decemlineata* ingestion γ/insect
M1557	1,70	0,200	3,00	>1000	60
M1668	1,70	0,100	2,00	800	80
M1556	1,80	0,310	4,00	1000	32
M1507	0,70	0,125	1,70	>1000	7
M1506	0,70	0,125	1,00	400	5
M1563	6,00	0,600	120,00	>1000	>80
M1669	3,20	0,500	2,00	>1000	60
M1553	1,25	0,320	1,40	200	27
M1565	2,00	0,150	3,50	>1000	>80
M1670	1,50	0,080	0,30	500	32
M1560	1,25	0,100	2,00	>1000	15
M1571	2,00	0,300	0,50	200	>80
M1671	0,70	0,120	0,40	46	40
M1567	0,80	0,160	0,20	44	60
M1626	1,40	0,160	1,25	>1000	46
M1625	1,30	0,130	1,20	60	17
M1555	1,20	0,100	3,00	>1000	>80
M1505	1,20	0,150	2,50	>1000	3
M1554	1,60	0,200	2,50	>1000	16
M1564	1,60	0,060	1,00	>1000	>80
M1568	0,50	0,050	0,40	64	8
M1624	1,25	0,100	4,00	>1000	15
Dimethoate	0,30	0,050	1,80	-	30
"F.A.C.20"	0,60	0,20	1,00	220	37
Parathion	1,30	-	3,00	-	1
Chlorfenson	-	-	-	300	-

Table 3. Acute LD50 on white rat of compounds used in field tests

Compound	Acute oral LD50 mg/kg	Acute intravenous LD50 mg/kg
M1568	21	13
M1567	25	17
M1506	4	5
M1553	11	12
M1571	31	28
Parathion	8,2	5,7

Table 4. Field test on Hyalopterus pruni

Compound	Quantity p.p.m. of a.s.	Diminution of infestation after:		
		6 hours	24 hours	48 hours
M1568	300	50% nearly	nearly total	total
M1506	300	50% nearly	nearly total	total
"F.A.C.20"	300	50% nearly	nearly total	total

Table 5. Field tests on Yezabura malifoliae

Compound	Quantity p.p.m. of a.s.	Observations 70 h. after treatment	
		No. of branches examined	No. of living aphids
M1568	600	16	0
M1506	600	45	0
M1553	500	50	0
M1567	250	50	0
M1571	500	41	0
"F.A.C.20"	300	46	0
Unsprayed	-	51	45 colonies

Table 6. Field tests on Aphis pomi

Compound	Quantity p.p.m. of a.s.	Diminution of infestation after:		
		6 hours	24 hours	48 hours
M1568	300	93%	100%	100%
"F.A.C.20"	300	78,3%	99,7%	100%

Table 7. First field test on *Metatetranychus ulmi*

Compound	Quantity p.p.m. of a.s.	Living adult females per/leaf after		
		2 days	10 days	16 days
M1506	300	0,01	0,3	0,8
M1553	300	0	0,2	0,1
M1568	300	0	0,07	0,02
"F.A.C.20"	300	0	0,16	0,3
Control	-	4,5	37	13,4

Sprayed 7th June 1960 each on three Stark Delicious apple trees at Cesena (Emilia). Adult females counted on 300 leaves per treatment.

Table 8. Second field test on *Metatetranychus ulmi*

Compound	Quantity p.p.m. of a.s.	Living adult females per/leaf after			
		2 days	9 days	15 days	23 days
M1506	300	0,30	0,16	5,6	2,6
M1553	300	0,07	0,02	3,0	0,7
M1567	150	0,13	0,19	3,3	1,5
M1568	300	0,02	0,01	0,3	0,03
M1571	300	0,15	0,17	2,5	0,6
"F.A.C.20"	300	0,18	0,21	2,3	1,1
Control	-	25	36	45	42

Sprayed 6th June 1960 on Stark Delicious apples at Cesena.

Table 9. Third field test on Metatetranychus ulmi

Compound	Quantity p.p.m. of a.s.	No. of living mites per/leaf after	
		6 days	18 days
M1506	500	27	13
	250	-	48
M1553	500	12,5	6
	250	60	30
M1567	250	13,5	11
	125	40	20
M1568	500	1,5	1,5
	250	9	9
M1571	500	27	43
	250	39	55
"F.A.C.20"	500	4,5	2
	250	4	8
Control		113	147

Table 10. Fourth field test on Metatetranychus ulmi

Compound	Quantity p.p.m. of a.s.	No. of living mites per/leaf after	
		8 days	21-22 days
M1506	600	9	3
M1553	500	4	0,5
M1567	250	2,5	1
	500	7	3
M1568	300	1,5	0,25
	500	0,3	0,15
M1571	500	7,5	7,5
"F.A.C.20"	300	11	8
	500	7,5	5

Table 11. Fifth test on Metatetranychus ulmi

Compound	Quantity p.p.m. of a.s.	No. of living mites per/leaf after 16 days
M1553	500	0,4
M1567	250	0,7
M1568	300	0,1
	500	0,02
"F.A.C.20"	300	0,7
	500	0,1
Unsprayed	-	19

References

FUSCO, R., LOSCO, G., PERI, C.A. (1959. Gazz. Chim. Ital. 89, 1282.
FUSCO, R., MARCHESE, G., PLACUCCI, G., LOSCO, G. (1960). Chimica e Industria, 42, 337.
LOSCO, G., PERI, C.A. (1959). Gazz. Chim. Ital. 89, 1298.
ROSSI, G. (1959). Gazz. Chim. Ital. 89, 1324.

INVESTIGATION INTO THE BIOLOGICAL ACTIVITY OF A SERIES OF BUTYLENE POLYMERS

by Ian Greenfield
F. W. Berk & Co. Ltd.

Introduction

The use of synthetic pesticides in the field creates many problems, not the least of which are toxicity to the operator, toxic residues on edible crops, development of resistant strains of pests, and the destruction of natural predators.

In view of these factors, the use of "Indopol"* polybutenes as experimental acaricides and fungicides in trials made by R. W. Fisher, of the Canada Department of Agriculture, Research Branch, Vineland Station, Ontario, Canada, were of interest for the activity of these polybutenes is based on physical rather than chemical properties.

Briefly, the "Indopol" polybutenes consist of a mixture of butylene polymers - about 85 - 95% being mono-olefines, the rest iso-paraffins. They are non-volatile, strongly viscous even at quite high temperatures, and non-drying: though insoluble in water and oxygenated solvents such as ethanol, they are miscible in common hydrocarbon and related chlorinated hydrocarbon solvents.

Product Grade	L-10	L-100	H-35	H-100	H-300	H-1500
Mean mol. wt.	300	520	730	830	1100	1800
Viscosity at 100° F, SSU	114	1040	7900	44000	140000	-
Viscosity at 210° F, SSU	40.6	93.8	375	1070	3000	15000
Specific Gravity, 60/60° F.	0.831	0.854	0.871	0.881	0.894	0.910
Flash Point, COC, ° F.	270	275	295	360	480	460

Their important physical property lies in their high viscosity at normal temperatures. The raw polybutene is almost impossible to use but effective water miscible emulsions can be made which may be sprayed or painted on to a plant surface to act as a relatively permanent non-drying tacky layer.

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* Manufactured in America by the Amoco Chemicals Corporation, 910 South Michigan Avenue, Chicago 80, Illinois.

