

## PROPINEB

### EXPLANATION

Propineb was evaluated in 1977, 1984 and 1985. The temporary ADI was withdrawn by the 1985 JMPR, but the CCPR maintained the guideline levels for propylenethiourea.

### USE PATTERN

Propineb is a protectant foliar-applied fungicide with long residual activity and belongs to the dithiocarbamate group of compounds. It is used as a protective treatment on several crops for the control of various fungi, especially Oomycetes, Ascomycetes, Basidiomycetes and Fungi imperfecti. Propineb controls blight on potatoes and tomatoes, downy mildew on hops and vines, apple scab, blue mould on tobacco and Sigatoka disease of bananas. It can also be used on gooseberries, black currants, celery and cereals.

Propineb is applied as a WG or WP formulation mainly as a spray. It is also applied, especially in southern Europe, in combination with oxadixyl, carbendazim, copper oxychloride, triadimefon or cymoxanil.

Table 1 shows the registered uses of propineb reported to the Meeting. However, the principal manufacturer intends to recommend the use of propineb only on the following crops: grapes, tomatoes, potatoes, pome fruit, onions, melons and bell peppers. In this monograph residue data are reviewed only for these crops.

Table 1. Registered or approved uses of propineb

Crop	Country	Application				PHI, days
		Form.	No.	g ai/hl	kg ai/ha	
Grapes	Austria	70 WP	1-4	0.21	up to 2.10	7
	France	70 WP	up to 2		up to 2.80	
	Germany	70 WG	up to 2	0.14	up to 1.12	56
		70 WG	up to 6		up to 2.52	56
	Greece	70 WP	3-4		1.40-1.75	7
		65 WP	3-4	0.16	1.30-1.63	7
	Italy	70 WP	2-5	0.14	1.05-1.40	28
		65 WP	2-5	0.13	0.98-1.30	28
	Portugal	70 WP	up to 7		1.45-2.10	7
	Spain	70 WP	up to 3	0.14-0.21	0.7-1.05	15,28
Thailand	70 WP	1-2	0.1	1.64-1.97	21	
Turkey	70 WP	2-3		up to 1.40	21	
Melons	Australia	70 WP	up to 7		up to 1.40	7
	Guatemala	70 WP	2-3		1.75-2.10	7
	Korea	70 WP	up to 3		up to 2.10	7
	Japan	70 WP	up to 3	0.17	2.34-3.50	7
	Turkey	70 WP	1-2		up to 0.84	7
Onions	Australia	70 WP	up to 4	0.14	up to 2.80	14
	Israel	70 WP	up to 2		up to 1.75	3

Crop	Country	Application				PHI, days
		Form.	No.	g ai/hl	kg ai/ha	
	Japan	70 WP	up to 5	0.17	1.75-2.63	7
	Spain	70 WP	up to 2	0.14-0.21	1.12-1.68	15
	Venezuela	70 WP	4-8		1.40-2.10	7
Pome fruit	Germany	70 WG	up to 12		up to 1.58	28
	Italy	70 WP 65 WP	3-5 up to 2		1.58-2.10 1.46-1.95	28 28
	Japan	70 WP	up to 4		up to 8.40	14
	Korea	70 WP	up to 3		up to 5.60	10
	Portugal	70 WP	up to 2		up to 2.10	7
	Taiwan	70 WP	7-10		up to 3.50	10
	Turkey	70 WP	4-5		up to 4.20	14
Potatoes	Australia	70 WP	up to 7	0.14	up to 2.10	7
	Colombia	70 WP	up to 6		1.05-1.75	3
	Germany	70 WG	1-6		1.05-1.26	7
	Greece	70 WP 65 WP	2-3 2-3	0.17 0.16	1.40-1.75 1.30-1.63	7 7
	Guatemala	70 WP	4-8		1.75-2.10	7
	Indonesia	70 WP	up to 10		1.05-1.75	14
	Peru	70 WP	3-4		1.05-1.75	7
	Portugal	70 WP	up to 8	0.17	up to 2.10	7
	Spain	70 WP	2-3	0.14-0.21	1.40-2.10	15
	Venezuela	70 WP	4 -6		1.40-2.10	7
Tomatoes	Australia	70 WP	up to 7		up to 1.40	3
	Germany	70 WP	up to 4		0,84-1.68	7
	Greece	70 WP 65 WP	3-4 3-4		1.40-1.75 1.30-1.63	3 3
	Indonesia	70 WP	up to 10		1.05-1.75	14
	Italy	70 WP 65 WP	1-2 1-2	0.14 0.13	up to 1.12 up to 1.04	28 28
	Morocco	70 WP	8-14		1.40-2.10	7
	Spain	70 WP	2-3	0.14	2.8 -4.35	15

#### RESIDUES RESULTING FROM SUPERVISED TRIALS

A number of trials were carried out with several crops in various countries. The residues determined were propineb, measured and calculated as CS<sub>2</sub>, as well as the major metabolite propylenethiourea (PTU) and in some cases propylenediamine (PDA). The results are discussed in relation to the current registered uses.

The following country codes are used in the Tables: ARG-Argentina, AUL-Australia, AUS-Austria, BEL-Belgium, CHI-Chile, CYP-Cyprus, DEN-Denmark, FIN-Finland, FRA-France, GER-Germany, HUN-Hungary, ISR-Israel, ITA-Italy, JPN-Japan, LUX-Luxembourg, MAL-Malaysia, MOZ-Mozambique, NET-Netherlands, NZE-New Zealand, POR-Portugal, SAF-South Africa, SPA-Spain, SWE-Sweden, SWI-Switzerland, TAW-Taiwan, TUR-Turkey, YUG-Yugoslavia.

Underlined residues are from treatments according to GAP.

