J. Pesticide Sci. **8**, 199–204 (1983)

Original Article

Stabilization of Buthiobate in the Wettable Powder of Buthiobate and Captan

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(Received November 15, 1982)

Stabilization of buthiobate in the combination wettable powder of buthiobate and captan was studied. Decomposition of buthiobate seems to be caused by the reaction between pyridine ring of buthiobate and hydrochloric acid produced by hydrolysis of captan. Hydroxides such as $Ca(OH)_2$ and $Mg(OH)_2$ and oxides such as CaO and MgO act as stabilizers, and these compounds do not influence captan stability significantly. In this way, a satisfactory combination wettable powder of buthiobate and captan could be obtained and shows good fungicidal efficacy.

INTRODUCTION

S-n-butyl S′-p-tert-butylbenzyl *N*-3-pyridyldithiocarbonimidate, buthiobate (Denmert®) is a fungicide invented by Sumitomo Chemical Co., Ltd., which shows excellent fungicidal efficacy against powdery mildew of fruit trees and vegetables.[1] The fungicidal spectrum of buthiobate, however, is narrow. As a way of using the excellent fungicidal efficacy of buthiobate against powdery mildew, combination formulations were developed in order to reinforce efficacy against powdery mildew of conventional fungicides. As one of them, the combination wettable powder with *N*-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide (captan) was formulated but buthiobate became very unstable by mixing it with captan. The combination wettable powder is thus not usable without stabilization. Therefore we conducted research to determine suitable stabilizers for buthiobate in a combination wettable powder with captan.

EXPERIMENTAL

1. *Materials*

Buthiobate was synthesized in the Pesticide Synthetic Laboratory, Pesticides Division, Sumitomo Chemical Co., Ltd. Captan technical material used in this work was supplied by Stauffer Chemical Co., Ltd. and chemical structures of these compounds are shown in Fig. 1. Additives used as stabilizers were of a reagent grade, and the stabilizers for polyvinylchloride were supplied from Sakai Chemical Co., Ltd.

2. *Methods*

Samples were prepared by blending 5% of buthiobate, 50% of captan, a certain amount of stabilizer and carriers with a household blender. Contents of buthiobate and captan in the combination formulation were analyzed after accelerated storage by gas chromatography (GC) under the conditions shown in Table 1. In the presence of captan, partial decomposition of buthiobate was observed in GC. Therefore, buthiobate was analyzed after extraction with *n*-hexane which hardly dissolves captan. After extraction of buthiobate from 1 g of the formulation with 5 ml of *n*-hexane, followed by centrifugation, 2 ml of the extract was pipetted out into a conical flask and 3 ml of chloroform solution of an internal standard (0.7 g/100 ml) was added to the conical flask and it was then applied to

Table 1 GC conditions for analysis of buthiobate and captan.

	Buthiobate	Captan
Apparatus	Shimadzu GC-5A (FID)	Shimadzu GC-5A (FID)
Column	0.5 m × 3 mm (glass)	1.0 m × 3 mm (glass)
Liquid phase	2% PEG-20M	2% Silicone XE-60
Support	Chromosorb W, AW, DMCS (60/80 mesh)	Chromosorb W, AW, DMCS (60/80 mesh)
Column temp.	220°C	170°C
Injection temp.	240°C	210°C
N_2 flow rate	80 ml/min	30 ml/min
Internal standard	Triphenylbenzene	Dibutylsebacate

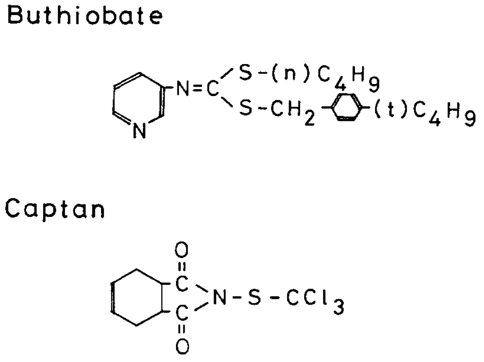


Fig. 1 Chemical structures of buthiobate and captan.

GC analysis. Captan was extracted from 0.5 g of the formulation with 25 ml of chloroform and 5 ml of chloroform solution of an internal standard (2.5 g/100 ml) was added to the extracts. After centrifugation, it was applied to GC analysis.