Work first published by Fisher (1959a) indicated that certain polybutenes, formulated as emulsions and used at a concentration of 5% active ingredient, effectively suppressed cucumber mildew (Erysiphe cichoracearum) for over three weeks while the untreated control became heavily infected. There was no evidence of phytotoxicity to the crop. Further experiments (Fisher, 1959b) on the control of mites (Tetranychus telarius) showed that the very viscous polybutene H-1500, applied as a 5% emulsion, killed adult mites, larvae and eggs on melons, lima beans, roses, honeysuckel, peach seedlings and other greenhouse crops. Protection from further infestation was obtained for eleven days.

Similarly, the Insecticide Newsletter, January 1960, p.16, summarizing the work at Vineland, claimed effective control of powdery mildew on cucumber, roses and grapes, and control of two-spotted mite, brown mite and European red mite on apples and peaches, and lecanium scales on plums with "Indopol" polybutenes.

At about this time the speaker visited the U.S.A. and observed experiments on powdery mildew of roses (Sphaerotheca pannosa) in progress at Cornell University under the direction of Dr. John Naegele. The results were most impressive and, with the Vineland work, suggested that an evaluation of the polybutenes in Europe might be worthwhile. Accordingly, after discussions with the Amoco Chemicals Corporation and subsequent correspondence with Dr. Fisher, a limited trial programme was begun in 1960 and continued throughout 1961 to test the efficacy of various grades of "Indopol" polybutenes under U.K. conditions.

Extension experiments 1960

By 1960, Fisher's work had indicated that the polybutene grades L-10, H-50 and H-1500 were promising. Later that year further tests showed grades L-100, H-35, H-100 and H-300 to be still more effective - even at concentrations as low as 1%, although strengths of 2 - 3% were necessary where an infection or infestation had become severe.

Since time was short we decided to use grade H-1500, initially formulated as a 50% emulsifiable concentrate but later the concentration was increased to 75%, on apples, hops, potatoes and sugar beet. In all cases applications were made at concentrations equivalent to 5 or 3% active ingredient. During the latter part of the summer L-100 was also tested on hops at a 3% concentration.

Summary of trial results 1960

Apples

H-1500 used at a concentration of 5% gave effective control of Metatetranychus ulmi and several different aphid species on Worcester and Cox.

Sugar beet

At the same concentration an effective control of Myzus persicae was obtained, thus reducing virus yellows to an extent comparable with demeton-methyl and dimethoate treatments. The control was superior to that obtained with phosphamidon.

Potatoes and Hops

At both 5 and 3% concentration of active ingredient effective control of aphid (Phorodon humuli) on hops was obtained, the foliage comparing favourably with that in the demeton-methyl treatments. The fungicides applied concurrently appeared to stick better on both potatoes and hops in comparison with the control plots to which no polybutene had been applied. As Fisher's latest work also showed that L-10, L-100 and H-50 were useful materials, a 75% emulsifiable concentrate formulation of L-100 was included which, used at a concentration of 3% a.i., showed promise as an aphicide.

Extension experiments 1961

During 1960 work in Canada progressed and more information was obtained about the use of these materials. These results, taken in conjunction with those obtained in this country, led to the initiation of a comprehensive experimental programme for 1961 both in this country and in Europe. Arrangements were also made to obtain toxicological data and to note the effect of these materials on predators.

It was decided to apply for approval through the Agricultural Chemicals Approval Organisation and, as a result independent trials on a wide variety of crops were carried out by the National Agricultural Advisory Service within the terms of the new scheme. In addition, independent trials were arranged at the Glasshouse Crops Research Institute and East Malling, and with collaborators in France and Holland. Most of our own trials in this country were confined to apples. Simultaneously, toxicological evaluation of the four grades under test was initiated at the Nutritional Research Unit at Huntingdon.

Summary of trial results 1961

U.K.

Apples

Berk trials with polybutenes L-100, H-35, H-100 and H-300

Site 1: Essex

Situation

Site aspect: Hilltop farm - gentle slope, frost free.
Soil: Boulder clay predominantly, with some gravel.
Soil cover: Arable.
Drainage: Generally satisfactory but poorer where L-100 and H-35 applied, though not affecting growth.
Variety: Cox/Scarlet Pimpernel; bush trees, age 4-5 years.
Tree health: Excellent - no scab; a little mildew on Cox; no phyto-

toxicity; very good extension growth particularly on Scarlet Pimpernel.

Pest status: Red spider mite - major pest; other pests present at a low level typical for "new" orchards.

Predators: Few present at the time of first spray; increased in numbers later on in the season.

Observations

1. Weather at time of spraying: Fine and clear on each occasion with still conditions so no drifting occurred. Weather remained fine for several days after spraying.

2. Red spider mite: Seasonal development. At the beginning of the season there was quite a high level of infestation. The winter egg hatch was early but comparable with adjacent orchards. First application was thus slightly earlier than usual, but the second one made at the time generally advised (mid-June). There was thus a longer time for build-up to occur. Full results of the spraying programme are given later. However, the effect of the polybutene formulations on the mites was briefly:
Adults - immobilized by the spray deposit and killed.
Eggs (summer) - those hatching within 7 - 14 days of spray deposition were "immobilized" while some inhibition of hatching also seemed to occur.

3. Predators: Polybutenes appeared to exercise no adverse effect on anthocorids and Ladybird beetles seen throughout the trial, while Black-kneed Capsid was observed by June 14th. All became more numerous.

4. Fruit and Foliage: No phytotoxic symptoms occurred on either variety.

5. Mixing in: This was very good for all four grades with H-100 and H-300 being rather less easy than the other two. A 50:50 initial mix for the H-100 and H-300 enables an excellent dispersion to take place.

6. Compatibility: All four grades produced an excellent dispersion when mixed with the standard pesticides and fungicides.

7. Disease incidence: No difference apparent between trees receiving polybutene formulations and those not sprayed with an acaricide or where demeton-methyl was applied.

Results

%		L-100 1	L-100 2	H-35 1	H-35 2	H-100 1	H-100 2	H-300 1	H-300 2	Demeton methyl 12 fl.oz/ac.	Untreated -
May 14th	M:	607	543	814	666	623	649	702	531	609	668
(pre-spray)	E:	52	49	98	83	41	41	104	67	59	44
May 20th	M:	130	66	200	151	52	48	60	35	21	751
	E:	41	20	77	102	62	50	57	45	37	205
May 28th	M:	121	41	72	31	20	11	29	5	32	1004
	E:	32	41	101	27	56	89	30	14	27	196
June 13th	M:	204	109	121	49	48	31	59	19	41	1302
(pre-2nd spray)	E:	63	42	77	33	12	31	11	16	22	205
June 25th	M:	40	31	35	20	16	19	12	12	3	2109*
	E:	45	37	25	21	6	6	3	5	21	285*
July 1st/2nd	M:	62	41	71	27	30	21	22	17	10	605
	E:	59	60	30	41	22	15	11	14	16	93
July 8th/9th	M:	103	62	114	52	32	19	18	23	25	542
	E:	69	71	39	44	33	27	31	17	21	107
July 15th	M:	171	98	119	79	42	32	34	22	29	311
	E:	83	66	47	36	53	41	27	29	39	88
July 23rd	M:	180	102	63	102	52	44	51	34	35	109
	E:	63	49	37	45	76	55	33	41	37	75
Aug. 9th	M:	253	200	84	98	80	39	69	59	71	291
	E:	71	53	52	74	41	52	45	33	49	112

%		H-100 2	H-100 2	H-300 2	H-300 2	H-100 1	H-100 2	H-300 1	H-300 2	Demeton methyl 12 fl.oz/ac.	Demeton methyl 12 fl.oz/ac
Aug. 20th	M:	41	62	15	22	4	15	9	22	12	42
Sept. 3rd	M:	55	42	12	3	13	7	11	10	6	5

Spray applications: May 17th when winter egg hatch approximately 90%. Second on June 14th: Applied by Drake & Fletcher knapsack.