Pome fruits. A total of 13 supervised trials were conducted in Germany with Antracol 70 WG/WP (10 on apples and 3 on pears), where up to 12 sprays

were applied at rates from 0.45 to 2.1 kg ai/ha. The dosage rates and pre-harvest intervals accord with those in effect in several countries. The results are summarized in Tables 2 and 3.

Residues of propineb in fruit 14-21 days after the last treatment ranged from <0.05 mg/kg to 0.96 mg/kg. For the main metabolite, PTU, the results were in the range <0.02 to 0.08 mg/kg.

Table 2. Residues of propineb in apples from supervised trials in Germany with Antracol 70 WP.

Sample, Year	Application			PHI, days	Residue, mg/kg		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
Fruit, 1982	10	2.1	0.14	21	<u>0.96</u>	0.03	8009-82
Juice					<0.05	0.03	
Puree					<0.05	0.02	
Fruit, 1982				28	<u>0.8</u>	0.03	
Fruit, 1982	10	2.1	0.56	21	<0.05	<0.01	8010-82
Juice					<0.05	<0.05	
Puree					<0.05	<0.05	
Fruit				28	<0.05	<0.01	
Fruit, 1987	12	1.6	0.105	0 5 7 14 21	1.5 1.4 0.85 0.31 <u>0.17</u>	0.02 <0.02	8008-87
Fruit, 1987	12	1.6	0.105	0 5 7 14 21	2.3 1.0 1.0 0.34 <u>0.48</u>	<0.02 <0.02	8058-87
Fruit, 1988	12	1.6	0.105	0 5 7 14 21	0.46 0.26 0.18 <0.05 <u>&lt;0.05</u>	<0.02 <0.02 <0.02 <0.02 <0.02	0023-88
Fruit, 1988	12	1.6	0.105	0 5 7 14 21	0.70 0.21 0.21 0.09 <u>0.09</u>	<0.02 <0.02 <0.02 <0.02 <0.02	0024-88
Fruit, 1991	12	1.6	0.105	0 3 7 13 21	0.81 0.59 0.68 0.34 <u>0.31</u>	<0.01 <0.01 <0.01 <0.01 <0.01	0038-91
Fruit, 1991	12	1.6	0.105	0 4 7 14 21	1.1 0.90 0.72 0.59 <u>1.0</u>	0.02 0.02 0.02 0.03 0.02	0039-91
Fruit, 1991	12	0.78	0.315	0 4 7 14 21	0.73 0.66 0.44 0.29 <u>0.24</u>	0.01 0.03 0.03 0.01 0.01	0040-91
Fruit, 1991	12	0.94	0.315	0 4 7 14 21	0.41 0.24 0.21 0.17 <u>0.11</u>	<0.01 <0.01 <0.01 <0.01 <0.01	0041-91
Fruit, 1991		1.58	0.14	0 3 7 13 21	0.81 0.59 0.68 0.34 0.31	<0.01 <0.01 <0.01 <0.01 <0.01	RA 2004/91
Fruit, 1991		1.58	0.14	0 4 7 14 21	1.1 0.90 0.72 0.59 1.0	0.02 0.02 0.02 0.03 0.02	RA 2004/91
Fruit, 1991		0.78	0.32	0 4 7	0.73 0.66 0.44	0.01 0.03 0.03	RA 2004/91

Sample, Year	Application			PHI, days	Residue, mg/kg		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
				14 21	0.29 0.24	0.01 0.01	
Fruit, 1991		0.45	0.32	0 4 7 14 21	0.41 0.24 0.21 0.17 0.11	<0.01 <0.01 <0.01 <0.01 <0.01	RA 2004/91

Table 3. Residues of propineb in pears from supervised trials in Germany.

Sample Year	Application			PHI, days	Residue, mg/kg		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
Fruit, 1982	10	2.1	0.14	21	0.52	0.06	8011-82
Puree					<0.05	<0.01	
Fruit				28	<u>0.55</u>	<u>0.05</u>	
Fruit, 1987	12	1.58	0.105	0 5 7 14 21	1.9 1.2 1.3 0.49 <u>0.40</u>	0.05 <u>0.05</u>	8010-87
Fruit, 1987	12	1.58	0.105	0 5 7 14 21	2.0 1.9 1.1 0.82 <u>0.82</u>	0.07 <u>0.08</u>	8060-87

Grapes. Many trials have been conducted in Germany and Turkey since 1981 with Antracol 70 WG and WP using a range of grape varieties and use patterns. At pre-harvest intervals of 49 to 69 days, residues of propineb and PTU were between <0.05 and 1.2 mg/kg and between <0.01 and 0.08 mg/kg respectively, except in one trial where 2.1 mg/kg propineb and 0.15 mg/kg PTU were measured (Table 4). With different application schedules, the results for propineb are more or less in the same range, although there is a slight tendency for the residue to increase with increasing dosage or number of applications. The variety of grape did not influence the residue levels.

Table 4. Residues of propineb in grapes, must and wine from supervised trials in Germany and Turkey.