RESULTS AND DISCUSSION

1. *Decomposition Mechanism*

Table 2 shows the stability of buthiobate and captan in the various kinds of formulations. It is clear that buthiobate is very unstable in the combination formulation while stable in the single active ingredient formulation. Table 3 shows pH change after accelerated storage of aqueous suspension of chloroform solutions of buthiobate and captan. Formation of acidic material from captan is suggested because pH changes to acidic side after accelerated storage of the samples containing captan. Captan is known to form hydrochloric acid by hydrolysis, as shown in Fig. 2.[2] Therefore the acidic material formed after accelerated storage seems to be hydrochloric

Table 2 Stability of combination formulation of buthiobate and captan.

Buthiobate (TG[a], 93.0%)	5.5		5.5	—
Captan (TG, 92.0%)	56.0		—	56.0
Tokusil GU-N	5.0		5.0	5.0
Radiolite 200	33.5		89.5	39.0
Decomposition (%)	B	C	B	C
0°C, 30 days	13.0	0	0	0
40°C, 30 days	100	1.0	1.2	0.8
50°C, 14 days	100	1.0	1.5	1.3

[a] technical grade, B: buthiobate, C: captan.

Table 3 pH change of chloroform solutions of buthiobate and captan after accelerated storage.

Buthiobate (TG, 93.0%)	15 mg	15 mg	—
Captan (TG, 92.0%)	150 mg	—	150 mg
chloroform	balance to 10 ml		
pH[a]			
0°C, 30 days	4.1	5.5	4.8
40°C, 30 days	3.7	5.5	4.5
50°C, 30 days	3.6	5.4	4.1

[a] condition for determination of pH: $CHCl_3$ solution (3 ml)/H_2O (50 ml).

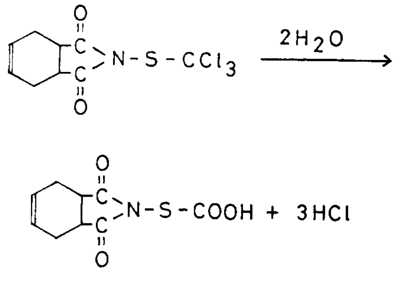


Fig. 2 Hydrolysis of captan.

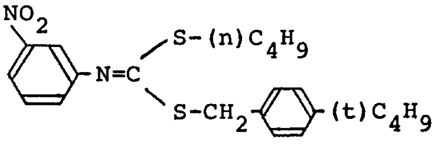
acid.

On the other hand, buthiobate is a base having pyridine ring, thus it is readily supposed that buthiobate forms hydrochloride by reaction with hydrochloric acid, followed by further decomposition. The proposed mechanism is supported by the fact that hydrochloride of buthiobate is very unstable in practice.[3] The proposed mechanism is also supported by the fact that 3-aminopyridine is decomposed by mixing with captan, as shown in Table 4. Moreover, as shown in Table 5, the addition of a drying agent such as $CaCl_2$ into the package of the formulation improved buthiobate stability remarkably.[4] Buthiobate stability after opening the package, however, is not good. It seems reasonable to conclude that hydrolysis of captan was suppressed by decreasing the moisture in the formulation by addition of drying agent. This result also supports hydrolysis of captan.

Table 4 Stability of buthiobate and its related compounds in the combination formulations with captan.

Buthiobate (TG, 93.0%)	5	—	—
Compound A[a]	—	5	—
3-Aminopyridine	—	—	5
Captan (TG, 92.0%)	55	55	55
Radiolite 200	40	40	40
Decomposition (%)			
0°C, 10 days	6.6	0	67.3
50°C, 10 days	100	5.7	100

[a] Compound A.



On the other hand, mechanism of action of captan is known to inhibit the SH group of an enzyme. Accordingly, interaction between $=C\begin{smallmatrix}\diagup SR\\ \diagdown SR'\end{smallmatrix}$, [R: (*n*)-$C_4H_9$, R′: $-CH_2-$⌬$-(tert)C_4H_9$] moiety of buthiobate and captan is considered as another decomposition mechanism.

Compound A having *m*-nitrobenzene ring (Hammet constant, $\sigma=0.71$) instead of pyridine ring ($\sigma=0.62$) of buthiobate, however, was not decomposed after mixing with captan as shown in Table 4. Moreover, it was also found that buthiobate is chemically compatible with Maneb which is known as an SH group inhibitor of the enzyme in the same manner as captan. From these results, the hypothesis of interaction of captan with $=C\begin{smallmatrix}\diagup SR\\ \diagdown SR'\end{smallmatrix}$ in buthiobate is not the case.

2. *Stabilization*

Captan is unstable in alkaline aqueous medium. For example, half lives of captan (50 ppm) in aqueous suspension at 20°C are 35 hr, 9.1 hr and 5 min at pH 4, 7 and 9, respectively. Therefore combined application with alkaline pesticides is inhibited.[5] In practice, captan is more unstable in Carplex

Table 5 Effect of HCl scavengers and $CaCl_2$ on stability of buthiobate.