Mite counts expressed per 50 leaves.

*June 25th: Predators active. Together with mite dispersal results were somewhat masked subsequently. By August 20th impossible to make summer egg counts. Winter egg laying had also begun.

Site 2: Essex

Situation

Site aspect: Valley site - free air movement, with little or no frost risk.

Soil: Brick earth with some gravel.

Soil cover: Arable.

Drainage: Good.

Variety: Cox/Worcester Pearmain; bush trees, 4 - 5 years.

Tree health: Generally excellent; but early in the season most trees were suffering from some growth depression owing to continued wet during the winter of 1960/61. Extension growth excellent for season. Mildew initially widespread on Cox. Scab-risk in area normally low but during 1961 some increase occurred.

Pest status: Red spider mite - major pest; other pests generally present at a low level.

Predators: Few present at time of the first spraying. Increase in numbers later on in the season.

Observations

1. Weather at time of spraying: On both occasions fine and clear with no wind. Weather remained fine for several days after spraying.

2. Red spider mite: Seasonal development: At the beginning of the season there was quite a high level of infestation, with a winter egg hatch of 85 - 90%. The first spray was applied sooner than usual because of an early hatch. The polybutene exerted the same type of control as at Site no. 1.

3. Predators: As at Site no. 1. these appeared to be unaffected by the polybutenes. From mid-June predators became much more active, especially on the untreated control trees.

4. Fruit and Foliage: No phytotoxic symptoms observed on either variety.

5. Disease incidence:

<u>Mildew</u>: It is possible that H-100 and H-300 caused a slight depression in the level of infection but a true assessment will have to wait until "green cluster" stage 1962.

<u>Scab</u>: Trees receiving polybutenes responded normally to the routine scab programme. Phytotoxicity was not observed on either variety.

Results

%		L-100 1	L-100 2	H-35 1	H-35 2	H-100 1	H-100 2	H-300 1	H-300 2	Demeton methyl 12 fl.oz/ac.	Untreated
May 7th	M:	841	703	887	490	547	907	829	755	1233	809
(pre-spray)	E:	15	22	24	11	20	24	27	30	43	14
May 21st	M:	156	83	98	63	31	44	56	29	21	906
(1)	E:	69	104	37	32	49	75	3	5	11	276
June 4th	M:	241	131	133	103	82	70	69	37	39	1096
(1)	E:	77	109	72	46	61	49	22	15	48	342
June 18th	M:	65	49	57	93	25	30	21	13	29	1401*
(2)	E:	40	21	41	5	21	17	41	12	32	141
June 19th	M:	204	102	94	104	59	77	86	63	77	1627*
(1)	E:	56	93	89	21	16	24	42	3	7	256*
June 25th	M:	204	251	150	111	102	61	215	49	114	825**
(1)	E:	78	25	61	49	35	32	41	51	38	103
June 25th	M:	131	98	147	171	47	51	27	21	30	1602
(2)	E:	53	49	104	61	35	13	48	30	30	368
July 9th	M:	198	88	194	132	101	69	68	39	32	1542
(2)	E:	175	92	201	75	25	41	17	20	31	409
July 23rd	M:	190	80	59	35	215	88	163	121	125	633
(1)	E:	82	102	162	98	72	93	62	101	107	33
July 23rd	M:	172	112	182	100	88	75	52	10	26	1011
(2)	E:	211	153	73	88	42	21	41	21	15	207**

M = mites; E = eggs.

Spray applications: May 11th when winter egg hatch 85-90% (1).
7th June (2).
(1) = one spray; (2) = two sprays.
Counts expressed per 50 leaves.
All sprays applied through knapsack - good cover obtained.
* Predators active.
** Thereafter predation and mite dispersal factors operated more noticeably, and masked results.

Site 3: Cambridgeshire

Control of red spider mite on Cox in the Wisbech area was similar to that obtained at Sites 1. and 2.

Other sites

Trials in Kent on three commercial orchards gave rather disappointing results. In part these could be attributed to the grade of polybutene used and the low rate of application, and also to formulation breakdown and inadequate spray technique. At one site another factor may have been the prolonged egg hatch.

Seasonal development:

As the preliminary results at Sites 1 - 3 seemed encouraging a further series of trials were made to establish whether it was the concentration of polybutene in the spray or a definite quantity of polybutene applied per unit area that mattered. Although more work is needed the results so far indicate that the latter is the more important. However, a good cover must be obtained, and with the minimum of run-off.

Other trials also confirmed that L-100 and H-35 were less effective than H-100 and H-300 in controlling red spider mite, even when used at three times the quantity of the latter materials.

N.A.A.S. trials with H-100, formulated as a 75% emulsifiable concentrate.

East Anglia - winter egg trial:

Spray made on February 20th on twigs heavily infested with winter eggs.

At 1.5% H-100 there was a slight effect on hatching but not really ovicidal.

Kent - on Cox:

Egg and spider counts both higher, especially eggs, than control.

Northern Ireland - 0.75% H-100 on Worcester Pearmain applied in May. By mid-June the control was bronzed but treatments satisfactory - healthy foliage and no evidence of mite attack. By mid-July, re-infestation showing but mites still only about one-seventh of the control population, on a per leaf basis. By late July, a second spray was made. The effect of this on winter egg deposition will be assessed later.

West Midlands - on Lane's Prince Albert:

Red spider mite well controlled by a high volume spray of 0.75% H-100. Control comparable with demeton-methyl.

Cucumber - Red spider (*Tetranychus telarius*)

Glasshouse Crops Research Institute, Littlehampton.

Polybutenes L-100, H-35, H-100 and H-300 were used at either 0.75 or 1.5% on plants artificially infested with red spider, and compared with two controls - an untreated one and 1% petroleum emulsion.

Three applications were made and, although it was not possible to assess yields owing to a severe attack of mildew on all but the petroleum-treated plants, the trial showed that all four grades of polybutenes at both concentrations were as effective as 1% petroleum emulsion (0.65% petroleum). Slight scorch was caused by 1.5% H-300.

A further trial with L-100 is still in progress. At 0.75% it is giving a satisfactory control of spider but either alone, or with dinocap for mildew, L-100 is more phytotoxic than certain other compounds except for petroleum. Final results are still to come.

N.A.A.S., Eastern Region - trials with H-100.

Phytotoxicity: Young plants (6-7 leaves) were sprayed to run-off on both surfaces. No damage was observed and the leaves were still tacky two weeks after spraying. At 1.5% and 3.75% the H-100 was also satisfactory.

Mite control: 1.5% H-100 sprayed to run-off. Compared with a control of 1% white oil. The plants were full grown and cropping had begun.

Assessments were made 5 days after spraying using the leaf disc technique when the numbers of eggs, live and dead mites were counted. Egg viability was also recorded.

Although a rather small mite population (350-400 per 20 discs), the results for the white oil spray were similar to those obtained on many other occasions, and in this one small trial there was no evidence that polybutene was in any way better.