Crop, product Year	Application			PHI, days	Residues (mg/kg) at days after application		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
Germany							
must, 1981 grape wine	6	2x1.4 4x2.8	0.14	69	0.07 0.13 <0.05	0.01 0.01 0.03	8000-81
must, 1981 grape wine	6	2x1.4 4x2.8	0.14	69	<0.05 <0.05 <0.05	<0.01 <0.01 0.02	8001-81
must, 1981 grape wine	6	2x1.4 4x2.8	0.14	69	0.41 0.75 0.05	0.07 0.05 0.10	8002-81
must, 1981 grape wine	8	2x1.4 6x2.8	0.14	40	0.10 0.49 <0.05	0.03 0.03 0.05	8003-81
must, 1981 grape wine	8	2x1.4 6x2.8	0.14	40	<0.05 0.19 <0.05	<0.01 0.02 0.01	8004-81
must, 1982 grape wine	6	2x1.4 4x2.8	0.28	41	0.1 <0.05 <0.05	0.03 <0.01 0.02	8025-82
must, 1982 grape wine	6	2x1.4 4x2.8	0.56	43	<0.05 <0.05 <0.05	0.03 0.01 0.04	8026-82
must, 1982 grape wine	6	2x1.4 4x2.8	0.56	41	0.1 0.2 0.1	0.2 0.05 0.2	8027-82

Crop, product Year	Application			PHI, days	Residues (mg/kg) at days after application		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
must, 1982 grape wine	6	2x1.4 4x2.8	0.56	35	0.1 0.5 0.1	0.2 0.03 0.1	8028-82
must, 1982 grape wine	6	2x1.4 4x2.8	0.28	42	<0.05 0.07 <0.05	0.1 0.01 0.06	8029-82
must, 1982 grape wine	6	2x1.4 4x2.8	0.28	42	0.08 0.07 <0.05	0.04 0.02 0.05	8030-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.28	55	<0.05 <0.05 <0.05	<0.01 <0.01 <0.01	8034-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.56	58	<0.05 <0.05 <0.05	<0.01 0.01 0.02	8035-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.56	56	<0.05 <0.05 <0.05	0.05 0.03 0.05	8036-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.56	49	0.05 0.2 0.05	0.02 0.08 0.07	8037-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.28	56	<0.05 <0.05 <0.05	0.08 <0.01 0.03	8038-82
must, 1982 grape wine	5	2x1.4 3x2.8	0.28	56	<0.05 <0.05 <0.05	0.05 0.02 0.05	8039-82
must, cold, 1984  must,heated grape  wine, cold  wine,heated	3	1.4;1.68; 1.96	0.14	42 49 56 42 28 42 49 56 42 49 56 42	1.2 0.24 1.5 0.57 1.1 1.6 0.74 0.52 <0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 0.10 0.13 0.07 0.14	8000-84
must, 1984  grape  wine	4	1.4;1.68 2x1.96	0.14	42 49 56 0 28 42 49 56 42 49 56	0.45 0.75 1.3 4.8 1.1 0.30 1.7 0.37 <0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 0.03 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	8001-84
must, cold, 1984  must,heated grape  wine, cold  wine, heated	5	1.4;1.68; 2x1.96; 2.24	0.14	42 49 56 56 0 28 42 49 56 42 49 56	1.5 1.8 2.5 0.21 3.7 2.1 0.22 1.5 1.1 <0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 <0.02 0.08 <0.02 <0.02 <0.02 <0.02 <0.02 0.17 0.24 0.14	8002-84
must, cold, 1984 must, heated  grape  wine, cold wine, heated	3	1.4;1.68; 1.96	0.14	42 42 49 56 28 42 49 56 42 42 49 56	<0.05 0.89 <0.05 0.12 0.74 1.3 0.50 0.68 <0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 0.10 0.10 0.04 0.05	8003-84
must, heated, 1984  grape	4	1.4;1.68; 2x1.96	0.14	42 49 56 28 42 49 56 42	0.34 0.73 0.80 3.2 1.4 0.61 0.51 <0.05	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 0.17	8004-84

Crop, product Year	Application			PHI, days	Residues (mg/kg) at days after application		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
wine, heated				49 56	<0.05 <0.05	0.09 0.09	
must, cold, 1984	5	1.4;1.68; 2x1.96;2.24	0.14	49	0.95	<0.02	8005-84
must, heated				56	0.46	<0.02	
				42	0.70	<0.02	
				49	0.83	<0.02	
grape				56	0.40	<0.02	
				0	2.4	0.06	
				28	<0.05	<0.02	
				42	0.35	<0.02	
				49	1.5	<0.02	
wine, cold				56	0.99	<0.02	
				49	<0.05	0.08	
wine, heated				56	<0.05	<0.02	
				42	<0.05	0.18	
				49	<0.05	0.09	
	56	<0.05	0.04				
mash, 1986	6	2x1.13;2x 1.68; 2.1; 2.52	0.42	56	0.17	<0.02	8000-86 G
must				56	<0.05	<0.02	
grape				0	1.9	0.02	
				56	0.32	<0.02	
wine				56	<0.05	0.03	
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1;2.38; 2.52	0.42	56	0.11	0.02	8000-86 N
grape				0	2.9	0.01	
				56	0.27	0.04	
wine				56	<0.05		
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1;2.38; 2.52	0.42	56	<0.05	0.03	8001-86 N
grape				0	4.8	0.11	
				56	1.1	0.02	
wine				56	<0.05	0.04	
must, 1986	6	2x0.84; 4x2.52	0.42	56	<0.05	0.02	8001-86 Z
grape				0	4.6	0.11	
				56	1.2	0.02	
wine				56	<0.05	0.04	
mash, 1986	6	2x1.13; 2x1.68; 2.1;2.52	0.42	56	0.18	<0.02	8002-86 G
must				56	<0.05	<0.02	
grape				0	3.1	0.06	
				56	0.35	<0.02	
wine				56	<0.05	0.03	
must, 1986	7	0.56;1.68; 1.68;1.96; 2.1;2.38; 2.52	0.42	56	0.15	0.02	8002-86 N
grape				0	3.0	0.03	
				56	0.28	0.01	
wine				56	<0.05	0.04	
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1;2.38; 2.52	0.42	56	0.25	0.03	8003-86 N
grape				0	4.7	0.08	
				56	0.78	0.01	
wine				56	<0.05	<0.05	
must, 1986	6	2x0.84; 4x2.52	0.42	56	0.10	0.03	8003-86 Z
grape				0	5.9	0.12	
				56	0.46	0.02	
wine				56	<0.05	0.04	
mash, 1986	6	2x1.13; 2x1.68; 2.1;2.52	0.42	49	0.46	0.02	8004-86 G
must				49	0.05	<0.02	
grape				0	1.7	0.04	
				49	0.38	<0.02	
wine				49	<0.05	0.04	
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1;2.38; 2.52	0.42	49	0.05	0.02	8004-86 N
grape				0	4.5	0.06	
				49	0.59	0.01	
wine				49	<0.05	0.05	
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1;2.38; 2.52	0.42	49	<0.05	0.04	8005-86 N
grape				0	3.3	0.07	
				49	0.71	0.01	
wine				49	<0.05	0.06	
must, 1986	6	2x0.84 4x2.52	0.42	49	0.10	0.02	8005-86 Z
grape				0	5.7	0.07	
				49	0.60	0.01	
wine				49	<0.05	0.04	
mash, 1986	6	2x1.13; 2x1.68 2.1;2.52	0.42	49	0.24	0.03	8006-86 G
must				49	<0.05	<0.02	
grape				0	2.4	0.04	
				49	0.30	<0.02	
wine				49	<0.05	0.03	
must, 1986	7	0.56;1.05; 1.68;1.96; 2.1; 2.38; 2.52	0.42	49	0.10	0.03	8006-86 N
grape				0	3.3	0.07	
				49	0.99	0.01	
wine				49	<0.05	0.04	
must, 1986	7	0.56;1.05; 1.68;1.96;	0.42	49	<0.05	0.03	8007-86 N
grape				0	3.4	0.03	