Storage conditions	Additive	Decomposition (%)				
		None	Lead sulfate tribasic	Lead stearate	Calcium stearate	Dioctyl tin maleate polymer
0°C, 30 days		13	0	0	0	0
40°C, 30 days		100	6.6	47	21	40
40°C, 30 days ($CaCl_2$, dry)		39	—	5.0	—	10

[composition]	
Buthiobate (TG, 93.0%)	5.5
Captan (TG, 92.0%)	56.0
Additive	5.0
Tokusil GU-N	5.0
Radiolite 200	balance
	100.0

#1120 which is an alkaline precipitated silica than in Carplex #80 which is a weak acidic one. Decomposition percentages in each carrier containing 10% captan are 86 and 22%, respectively, after accelerated storage at 50°C for 14 days. Therefore, at first, neutral stabilizers for PVC acting as HCl scavengers were tested for buthiobate stabilization, considering captan instability in basic medium. As shown in Table 5, acid scavengers tested here showed a stabilizing effect to some extent. Especially, lead sulfate tribasic [$(PbSO_4)(PbO)_3H_2O$] showed remarkable stabilizing effect, although this material is slightly basic. Therefore these results support the decomposition mechanism proposed in the preceding section 1.

Next, weak alkaline inorganic salts were tested although influence on captan stability might be expected. $CaCO_3$, $NaHCO_3$, Na_2CO_3, $Na_2B_4O_7$ and Na_2HPO_4 showed considerable stabilizing effect without any significant influence on captan stability, as shown in Table 6. Especially, carbonates showed a high stabilizing effect but expansion of the package attributed to CO_2 gas evolution was observed when the formulation was stored in a polyethylene-laminated aluminium foil bag. Then, oxides such as CaO and MgO and hydroxides such as

Table 6 Effect of carbonates, borate and phosphate on stability of buthiobate.

Storage conditions	Additive	Decomposition (%)											
		None		$CaCO_3$		$NaHCO_3$		Na_2CO_3		$Na_2B_4O_7$		Na_2HPO_4	
		B	C	B	C	B	C	B	C	B	C	B	C
0°C, 30 days		13	0	0	0	0	0	0	0	0	0	0	0
40°C, 30 days		100	1.0	7.8	1.3	0	2.0	2.7	0.9	14	1.2	8.1	1.1
40°C, 60 days		100	2.2	13	2.0	0.5	2.5	—	—	18	—	20	—
50°C, 30 days		100	1.7	40	2.1	16	2.0	11	2.6	100	2.3	57	2.2

B: buthiobate, C: captan.

[composition]

Buthiobate (TG, 93.0%)	5.5
Captan (TG, 92.0%)	56.0
Additive	5.0
Tokusil GU-N	5.0
Radiolite 200	balance
	100.0

Table 7 Effect of oxides and hydroxides on stability of buthiobate.

Storage conditions	Additive (content)	Decomposition (%)									
		CaO (2.5%)		MgO (2.5%)		$Ca(OH)_2$ (4%)		$Mg(OH)_2$ (4%)		NaOH (2.5%)	
		B	C	B	C	B	C	B	C	B	C
0°C, 30 days		0	0	0	0	0	0	0	0	3.5	0
40°C, 30 days		4.1	1.9	3.3	2.0	5.4	2.0	4.7	2.3	15	2.1
50°C, 30 days		7.8	2.4	6.9	2.2	7.4	2.7	7.6	2.6	48	2.9

B: buthiobate, C: captan.

[composition]

Buthiobate (TG, 93.0%)	5.5
Captan (TG, 92.0%)	56.0
Additive	2.5 or 4.0
Tokusil GU-N	5.0
Radiolite 200	balance
	100.0

Table 8 Effect of content of hydroxides on stability of buthiobate.

Storage conditions	Additive (content)	Decomposition (%) $Ca(OH)_2$ (1.0%)	$Ca(OH)_2$ (3.0%)	$Ca(OH)_2$ (5.0%)	$Mg(OH)_2$ (0.5%)	$Mg(OH)_2$ (1.0%)	$Mg(OH)_2$ (3.0%)
40°C, 30 days		3.7	4.6	8.0	3.9	2.2	5.0
40°C, 90 days		12	—	—	—	5.9	—
50°C, 30 days		100	5.6	9.5	100	8.5	8.4

[composition]	
Buthiobate (TG, 93.0%)	5.5
Captan (TG, 92.0%)	56.0
Additive	0.5–5.0
Tokusil GU-N	5.0
Radiolite 200	balance
	100.0

Table 9 Effect of NaOH on stability of buthiobate and captan.