In a similar unreplicated trial on another nursery, plants showed severe leaf scorch a few days after spraying; subsequently most of the leaves died and the plants were severely affected. The plants had been sprayed with white oil about 10 days earlier and this also was used on the other plants in the house soon after the trial. Possibly traces of oil on the leaves or drift from the latter spraying proved incompatible with the polybutenes. The plants later recovered and continued to grow normally, but the damage rather took the grower by surprise.

Further observations on leaves and glass plates sprayed with 1.5% polybutene showed that any mites present on leaves at the time of spraying seemed to be killed, but if much webbing is present the mites underneath appeared to be unaffected. Mites moving on to sprayed surfaces do not seem to be affected until they come into direct contact with droplets on the webbing or leaves. On plates, the same thing was noticed, mites being able to move normally on the plates sprayed evenly with 1.5% H-100 but not at 3.75%.

In a third replicated trial, using single plant plots, mite mortality was again about 50% of the total population.

However, these results show only the short term effect of single sprays, and a full programme using these materials might give much better results.

N.A.A.S. Northern Region - trials with H-100

In an observation trial, using H-100 at 0.75 and 1.5%, no phytotoxicity was observed. The 0.75% treatment proved largely ineffective but the higher rate was more successful, comparing favourably with that obtained by azobenzene-parathion smokes in another house of the same nursery.

Sugar beet - Aphis (Myzus persicae and Aphis fabae)

As 2.5% H-1500 had proved comparable with dimethoate and phosphamidon, and only slightly inferior to demeton-methyl, in a 1960 Rothamsted trial, arrangements were made to include H-35 in the 1961 series.

The results were extremely disappointing as, although applied at 3.75%, H-35 proved totally ineffective, which was in marked contrast to demeton-methyl. It would appear that only the more viscous polybutenes might be effective.

Other crops

Blackcurrant - Gall mite (Eriophyes ribis)

Trials were made at several N.A.A.S. centres. Detailed results are not yet available as it is too early in the season for these, but the results so far are fairly encouraging.

N.A.A.S. Eastern Region - trials with H-35.

3.75% H-35 proved non-phytotoxic. Large number of dead mites were present on buds and shoots but final assessments will have to wait until the buds have swollen.

A preliminary bud dissection to assess mite invasion did not give very encouraging results as mites had invaded new buds, although as the level of infestation was extremely high no material could be expected to hold this population during migration.

West Midlands

Preliminary results, where H-35 was used at 0.75% against T. telarius, were less hopeful.

Results from several other centres have not yet been received.

Swede - Swede midge (Contarinia nasturtii)

0.75% H-100 failed to control this pest, the eggs of which are laid in the heart of the plant.

France

Apple

Station de Zoologie Agricole, Antibes.

Preliminary tests show L-100, H-35, H-100 and H-300 to be very satisfactory in controlling red spider. The Braconid, Opius concolor, and several other predators were unaffected. It is not yet possible to distinguish between the four grades.

M. Lambert, Antibes

All four grades were used, and applied three times at 10-day intervals, to the variety Canadian Pippin.

Spider mite was not present but powdery mildew (P. leucotricha) was checked on badly affected shoots. The foliage was otherwise in a very good condition and retained its glossy aspect.

Vine

Station Viticole, Cognac

Against downy mildew (P. viticola) all four grades at 0.75 and 1.5% obtained a control better than 0.5% Bordeaux and comparable with 2% Bordeaux and organo-copper preparations commercially available. Both in efficiency of disease control and persistency the polybutenes were superior to zineb and its analogues, and to maneb. None of the polybutenes proved to be phytotoxic to the foliage or crop. More definite results ought to be available after mid-October.

Other crops

M. Lambert, Antibes.

Carnations/Pinks

Work carried out at Antibes showed that all four polybutenes, used at 0.75 or 1.5%, were phytotoxic; both blooms and foliage were damaged.

Rose

All growth safe when polybutenes applied up to six times normal dosage (0.75%). Excellent control of powdery mildew (Sphaerotheca pannosa) and downy mildew (P. sparsa), and of the mite (T. urticae) and aphid (Macrosiphum rosae) but this incidence was low.

Compatibility

Polybutenes H-100 and H-300 were tested for compatibility with pesticides commonly in use on apples. The tests were made at both high and low volume rates of application with the following results. With high volume applications, both polybutenes were used at 1.5% and the test materials were used at the makers' recommendations.

Miscible liquid/emulsifiable concentrate formulations based on DDT (20, 25%), gamma BHC (20%), malathion (60%), demeton-methyl, and dimethoate were compatible.

Wettable powders containing captan, dinocap, phenyl mercury dimethyl dithiocarbamate (3%), sulphur (75%) or thiram (80%) were compatible. A DDT (50%) formulation was also satisfactory. Dodine acetate (65%) was found to be incompatible. Urea and lead arsenate were found to be compatible.

For low volume applications, H-100 and H-300 were used at 5% concentration in 20 gallons of water.

Miscible liquid/emulsifiable concentrate formulations of DDT 20%, demeton-methyl and malathion (60%) were incompatible. Dimethoate was satisfactory if used immediately, but on standing was incompatible.

Wettable powder formulations of DDT 50%, captan, phenyl mercury dimethyl dithiocarbamate were compatible - indeed, the suspensibility was better where polybutenes were used. Some separation occurred on standing with lime sulphur but the liquids were completely miscible on agitation. A slight build-up of a sticky material occurred on nozzles of the spray equipment, which was presumed to be polybutene.

Mixtures of H-100 and H-300 at both high and low volume concentrations were compatible with colloidal sulphur.

Toxicology

Polybutenes L-100, H-35. H-100 and H-300 both in the raw state and formulated as 75% emulsifiable concentrates were tested for oral and dermal toxicity on rats. These tests showed quite clearly that all were non-toxic even at doses as high as 80 ml. polybutene per kg.

Discussion

The results of our investigations to date enable the following conclusions to be drawn.

1. Toxicity

Polybutenes can be regarded as non-toxic to mammals. With the posible exception of cucumbers and carnations, the polybutenes are unlikely to be phytotoxic. Where damage occurs it seems that the formulation rather than the polybutene is responsible, a point which is being further investigated.

2. Biological activity

In general, grades of higher viscosity are more effective and persistent acaricides than less viscous ones. A better control seems to be obtained when the polybutenes are applied at high volume rather than low, but it is probable that effective coverage can be obtained in volumes around 20 and even as low as 2 or 3 gallons per acre. However, as the mode of action of these materials seems to be purely physical, direct application of the polybutene formulation to eggs, larvae, and adults is necessary.

Where a high population exists more polybutene is probably required initially but a lower rate appears to be effective when the population is smaller. Timing of application is critical and for the greatest effect sprays should be applied at the 80-90% hatch stage.

The question of resistant strains of mites does not arise, whilst there appears to be no adverse effect on desirable insects, enabling a build-up of an effective predator population.

Although a good control of vine downy mildew, powdery mildew of roses and apple mildew was obtained at some sites, in other fungicide trials the polybutenes were ineffective and, so far, results are not comparable with those in North America. These variations seem to indicate that further work is necessary to establish the most effective grades and to determine suitable application techniques.

Practical applications

Four major disadvantages of acaricides currently in use have been mentioned. Formulations based on polybutene are free of these drawbacks for they are non-toxic to operators, leave no toxic residues and have no adverse effect on predators; nor do they encourage the formation of resistant strains of pests.