Crop, product Year	Application			PHI, days	Residues (mg/kg) at days after application		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
wine		2.1; 2.38; 2.52		49 49	0.83 <0.05	<0.01 0.05	
must, 1986 grape	6	2x0.84 4x2.52	0.42	49 0 49 49	0.05 5.6 0.60 <0.05	0.05 0.08 <0.02 0.06	8007-86 Z
wine							
mash, 1986 must grape	6	2x1.13; 2x1.68; 2.1; 2.52	0.42	56 56 0 56 56	0.13 0.06 2.6 0.30 <0.05	<0.02 <0.02 0.06 <0.02 <0.02	8008-86 G
wine							
must, 1986 grape	7	0.56;1.05; 1.68;1.96; 2.1; 2.38; 2.52	0.42	56 0 56 56	0.10 3.1 0.69 <0.05	0.20 0.06 0.01 0.28	8008-86 N
wine							
must, 1986 grape	7	0.56;1.05; 1.68;1.69; 2.1;2.38; 2.52	0.42	56 0 56 56	0.20 3.5 1.1 <0.05	0.50 0.14 0.03 0.67	8009-86 N
wine							
must, 1986 grape	6	2x0.84; 4x2.52	0.42	56 0 56 56	0.08 6.8 1.0 <0.05	0.25 0.16 0.02 0.26	8009-86 Z
wine							
must, 1987 grape	6	1.12;2x1.68 3.8;2x3.5	0.14	56 0 28 35 56 56	<0.05 20 1.6 1.3 0.9 <0.05	<0.02 0.6 0.03 0.03	8000-87
wine							
must, 1987 grape	6	0.84;1.05; 1.68;2x2.1 2.52	0.42	56 0 28 35 56 56	0.05 4.6 1.1 0.38 0.72 <0.05	<0.02 <0.02 0.02 <0.02	8001-87
wine							
must, 1987 grape	6	2x0.84; 4x2.52	0.42	56 0 28 35 56 56	0.05 7.2 1.5 0.62 0.46 <0.05	0.04 0.07 0.04 0.04	8002-87
wine							
must, 1987 grape	6	0.7;1.12; 2.1;2.52; 2.8;3.5	0.14	56 0 28 35 56 56	<0.05 4.3 1.2 0.50 0.42 <0.05	<0.02 0.03 <0.02 <0.02	8050-87
wine							
must, 1987 grape	6	0.84;1.05; 1.68;2x2.1; 2.52	0.42	56 0 28 35 56 56	0.05 4.7 1.0 0.44 0.75 <0.05	<0.02 <0.02 <0.02 <0.02	8051-87
wine							
must, 1987 grape	6	2x0.84 4x2.52	0.42	56 0 28 35 56 56	0.11 13 2.1 2.0 2.1 <0.05	0.06 0.12 0.15 0.04	8052-87
wine							
bunch, 1988 must wine	4	2x0.84 2x1.68	0.42	0 70 70 70	6.9 0.06 <0.05 <0.05	0.27 <0.02 <0.02 <0.02	0406-88
bunch, 1988 must wine	5	2x0.84 3x2.1	0.42	0 70 70 70	0.50 0.66 <0.05 <0.05	<0.02 0.03 0.07 0.10	0408-88
bunch, 1988 must wine	5	2x0.84 3x2.1	0.42	0 70 70 70	5.8 0.53 <0.05 <0.05	0.16 0.04 0.10 0.11	0409-88
Turkey							
grape, 1990	4	1.4	0.14	0 76	2.6 <0.1		0610-90
grape, 1990 raisin	4	1.4	0.14	0 62 62	1.2 0.15 <0.1	<0.01	0611-90