Buthiobate (TG, 93.0%)	5.5		5.5		5.5	5.5	—	—
Captan (TG, 92.0%)	56.0		56.0		—	—	56.0	56.0
NaOH	—		2.5		—	2.5	—	2.5
Tokusil GU-N	5.0		5.0		5.0	5.0	5.0	5.0
Radiolite 200	33.5		31.0		89.5	87.0	39.0	36.5
Decomposition (%)	B	C	B	C	B	B	C	C
50°C, 20 days	100	1.0	19	10	1.5	1.9	1.0	7.2
60°C, 20 days	100	1.5	100	14	2.3	2.5	1.3	10

B: buthiobate, C: captan.

$Ca(OH)_2$ and $Mg(OH)_2$ were tested. Consequently, it was found that these oxides and hydroxides showed remarkable stabilizing effect[6] as shown in Table 7 and did not significantly influence captan stability. However, there seems to be an optimum value in the amount of hydroxides to be added as shown in Table 8. That is, the durability of the stabilizing effect was not as good when the amount of hydroxides added was small (1%) and a larger decomposition of buthiobate was observed when the amount of hydroxides added was too great (5%). It is supposed that acceleration of hydrolysis of captan takes place by addition of an excess amount of hydroxides. Therefore a suitable amount of hydroxides to be added seems to be about 3%.

In the case of NaOH, as shown in Table 9, its addition accelerated captan decomposition and showed a stabilizing effect on buthiobate to some extent by trapping HCl, but the effect was not good enough for practical use. In the case of aqueous solution or suspension, captan is unstable in alkaline medium, but the influence of hydroxides such as $Ca(OH)_2$, $Mg(OH)_2$ and NaOH on captan stability is little in the case of mixing in the formulation as mentioned above. From these results, it is understood that the influence of alkaline materials on captan stability is not as large under a low moisture condition such as in the formulation (1–2%). In Carplex #1120, captan is slightly unstable because of higher moisture content (4–9%). Therefore, it is clear that the influence of water on captan stability is very large.

3. *Bioassay*

The fungicidal efficacy of a combination wettable powder of buthiobate and captan stabilized by the addition of $Mg(OH)_2$ against powdery mildew and downy mildew (cucumber) was tested in a greenhouse. Fifty ml of suspension containing the prescribed dosage was applied to cucumber foliar using a spray gun. Spore suspension was inoculated at 0, 3 and 7 days after treatment and then the plants

Table 10 Efficacy of combination wettable powder of buthiobate and captan.
Percentage of powdery mildew (cucumber) control

	Conc. of a.i.[a)] (ppm)	Inoculation (days after treatment)		
		0	3	7
Buthiobate 20 WP	2.5	43	13	5
	5	77	45	38
	10	100	93	82
	20	100	99	95
Combination WP (5/50)	2.5/25	55	45	37
	5/50	97	78	67
	10/100	100	99	82
	20/200	100	100	100

a): Active ingredient.

Table 11 Efficacy of combination wettable powder of buthiobate and captan.
Percentage of downey mildew (cucumber) control

	Conc. of a.i. (ppm)	Inoculation (days after treatment)		
		0	3	7
Captan 80 WP	12.5	96	0	0
	25	99	49	13
	50	100	79	35
	100	100	98	77
Combination WP (5/50)	1.25/12.5	77	3	0
	2.5/25	92	47	17
	5/50	100	81	23
	10/100	100	97	68

were kept at 25°C in a greenhouse. After 10 days, disease control percentage was calculated in accordance with the usual method. As shown in Tables 10 and 11, a combination wettable powder of buthiobate and captan showed good fungicidal efficacy against both powdery mildew and downy mildew.

ACKNOWLEDGEMENT

Thanks are due to Dr. S. Tanaka for his kindness in supplying us with several samples. Thanks are also due to Misses K. Morishita and S. Ito for their technical assistance.

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要 約

ブチオベート・キャプタン混合水和剤中でのブチオベートの安定化

堀出文男，辻 孝三

ブチオベート・キャプタン混合水和剤でのブチオベートの安定化について検討した．ブチオベートの分解はキャプタンの加水分解によって生じる塩酸とブチオベートのピリジン環の反応によるものと考えられる．ブチオベートの安定化には $Ca(OH)_2$，$Mg(OH)_2$ 等の水酸化物あるいは CaO, MgO 等の酸化物の添加が有効であったが，これらの化合物はキャプタンの安定性に対して有意な影響を与えることはなかった．このようにして，実用的なブチオベート・キャプタン混合水和剤 (5+50%) が得られ，効力面でも優れた防除効果を示した．