When applied thoroughly, the control of fruit tree red spider mite is comparable with that obtained by the use of systemic acaricides based on chemical action. The emphasis must be on effective spray technique if adequate mite control is to be obtained.

Formulated as emulsifiable concentrates, these materials are compatible with a wide range of commonly used pesticides and work is in hand to stabilize mixtures of organo-phosphorus and polybutene formulations. There may well be a case for spray programmes where polybutene and conventional acaricides are used alternately, or where mixtures of polybutenes and established acaricides may be more effective than when either are used separately. However, with regard to the latter, some of the advantages of polybutenes when used alone will be lost.

The problems before the chemical industry and the grower, today, require rapid resolution. The intelligent use of control measures based on physically active compounds can do much to help, as, comparable in cost, they offer all the advantages of a new approach based on an old principle.

References

FISHER, R.W. (1959a). Plant Disease Reporter. 43, (8), 878.
FISHER, R.W. (1959b). J. Econ. Ent. 52, 1015.

SPECIAL FORMULATIONS FOR LOW VOLUME SPRAYING

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1. PHYSICAL PROBLEMS OF LOW VOLUME SPRAYING

In modern spray operations it is desirable to work at as low volume as possible for economic reasons. When using aircraft this is particularly important since flying time is so costly. High volume was used in the past since spraying to "run off" gave a very even coverage although much of the chemical was wasted. Spraying to run off has the advantage that only the concentration of toxicant need be fixed, but when using more costly chemicals and machines more efficient use of the chemical must be made. However, with the use of low or ultra low (1 to 2 gal/acre) volumes come new problems, some of which are inherent and some of which can be solved by the special design of formulations with which this paper is concerned.

Very low volume spraying cannot leave as even a deposit as spraying to run off. Instead of a general wash the deposit is as discrete droplets and this makes it more vulnerable to displacement by rain or by mechanical means. The use of stickers is therefore more important.

In high volume work a mean droplet size may be of the order of 300-500μ. Assuming a mean droplet size of 300μ, if we spray at 100 gallons per acre, we will achieve about 800 drops per sq. cm. on a plane surface or, since the crop may be 5-15 acres of leaf per field acre, about 50-150 drops per sq. cm. of leaf. However, at 1 gallon per acre we would get only 0.5 - 1.5 drops per sq. cm. and therefore a much greater variation of deposit on individual leaves would result. Thus the droplet size must be reduced. If a mean droplet size of 100μ is used we will get 15-40 drops per sq. cm. of leaf. The deposit, although more uniform, will still be discrete since these small droplets will not coalesce. Droplet size reduction, however, brings with it another problem, namely that of the evaporation of the spray before it reaches the crop. The life of a drop in given air conditions is proportional to the square of its diameter, and it is in the size range of interest that the life becomes critically short.

2. REDUCTION OF EVAPORATION

The obvious method of reducing evaporation is to replace water as the carrier by an involatile oil, but a gallon of oil must always be more expensive than a gallon of water and since the object of this exercise was to cut costs, we may lose more than we gain. The risk of damage is also increased since all the cheaper oils are considerably phytotoxic. If, while using water as our carrier, we may, by the addition of a comparatively cheap ingredient, reduce evaporation, and if this same ingredient can stick our toxicant to the leaf to prevent wash off by rain or accidental brush off, we have solved these two major problems at once.

These problems, particularly that arising from evaporation, are particularly important with solid substances which are presented as wettable powders. With an involatile active ingredient, if present in a concentration as high as 12% v/v in the spray, even the complete evaporation of the water will result in the diameter of the drop being only halved. If the active ingredient were a solid these residual particles would be dry and therefore will neither adhere to the leaf nor spread on contact. The advantage of reducing evaporation is therefore far more important in the formulation of solids than of liquids.

That the problem of evaporation is a real one even on a cool day in this country, is not always appreciated. It may be shown that the rate of evaporation is proportional to the difference in wet and dry bulb temperatures and radiation has little effect. Even in relatively cool humid conditions with the wet bulb perhaps 1.5° C below the dry bulb a 50μ drop would only fall 2 metres before its radius is reduced to half and the particle becomes dry. In arid conditions, with the wet bulb perhaps 15° C lower than the dry, the distance of fall of a 100μ drop would be little more than 1 metre although under the same conditions a 250μ drop would fall nearly 40 metres.

However, if we interpose at the surface of the drop a monolayer of a fatty substance the droplet life may be increased considerably. The best substances for this use are undoubtedly long chain fatty alcohols (Eisner et al., 1960) but we find that their very low solubility makes them difficult to formulate satisfactorily in the presence of absorbent solids. We have, however, successfully shown that a fatty acid may be used to form the monolayer and that it gives adequate protection.

To illustrate both the importance of evaporation and successful control of it we carried out a field experiment in which a copper oxychloride formulation containing the fatty acid preparation was sprayed along side an orthodox wettable powder by a drift spraying technique.

The spray was produced in an airblast machine directed upwards and allowed to drift with the wind. Samples were collected at 10 yard intervals in a grid pattern on young pea plants and microscope slides inclined at 45° to the horizontal. The results of our experiments in which the air temperature was 78° F and 55% R.H. (Δt 6.5° C) have been shown as contour maps (Figure 1), the results being expressed as γ per sample point (i.e. per 3" x 1" slide or pea plant). Thus it may be seen that a usable plume (greater than 5 γ per sample) of about 100 yards can be expected from the fatty acid formulation and only 35-40 yards in the case of the orthodox wettable powder. That this is mainly due to evaporation was shown by the fact that particles were received on black glass plates held by an operator at up to 150 yards in both cases, but in the case of the orthodox material they rolled off as coarse dust and in the case of the fatty acid preparation no such dust was observed. The average size of the spray droplets was about 60μ for the fatty acid preparation and 80μ for the orthodox material. Over seven times the total amount of copper was recovered compared with the orthodox formulation.

The additive which we worked with was simply a fatty acid, stearic acid, dissolved in an excess of a volatile amine. When dissolved in water a solution of the amine stearate results which has excellent wetting and suspending properties for our active ingredient. On spraying, the amine stearate migrates to the surface of the drop by normal surface activity effect and the amine, being volatile, evaporates leaving a monolayer of stearic acid which reduces evaporation of the water. In selecting our formulant we have used a tower, twenty feet high and maintained at 10 - 30% R.H at 40° C. These conditions may be considered stringent but we feel that they are not totally unrealistic. The top and bottom of the tower are closed by small air locks to prevent "chimneying" of the air in the tower. In the bottom air lock provision is made to hold glass slides, leaves or small potted plants. At the top is a droplet producing device, either a constant droplet device producing discrete single drops, or a spray nozzle similar to that used in the field. Using the constant droplet device we have shown that no evaporation of spray containing the amine stearate preparation can be detected on droplets down to 80μ although 150μ droplets of a conventional spray are almost dry on reaching the bottom. A more graphic picture results when using the spray jet. A normal wettable powder sprayed at ultra low volume gives a rather broad spectrum with a peak at about 70μ. After passage down the tower at 40° C and 20% R.H. the peak is now at about 30μ. However all material below 120μ is a non-adherent dust which is readily blown off the glass surface. When the same active ingredient is formulated with the amine stearate preparation and sprayed through the same nozzle, the droplet spectrum is narrower, due to the low surface tension, with a peak at about 40μ and after passage down the tower is virtually unaltered although some evaporation below 30μ may have taken place. All droplets received at the bottom of the tower are moist and stick to glass.