Crop, product Year	Application			PHI, days	Residues (mg/kg) at days after application		Ref.
	No.	kg ai/ha	kg ai/hl		CS <sub>2</sub>	PTU	
grape, 1990	4	1.4	0.14	0 48	1.5 0.15		0612-90
grape, 1990 raisin	4	1.4	0.14	0 76 76	3.2 0.22 <0.1	0.29 <0.01 <0.01	0613-90
grape, 1990	4	1.4	0.14	0 62	2.2 <0.1	0.16 <0.01	0614-90
grape, 1990 raisin	4	1.4	0.14	0 48 48	0.99 0.29 <0.1	0.01 0.01 <0.01	0615-90
grape, 1990 raisin	4	1.4	0.14	0 76 76	4.2 0.11 0.20	0.12 <0.01 <0.01	0616-90
grape, 1990	4	1.4	0.14	0 62	1.8 0.11	0.12 <0.01	0617-90
grape, 1990 raisin	4	1.4	0.14	0 48 48	3.2 0.39 0.12	0.08 0.02 0.01	0618-90
grape, 1990	4	1.4	0.14	0 76	3.8 0.15	0.10 <0.01	0620-90
grape, 1990 raisin	4	1.4	0.14	0 62 62	2.1 0.67 <0.1	0.09 0.02 <0.01	0621-90
grape, 1990	4	1.4	0.14	0 48	2.2 0.18	0.07 0.01	0623-90

Onions. In 1987, 2 residue trials were conducted in Australia with rates of 1.4 or 2.8 kg ai/ha applied 5 times per season, according to the current registered use. 14 days after the last treatment no residues of propineb were found above the lower limit of determination (0.2 mg/kg). In these trials PTU was not analyzed.

In Japan 6 residue trials were conducted according to the current use pattern. Applications were made 5 or 7 times at a rate of 1.4 or 1.75 kg ai/ha. Seven days after the last treatment the residues of propylenediamine (PDA) were <0.05 mg/kg in four samples and 0.05 and 0.08 mg/kg in the other two. Residues of PTU were below the lower limit of determination (<0.01 mg/kg). Propineb was not determined in these trials.

Melons. Four residue trials were conducted in Australia, where 7 or 8 sprays at 1.4 or 2.8 kg ai/ha were applied to melons, according to the current use pattern or at double rate. Seven days after the last treatment no measurable residues of propineb were found (<0.1 mg/kg).

In Japan, residue trials were conducted with application rates from 2.63 to 3.5 kg ai/ha, applied 3-5 times per season, according to the current use pattern. Seven to 21 days after the last application residues of propineb were in the range <0.01 to 0.03 mg/kg, and those of PDA 0.06 to 0.72 mg/kg. The results are shown in Table 5. Residues of PTU were below the lower limit of determination (0.01 mg/kg) in every sample.

Table 5. Residues of propineb in melons from supervised trials in Australia and Japan.

Country, Year	Application		Residues (mg/kg) at days after last application							Ref.	
	No.	kg ai/ha	Residue	1	3	5-6	7-8	9-14	21		28
AUL, 1985	7	1.4	CS <sub>2</sub>	0.3	0.4	0.4	<0.2	<0.2			12/85A 12/85B
	7	2.8	CS <sub>2</sub>	1.4	0.8	0.4	<0.2	<0.2			
AUL, 1985	8	1.4	CS <sub>2</sub>	1.3	0.3	0.2	<0.1	<0.1			56/85A 56/85B
	8	2.8	CS <sub>2</sub>	0.4	0.5	0.5	<0.1	<0.1			
JPN, 1977	3	2x2.63 3.5	CS <sub>2</sub> PDA					<0.03 0.06- 0.15*		<0.03 0.18- 0.42*	N559 A N560 A
	5	3x2.63 2x3.5	CS <sub>2</sub> PDA				<0.03 0.18- 0.4*		<0.03 0.38- 0.72*		N559 B N560 B



JPN, 1977	3	3.0	CS <sub>2</sub> PDA					<0.03 0.09- 0.3*		<0.03 0.16	N562 A N563 A
	5	3.0	CS <sub>2</sub> PDA					<0.03 0.17- 0.32*		<0.03 0.20- 0.38*	N562 B N563 B
JPN, 1984	4	3.5	CS <sub>2</sub>	0.1			0.02				N1097
JPN, 1984	4	3.5	CS <sub>2</sub>	0.03		<0.01					N1098

\* Samples were analyzed in two laboratories.

**Tomatoes.** A total of 14 supervised trials were conducted in Germany in 1978, 1982 and 1987. Antracol 70 WP was applied 4 to 6 times at rates of 0.84 to 2.94 kg ai/ha. When the treatments were according to German GAP, seven days after the last application residues of propineb ranged from 0.08 to 0.55 mg/kg and those of PTU were at or below the lower limit of determination of 0.02 mg/kg (Table 6).

**Potatoes.** A summary of 9 supervised residue trials in Germany was provided. Three trials were conducted in 1971 in which 3 sprays, each at 1.68 kg ai/ha, were applied. No residues of propineb were found above the lower limit of determination (0.2 mg/kg) after 8, 48 or 69 days. In a further three residue trials in 1973, where 1.26 kg ai/ha was applied 4-5 times, no residues of propineb were measured above the lower limit of determination (0.1 mg/kg) after 22, 51 or 60 days. In 1979, 3 residue trials were carried out in which 8 sprays, each at 1.26 kg ai/ha, were applied. The analyses showed no measurable amounts of either propineb (<0.04 mg/kg) or PTU (<0.01 mg/kg) 7 days after the last treatment.

7 supervised trials were conducted in Australia with rates between 1.1 and 2.8 kg ai/ha applied up to 9 times per season. Although Australian GAP allows a maximum of 7 applications at 2.1 kg ai/ha, no residues of propineb could be detected in the potatoes. The results are comparable to those found in the German trials.

Table 6. Residues of propineb in tomatoes from supervised trials with Antracol 70 WP applied in 0.14 kg ai/hl in Germany.

Sample, Year	Application		Resi- due	Residues (mg/kg) at days after last applicn.						Ref.
	No.	kg ai/ha		0	1	3	4-5	7	10-14	
fruit,1978	6	0.84; 2x1.26; 3x1.68	CS <sub>2</sub> PTU	0.66 0.04	0.22 0.05		0.3 0.05	0.08 0.02	<0.05 0.02	8005-78
fruit,1978	6	0.84;2x1.26; 3x1.68	CS <sub>2</sub> PTU	0.54 0.03	0.43 0.05		0.38 0.04	0.32 0.02		8017-78
fruit,1982 juice ketchup	4	0.84; 1.68; 2.52; 2.94	CS <sub>2</sub> PTU CS <sub>2</sub> PTU CS <sub>2</sub> PTU					0.3 0.04 <0.05 0.02 <0.05 0.02		8019-82
fruit,1982 juice ketchup	4	0.84; 1.68; 2.52; 2.94	CS <sub>2</sub> PTU CS <sub>2</sub> PTU CS <sub>2</sub> PTU					0.2 0.01 <0.05 <0.01 <0.05 <0.01		8020-82
fruit,1982 juice ketchup	4	2x1.68; 2x2.52	CS <sub>2</sub> PTU CS <sub>2</sub> PTU CS <sub>2</sub> PTU					0.7 0.03 <0.05 0.02 <0.05 0.01		8021-82
fruit,1982 juice ketchup	4	0.84; 1.68; 2.52; 2.94	CS <sub>2</sub> PTU CS <sub>2</sub> PTU CS <sub>2</sub> PTU					0.6 0.04 <0.05 0.02 <0.05 0.02		8022-82
fruit,1982 juice ketchup	4	2x1.68; 2x2.52	CS <sub>2</sub> PTU CS <sub>2</sub> PTU CS <sub>2</sub> PTU					0.8 0.03 <0.05 0.02 <0.05 0.02		8023-82
fruit,1982	4	2x1.68; 2x2.52	CS <sub>2</sub> PTU					0.7 0.03		8024-82

Sample, Year	Application		Resi- due	Residues (mg/kg) at days after last applicn.						Ref.
	No.	kg ai/ha		0	1	3	4-5	7	10-14	
juice			CS <sub>2</sub>					<0.05		
ketchup			PTU					0.01		
			CS <sub>2</sub>					<0.05		
			PTU					0.02		
fruit,1987	4	0.84; 1.26; 2x1.68	CS <sub>2</sub>	1.5		0.41	0.44	0.55	0.22	8005-87
			PTU					<0.02	<0.02	
fruit,1987	4	4x1.26;	CS <sub>2</sub>	0.80		0.39	0.21	0.06	<0.05	8006-87
			PTU					<0.02	<0.02	
fruit,1987	4	0.84; 1.26; 2x1.68	CS <sub>2</sub>	0.87		0.38	0.20	0.11	<0.05	8007-87
			PTU					<0.02	<0.02	
fruit,1987	4	0.84; 1.26; 2x1.68	CS <sub>2</sub>	0.83		0.61	0.57	0.29	0.40	8055-87
			PTU					0.02	0.02	
fruit,1987	4	4x1.26	CS <sub>2</sub>	0.65		0.24	0.22	0.15	0.18	8056-87
			PTU					<0.02	<0.02	
fruit,1987	4	0.84; 1.26; 2x1.68	CS <sub>2</sub>	0.45		0.29	0.21	0.14	0.06	8057-87
			PTU					<0.02	<0.02	

### FATE OF RESIDUES

#### In processing

The effects of processing on propineb residues were studied with various crops. Transfer factors were calculated which indicate the relation between the residue concentrations in the processed product and the initial commodity (Walz-Tylla, 1992). The average ratio of PTU to propineb in raw commodities (P), and transfer factors (F), number of trials (n) and standard deviation of the factors ( $s_{n-1}$ ) are summarized in Table 7.

Table 7. Transfer factors for propineb and PTU from raw to processed products (propineb/propineb, PTU/propineb, and PTU/PTU).

Commodity/compound		P <sup>1</sup>	F	n	S <sub>n-1</sub>
Raw	Processed				
Apple/propineb	Apple/PTU	0.06		7	0.03
Apple/propineb	Puree/PTU		0.04	6	0.03
Apple/PTU	Puree/PTU		0.7	6	0.29
Cherry/propineb	Cherry/PTU	0.2		5	0.2
Cherry/propineb	Jam/propineb		0.4	4	0.16
Cherry/propineb	Juice/propineb		0.4	3	0.25
Cherry/propineb	Jam/PTU		0.1	4	0.13
Cherry/propineb	Juice/PTU		0.2	4	0.25
Cherry/PTU	Jam/PTU		1.2	4	1.2
Cherry/PTU	Juice/PTU		1.9	4	2.27
Grape/propineb	Grape/PTU	0.08		45	0.087
Grape/propineb	Must/propineb		0.5	38	0.51
Grape/propineb	Wine/propineb		*	52	
Grape/propineb	Must/PTU		0.2	40	0.28
Grape/propineb	Wine/PTU		0.2	47	0.21
Grape/PTU	Must/PTU		3.1	37	4.49
Grape/PTU	Wine/PTU		3.6	43	5.23
Hop/propineb	Hop/PTU	0.03		5	0.013
Hop/propineb	Beer/PTU		0.003	10	0.005
Hop/PTU	Beer/PTU		0.08	4	0.049
Tomato/propineb	Tomato/PTU	0.09		13	0.06
Tomato/propineb	Ketchup/PTU		0.2	13	0.34
Tomato/propineb	Juice/PTU		0.1	12	0.15
Tomato/PTU	Ketchup/PTU		1.5	12	1.52
Tomato/PTU	Juice/PTU		0.9	10	0.75

\* No residue was detected in the wine.

<sup>1</sup> PTU/propineb in raw commodity.

Apples were processed to juice and puree according to household procedures. After sorting, washing and cutting the apples they were crushed in a punched disc mill produce puree, which was separated in a high-pressure press into juice and pomace. The juice was then pasteurized at 85°C for 15 to 150 seconds.