This behaviour is illustrated in Figure 2.

3. IMPROVEMENT OF RESISTANCE TO WEATHERING

When the droplet reaches its target, its high surface activity prevents reflection and assists spread on the leaf. The rest of the amine now evaporates and free stearic acid is left. This always crystallises quickly and its crystal structure is similar to that of the natural leaf waxes, so that molecular bridging occurs. The bulk of the stearic acid forms a matrix of interlocked micro crystals which enmesh the active ingredient. A firm, water proof adhesion of the latter to the leaf results. Adhesion is notably better to the leaf surface than to glass.

In the case of insoluble stomach-acting insecticides, used against phytophagous insects, resistance to weathering is unambigously desirable. There is doubt whether it is so desirable in the case of protectant fungicides, where some redistribution in rain and dew may be necessary. It has been shown that additional non-ionic wetters may be used controllably to reduce the resistance to rain although there is then a slight loss of anti-evaporation properties.

We carried out a comprehensive test of resistance to rain, using two active ingredients and the leaves of twelve species of plants. Three leaves of each species were sprayed from a spinning disc with each formulation.

One leaf was kept for reference and the other two were subjected to artificial rain at the rate of $2\frac{3}{4}$" in $2\frac{1}{4}$ minutes, falling from 10 ft. with an average droplet size of 4-5 mm. diameter. The proportions of initial deposit retained after artificial rain 1 hr. after spraying are summarised in the Tables below.

Table 1. Active ingredient - N-methyl α naphthyl carbamate

Leaf surface	% Retained (Orthodox W.P.)	% Retained (Amine stearate prep.)
Banana	0	80
Field bean	2	50
French bean	0	80
Cabbage	0	75
Cocoa	0	95
Cotton	0	25
Maize	2	95
Pea	0	90
Rubber	0	95
Sugarbeet	0	95
Tomato	0	100
Vine	0	90
Mean	0.3	81

Table 2. Active ingredient - Copper oxychloride

Leaf surface	% Retained (Orthodox W.P.)	% Retained (Amine stearate prep.)
Banana	0	98*
Field bean	5	50
French bean	5	80
Cabbage	0	10
Cocoa	0	20
Cotton	0	80
Maize	1	100
Pea	0	100
Rubber	0	50
Sugarbeet	10	50
Tomato	0	75
Vine	1	50
Mean	1.8	64

* Microscopic examination showed some erosion allowed for.

Estimates of the proportion of deposit retained after the application of artificial rain were made visually. We find that the discrete deposits either remain intact or are dislodged as a whole but leaving a visible "ghost" ring where they have been. The proportion of drop residues dislodged can therefore be estimated fairly accurately.

It is of course possible that some invisible erosion occurs, and that chemical estimate of amount retained might give lower values than the visual method. We have therefore made comparisons of estimates of deposit removal in the case of some experimental formulations of N-methyl α naphthyl carbamate, some of which were much less adherent than those finally selected. Good agreement between these methods is shown in Table 3.

Table 3. Estimates of removal by 1" of artificial rain

Visual assessment	Chemical estimation
5%	3%
15%	12%
50%	65%
75%	76%
80%	82%
85%	91%

R.J. Courshee and M.J. Iresan (1961) claimed that 80% of visual assessments are within 15% of chemical estimation in a wider variety of types of deposit.

4. THE FORMULANT IN USE

The amine stearate formulants as supplied are mobile, completely stable liquids. They have low setting points and, if frozen, may be remelted without detriment to their properties. It is necessary to keep containers closed to avoid evaporation of the volatile amine. The formulants are separately supplied, to be mixed in the spray tank with finely ground technical active ingredient, which may contain inert fillers. Any inconvenience in this two-pack supply is compensated by the greater flexibility in ratio of formulant and active ingredient which is permitted to the user.

The use of the formulants with already formulated wettable powders is undesirable. The other wetting agents so introduced may adversely affect reduction of evaporation and always reduce the resistance to rain washing. Also, when the wettable powders contain sodium or calcium salts, the spray liquor may gell or cause nozzle blockage due to the formation of the sparingly soluble stearates. The calcium content of hard waters is not sufficient to cause any trouble in the low volume application for which these formulations are designed.

The formulants are freely soluble in water and promote very easy mixing and good suspension of the solid ingredients. Even at so high a concentration as 5 lb of copper oxychloride per gallon a very mobile spray liquor is obtained. The spraying properties of the liquors are excellent and the high soap concentration promotes finer division of the spray than is obtained from orthodox spray liquors under the same conditions.

The high concentration of soap does of course facilitate the formation of froth, but the use of excess of the lipophilic amine reduces this tendency and no difficulty need arise if reasonable care is taken to stop air being introduced into the mixing tanks.

The formulants introduce no toxic or dermatological hazards in use.

They are in no way corrosive and indeed have some inhibiting effect on corrosion of metals by other agents.

It must be remembered that they are designed to leave very tenacious residues on evaporation, and therefore unused liquor should never be left for long in spray tanks. In fact the normal hygiene of spray machinery maintenance should be enforced.

5. IMPROVEMENT OF RESIDUAL INSECTICIDAL ACTION

Numerous tests have been carried out in the laboratory and one large scale aerial spraying experiment on pine forest infested with pine looper, *Bupalus pinearius*. These involved the solid insecticides D.D.T., N-methyl α naphthyl carbamate and dried *Bacillus thuringiensis* culture, comparing product formulated as orthodox wettable powder and in amine stearate formulation. These experiments are described by Q.A. Geering and J.H. Lloyd (in the press) and illustrative Tables are quoted below.

Table 4. Laboratory spraying on Brussels sprouts (*Brassica oleracea* var. *capitata*). Observation of mortality of Pieris brassicae larvae 48 hours after infestation on fresh deposits

Treatments (at 1 gal./acre)		Washed (1" rain)	Unwashed
¼ lb/a.	N-methyl α naphthyl carbamate + 4% amine stearate formulant	80	92
½ lb/a.		76	80
1 lb/a.		80	84
¼ lb/a.	N-methyl α naphthyl carbamate in wettable powder	20	68
½ lb/a.		12	56
1 lb/a.		32	56
Control		0	4
L.S.D. (5%)		33%	

Table 5. Laboratory spraying on Brussels sprouts. Observation of mortality of Pieris brassicae larvae 10 days after infestation on fresh deposits

Treatments (at 2 gal. /acre)		Washed (1" rain)	Unwashed
½ lb/a.	Bacillus thuringiensis w.p. + 4% v/v amine stearate formulant	95	100
1 lb/a.		95	100
2 lb/a.		85	95
½ lb/a.	Bacillus thuringiensis w.p.	40	65
1 lb/a.		20	95
2 lb/a.		60	80
Control		25	10
L.S.D. (5%)		24.3%	

Table 6. Laboratory spraying on Brussels sprouts. Observation of mortality of Pieris brassicae larvae 2 days after infestation on fresh deposits

Treatments (at 1 gal. /acre)		Washed (2" rain)	Unwashed
2 oz/a.	DDT a.i. wettable powder	40	100
16 oz/a.		52	100
2 oz/a.	DDT a.i. technical + 12% v/v amine stearate formulant	80	72
16 oz/a.		100	96
Control		8	8
L.S.D. (5%)		27%	

Table 7. Field data for aerial spraying of forest of 40 year old mixed stand of Pinus silvestris and P. nigra. Population reduction of Bupalus pinearius larvae corrected for natural population reduction