It was found that propineb residues in fruit (up to 1.0 mg/kg) were reduced below the lower limit of determination (0.05 mg/kg) during processing to apple juice and puree. The residues of PTU in apple juice and puree ranged from <0.01 mg/kg to 0.025 mg/kg and were similar to or marginally less than the residues found in fruit 21 days after the last treatment.

Grapes were processed to must and wine according to the BBA-Guideline part IV, 3-3.4. Propineb residues were significantly reduced by processing, while PTU residues were generally increased in the must and wine.

Grapes were also processed to raisins by drying grapes in the air in Turkey. The results show that during the production of raisins the concentration of propineb residues was markedly reduced, while PTU residues remained at or about the lower limit of determination (<0.01 mg/kg) in all analyzed commodities.

Tomatoes were processed to juice and puree according to industrial procedures. After sorting, washing, cutting and blanching the tomato pulp

water was added and the mixture was heated for 2 to 5 minutes at 70°C.

To obtain ketchup the tomato pulp was strained and concentrated, and other ingredients were added. After canning, the tomato ketchup was pasteurized at 93°C for 5 to 10 minutes.

To produce juice the tomato pulp was strained and sodium chloride was subsequently added. After canning, the juice was pasteurized at 93°C for 5 to 10 minutes.

No residues of propineb could be detected in the juice or ketchup, showing a substantial reduction from the residue found in the fruit (0.11 to 0.70 mg/kg).

In all 6 trials the residues of PTU in the juice and ketchup were similar to the levels found in the fruit (0.01-0.04 mg/kg) at a 7-day pre-harvest interval.

## METHODS OF RESIDUE ANALYSIS

### Propineb

Residues of fungicides belonging to the dimethyldithiocarbamate and ethylene-bis(dithiocarbamate) groups can be determined by colorimetric as well as gas-chromatographic methods.

Several colorimetric methods for the residue analysis of propineb have been developed. Some of these were referred to in the 1977 and 1984 JMPR monographs (Keppel, 1969; Otto *et al.*, 1977; Thier, 1977). The principle of these methods is the determination of propineb by acid decomposition and spectrophotometric measurement of the evolved carbon disulphide (CS<sub>2</sub>). The method of Thier (1979) is based on the same principle and is suitable for enforcement purposes.

Nakahara and Aizawa (1978) developed a gas-chromatographic method for the determination of propineb residues in crops. The method is based on the measurement of the carbon disulphide (CS<sub>2</sub>) and propylenediamine (PDA) produced by acidic hydrolysis in the presence of stannous chloride. The CS<sub>2</sub> is quantified by GLC in a gas chromatograph equipped with a flame-photometric detector. After derivatization to 1,2-bis(trifluoroacetamido)propane, PDA is determined by GC-MS with selective ion monitoring. A modified version of this method has been validated by Specht (1993) in apples, grapes, grape juice, wine, potatoes and tomatoes. The recoveries ranged from 71 to 113%. The limit of determination was 0.05 mg/kg.

### Propylenethiourea (PTU)

Kobayashi *et al.* (1981), Ohs (1988) and Meier (1982) described methods for the determination of ethylenethiourea (ETU) and propylenethiourea (PTU) in plant materials and their processed products, especially beer and wine.

In these methods the residues are determined by HPLC with UV detection after extraction and clean-up. The recoveries ranged from 70 to 110%. The limit of determination was reported as 0.02 mg/kg in plant commodities and 0.004 mg/kg in beer, wine and fruit juices.





## Section 2: Luxembourg - Yugoslavia

Commodity Country	LUX <sup>1</sup>	MAL <sup>1</sup>	MOZ	NET <sup>1</sup>	NZE	POR <sup>1</sup>	SAF <sup>1</sup>	SPA <sup>1</sup>	SWE <sup>1</sup>	SWI <sup>1</sup>	TAW	TUR	YUG
Apple											1		
Asparagus											0.1		
Aubergine											0.5		
Bamboo											0.1		
Banana											1 0.2		
Bean												2	
Bell pepper											0.5	1	
Berries + Small fruits				3									
Boysenberry							3						
Bulb vegetables				0.5									
Carrot									0.5		0.1		
Cereals		0.5		0.5					0.1 <sup>3</sup>	0.1			
Cereals, processed									0.1 <sup>3</sup>				
Chick-pea												1	
Cucumber				1								1	
Dewberry							3						
Egg plant											0.5		
Fruit	2	5							1	2			2
Ginger											0.1		
Grape			3				3 2 <sup>4</sup>	4					
Grapefruit											1 0.2 <sup>5</sup>		
Hop								4					
Leafy vegetables		5											
Leguminosae				0.2									
Lemon											1 0.2 <sup>5</sup>		
Lettuce												1	
Lettuce, head				4						2			
Litchi											1 0.2 <sup>5</sup>		
Longan											1 0.2 <sup>5</sup>		
Loquat											1		
Mango											1 0.2 <sup>5</sup>		
Melon	1			1							1 0.2 <sup>5</sup>		
Melon, netted (musk)											1 0.2 <sup>5</sup>	1	
Melon, water-											1 0.2 <sup>5</sup>	1	
Nut, pea-							0.5						

Commodity Country	LUX <sup>1</sup>	MAL <sup>1</sup>	MOZ	NET <sup>1</sup>	NZE	POR <sup>1</sup>	SAF <sup>1</sup>	SPA <sup>1</sup>	SWE <sup>1</sup>	SWI <sup>1</sup>	TAW	TUR	YUG
Onion					0.5						0.1		
Orange											$\frac{1}{0.2^5}$		
Other fruits				2				3					
Other plant commodities	0.05			0				0.2					0.05
Other vegetables	2	3		2									
Papaya											$\frac{1}{0.2^5}$		
Pea, Chick-												1	
Peach											1		
Peanut							0.5						
Pear											1		
Pepper, Cayenne-											0.5	1	
Pineapple											$\frac{1}{0.2^5}$		
Plum											1		
Potato			0.5	0.2		0.05	0.5	0.2	0.1	0.05	0.1		
Pummelo											$\frac{1}{0.2^5}$		
Radish, small											0.1		
Root vegetables		1											
Strawberry								4					
Taro (Dasheen)											0.1		
Tobacco		25								50			2
Tomato	1		3				3				0.5	1	
Vegetables										2			2
Vegetables exc. carrots									1				
Vegetables exc. potatoes								3					

<sup>1</sup> Total dithiocarbamates expressed as CS<sub>2</sub>

<sup>2</sup> Produced for canning.