Treatments (acre-dosage at 1 gallon/acre)		Weeks after spraying						
		1	2	3	4	5	6	7
$\frac{1}{4}$ lb	N-methyl α naphthyl carbamate wettable powder	0	6.4	3.4	0	0	0	11.0
$\frac{1}{2}$ lb		23.4	41.3	33.7	13.9	0	0	17.9
1 lb		20.7	45.4	56.2	39.1	21.5	54.2	75.2
$\frac{1}{4}$ lb	N-methyl α naphthyl carbamate + 12% v/v amine stearate formulant	21.5	56.0	57.8	26.0	20.6	55.9	59.4
$\frac{1}{2}$ lb		22.3	39.7	41.4	55.9	68.2	63.0	63.0
1 lb		25.2	40.0	51.6	60.1	56.4	49.3	65.1

Notes to Tables

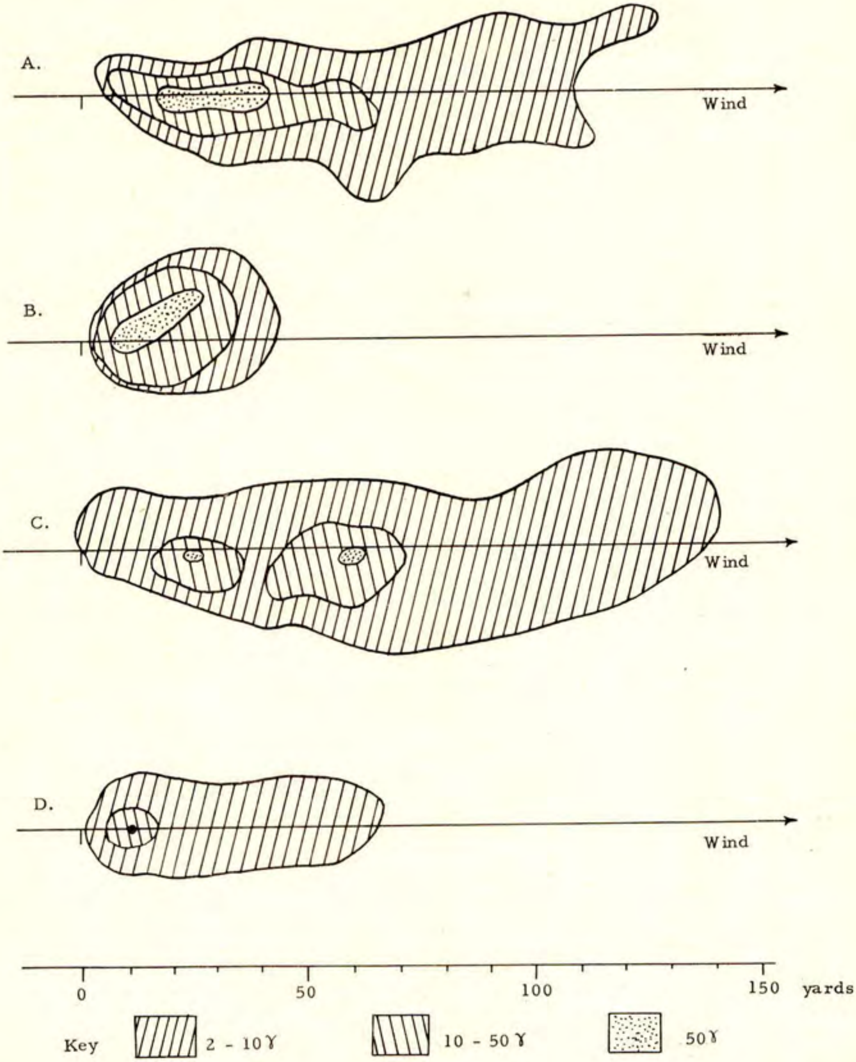
(1) The amine stearate formulation recorded in Tables 4 and 5 was a solution of 61% stearic acid in 39% methyl dibutylamine. That in the other experiments was 22% stearic acid, 14.5% methyldibutylamine and 63.5% inactive solvent to lower setting point.

(2) In some cases it will be noticed that the special formulation is more effective even before washing. This is due to improved initial retention (i.e. reduction of droplet reflection from the leaf.)

References

COURSHEE, R.J. and IRESON, M.J. (1961). J. Ag. Eng. Res. 6(3), 175.
EISNER, H.S., QUINCE, B.W. and SLACK, C. (1960). Disc. Faraday Soc. 30, 86.
GEERING, Q.A. and LLOYD, J.H. (in the press). XIIIth International Symp. on Crop Protection, Ghent, 1961, in press.

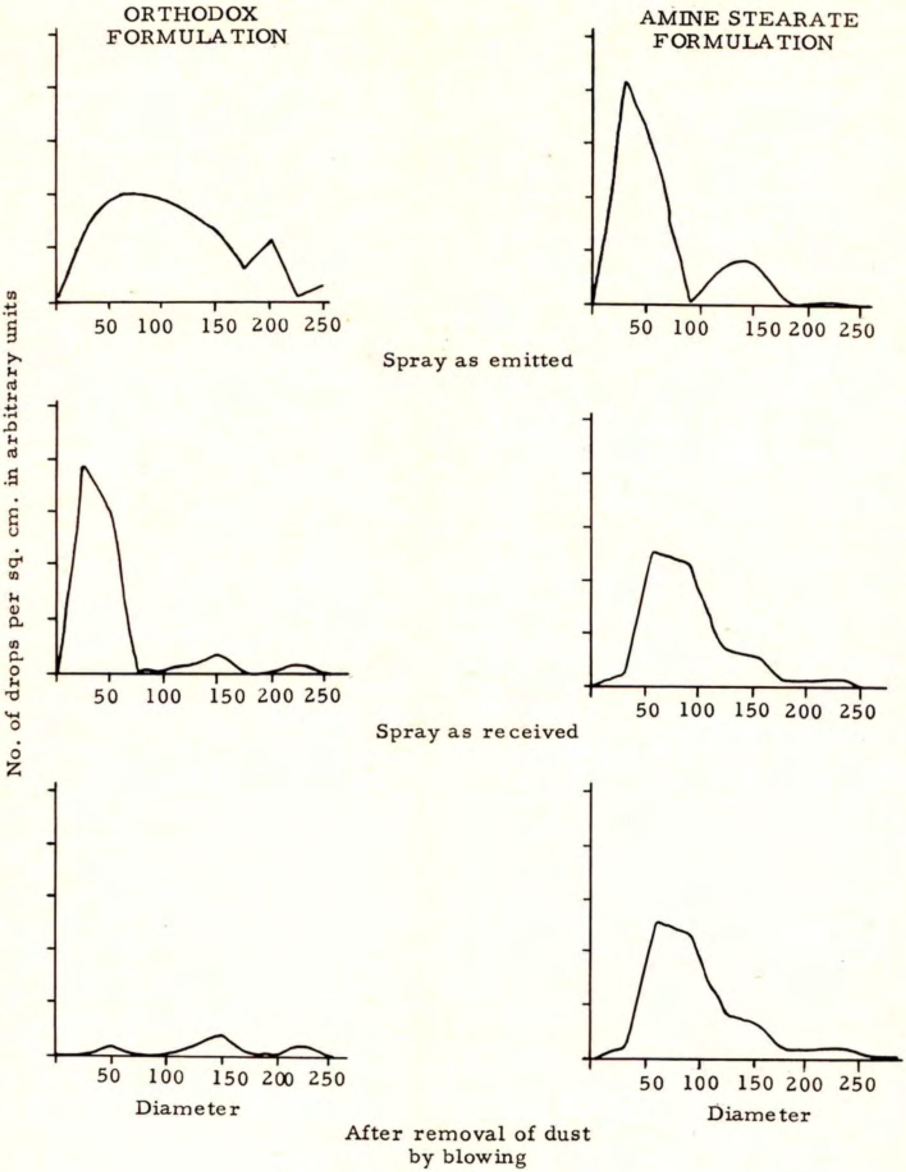
FIGURE 1



Contours of copper deposits in γ per sampling point.

A. Fatty acid preparation on 3" x 1" microscope slides.
B. Orthodox formulation on 3" x 1" microscope slides.
C. Fatty acid preparation on young pea plants.
D. Orthodox formulation on young pea plants.

FIGURE 2


ORTHODOX FORMULATION
AMINE STEARATE FORMULATION
No. of drops per sq. cm. in arbitrary units
50 100 150 200 250
Spray as emitted
Spray as received
Diameter
After removal of dust by blowing

Discussion

Q. Mr. P.G. Clinch

Has Dr. Linke any evidence of the effectiveness of thioquinox against Fruit Tree Red Spider mites resistant to any of the groups of chlorinated hydrocarbon acaracides?

A. Dr. Linke

No. We have no own evidence from trials in this country. However, experiments carried out by colleagues in Italy have shown thioquinox to be effective against Fruit Tree Red Spider mites resistant to "Kelthane".

Q. Dr. H. Martin

Is there any evidence of the spontaneous oxidation, after application, of the sulphide to the sulphoxide and ultimately the sulphone?

A. Dr. Meltzer

We have no definite results of the investigation of the metabolism of the sulphide within the plants, but there is some evidence that after its application there appears some sulphoxide and sulphone in the leaves.

Q. Dr. W.E. Ripper

When referring to the selective action, did Dr. Meltzer mean by insect predators to include predacious mites?

A. Dr. Meltzer

When I am speaking of insects, I really mean insects, and not - like the Americans - all small animals, which are not mammals. But as to the sulphide we have no evidence so far that it is affecting predacious mites. We know that the sulphone tetradifon is completely safe for predacious mites, and therefore we may assume that the sulphide behaves similarly.

Q. Mr. D. Tyson

Do the butylene polymers offer advantages, when used high volume under glass on cucumbers, over the accepted use of white oils for red spider control?

A. Mr. Greenfield

Further work is in progress on cucumbers. Phytotoxicity we have experienced to date has been very slight and the materials are certainly effective against red spider mite. We shall be in a better position to answer your question more fully when we have the results of next year's trials.

Q. Mr. N.B. Van Buren

Could you give us the advantages, if any, of polybutenes over the classic oil sprays?

A. Mr. Greenfield

I think the main point is that there is less likelihood of phytotoxicity using properly formulated polybutenes. However further evidence is needed to enable a complete answer at this stage.

Q. Dr. G.S. Hartley

In the film were the aphids shown in an active state not contaminated with polyisobutene? Was their abnormal activity due to the bright photographic light?

A. Mr. Greenfield

Aphids are normally stimulated by light. The source of activation here was sunlight. The object of the film was to demonstrate the immediate cessation of activity as a result of a high volume polybutene spray, in other words the reverse of stimulation.

Q. Mr. D. Tyson

How residual is the action of Butylene Polymers on crops under glass against spider mite and aphids, i.e. the length of time between sprays?

A. Mr. W. H. Read

The persistence of adhesive action of polybutenes at 5% is up to ten days but these concentrations are highly phytotoxic. At 0.75% the adhesive action does not persist more than 24 hours except on portions of the leaves, e.g. positions adjacent to the veins.

Mr. Greenfield then commented:

We have got Dr. Fisher, who has carried out all the original work, here from Canada and I think it would be useful to have his observations. In our own U.K. trials on apples, cucumbers, sugar beet, blackcurrants, potatoes and hops, we noticed the adhesive effect persisting from 7 - 14 days. I agree that it is only acaricidal for possibly something up to 5 days but we have also noticed that the mites dislike walking over tacky surfaces and, in addition, it tends to dissuade them from laying eggs. I think Dr. Fisher would like to add a comment.

Dr. Fisher then spoke:

Polybutenes used at 0.75% do not last for many days, however, they do control all active stages and if applied at weekly intervals for 2 or 3 weeks, will provide quite good control. In North America polybutenes of lower viscosity have been used because they had to compete with spray oils in cost to the grower. Two sprays of L-100 or H-35 at 2% give good control of European red mite on peach. Bi-weekly application of L-100 at 1% gave me good control of powdery mildew of cucumbers. At Geneva, N.Y., it was found that a residue of polybutene reduced the egg laying of pear psylla to about one tenth, but had no effect whatever on the adults.

Q. Dr. H. Martin

Has Mr. Howes any evidence that the fungicidal efficiency of a particle of copper oxychloride is impaired if it is treated with a film of stearic acid?

A. Mr. Howes

No, we have no evidence to this effect, rather to the reverse. Certainly not that it is impaired in any way but we have in certain trials got better effect - about 30% better - by using the amine stearate formulation rather than a straightforward formulation at high volume.

Dr. Hartley added:

Aqueous hydrochloric acid rapidly extracts copper oxychloride from the deposits, leaving a porous matrix of stearic acid crystals.

Q. Mr. M. J. Way

In view of the fact that the action of systemics like Menazon depends on persistence on the leaf surface, do the Lovo formulations benefit the persistence of systemic residues?

A. Mr. Howes

We really have no information on how it affects systemic insecticides. It may well have an effect on it but in the first case the formulation was designed specifically for active ingredients which are insoluble solids and therefore more difficult to formulate for low volume spraying. We are, of course, open to suggestions and will try this. We have thought that it will help systemic insecticides to get in but we have no evidence to this effect as yet.

Q. Dr. W. E. Ripper

The findings of Dr. Hartley and Mr. Howes seem to conflict with the generally accepted hypothesis that resuspension of copper fungicides in dew was essential for good results of low volume spraying. The work of Kerssen and Courshee showed that rain fastness and fungicidal action were inversely correlated. Are we to deduce that the Lovo compounds lead to a greater fungicidal activity because of larger deposition of fine droplets or is the above cited hypothesis untenable in the face of the new findings reported here today?

A. Mr. Howes

Actually, we have not found this effect which you reported. We find that provided the copper reaches the leaf and actually does stick to the leaf we do get fungicidal activity. We have, however, bowed to this belief; as I said at the end of my paper, we have incorporated a permanent non-ionic wetter in our formulation for fungicides, to promote redistribution. Indeed, we can get quite considerable redistribution and yet still approach the results achieved at 20 - 30 gallons per acre. You get much more shift of the copper, but even when sticking it very firmly as in our initial experiments, using an extremely strong sticker, we have a very good result. All I can suggest is that the copper is capable of being leached out by water and small quantities which we may not be able to detect are redeposited over the leaf. Indeed, that copper may be leached out with water can be shown by the fact that dilute hydrochloric acid will remove all the copper from the deposit.

Dr. Hartley added:

It is possible that the low volume spray protected from evaporation may convey more very small (satellite) drops to the leaf, which drops would be lost from a normal spray.