<sup>3</sup> Level at or about the limit of determination

<sup>4</sup> In export commodities

<sup>5</sup> Without peel

## APPRAISAL

Propineb was evaluated in 1977, 1984 and 1985. The temporary ADI was withdrawn by the 1985 JMPR, but the CCPR maintained the Guideline Levels for propylenethiourea (PTU). The compounds are included in the CCPR periodic review programme.

Propineb is currently registered on a large number of crops in several countries around the world, but the Meeting was informed that its actual use is restricted to a few crops. The results of numerous supervised field trials and processing studies were provided by the principal manufacturer only for grapes, tomatoes, potatoes, pome fruits, onions and melons. The use of the compound will still be recommended on these crops and on bell peppers, but the use recommendations for other crops are due to be withdrawn.

The metabolism in plants has been sufficiently presented in the 1984 Evaluations. The laboratory animal metabolism studies are discussed in the Toxicological Evaluations. The



metabolic pathways in plants and animals are essentially the same. Propylenediamine and 4-methylimidazoline identified in animals were present in the form of *N*-formylpropylenediamine and 2-methoxy-4-methylimidazoline, respectively. No information was available on metabolism by farm animals or on animal transfer studies.

In the supervised trials, propineb residues were determined and expressed as mg/kg CS<sub>2</sub>, and propylenethiourea (PTU) residues were determined and expressed as mg/kg PTU throughout.

In apples and pears, the residues of propineb ranged from <0.05 mg/kg to 0.96 mg/kg 14-21 days after the last treatment. For the main metabolite, PTU, the results were in the range of <0.02 mg/kg to 0.08 mg/kg. If propineb were used alone the estimated maximum residue levels on apples and pears would be 2 mg/kg propineb and 0.1 mg/kg PTU.

In grapes, at pre-harvest intervals ranging from 49 to 69 days, residues of propineb and PTU were between <0.05 and 1.2 mg/kg, and <0.01 and 0.08 mg/kg respectively, except in one trial where 2.1 mg/kg propineb and 0.15 mg/kg PTU were measured. Following a different application schedule, the residues of propineb were more or less in the same range. The variety of grape did not influence the residue levels. If propineb were used alone the estimated maximum residue levels on grapes would be 2 mg/kg propineb and 0.1 mg/kg PTU.

In onions, 14 days after the last treatment, no residues of propineb were found above the limit of determination (0.2 mg/kg) in Australia. PTU was not determined. In Japanese trials seven days after the last treatment the residues of propylenediamine (PDA) were <0.05 mg/kg in four samples and 0.05 and 0.08 mg/kg in two samples, while the residues of PTU were below the limit of determination (<0.01 mg/kg). Propineb was not determined. The data are not sufficient to estimate a maximum residue level for the use of propineb on onions.

In melons, 7 to 21 days after the last treatment the residues of propineb and PTU were below the limits of determination (0.01-0.2 and 0.01 mg/kg respectively) in all samples, while PDA ranged between 0.06 and 0.72 mg/kg. If propineb were used alone the estimated maximum residue levels in melons would be 0.2 mg/kg propineb and 0.05 mg/kg PTU, both levels being at or about the limit of determination.

In tomatoes treated according to German GAP, seven days after the last application residues of propineb ranged from 0.08 to 0.55 mg/kg and residues of PTU were at or below the limit of determination of 0.02 mg/kg. If propineb were used alone the estimated maximum residue levels in tomatoes would be 1 mg/kg for propineb and 0.05 mg/kg for PTU.

In potatoes no residues of propineb or PTU were found above the limits of determination (0.2 mg/kg and 0.01 mg/kg respectively) within 8 to 69 days after the last treatment. These residue trials do not completely correspond to the current registered uses but they cover present good agricultural practice as the application rate was higher. All trials showed that in spite of the great variations in pre-harvest interval no residues of propineb or the major metabolite PTU could be detected in potatoes. If propineb were used alone the estimated maximum residue levels in potatoes would be 0.2 mg/kg propineb and 0.05 mg/kg PTU (the limits of determination).

The effects of processing on the residues were extensively studied on apples, cherries, grapes, hops and tomatoes. These studies showed that the concentration of propineb residues was reduced to non-detectable (<0.02 mg/kg) in the case of apple juice and puree, wine, beer, and tomato juice and ketchup, while in cherry juice and jam the average propineb residue was 40% of that in the fruits. The residue level of PTU in processed products is primarily influenced by the level of propineb and the mode of processing. The ratio of PTU in the processed product to propineb in the raw commodity was 0.04 for apple puree, 0.003 for beer, 0.2 for cherry juice, 0.1 for cherry jam, 0.2 for must and wine, 0.1 for tomato juice and 0.2 for ketchup. The residue levels of PTU were higher in products where the processing involves extensive contact with the peel of the harvested crop as in red

wine and tomato ketchup.

The freezer storage stability of the residues in samples has not been studied systematically. However the Meeting was informed that the repeated analyses of samples analysed when taken and after prolonged freezer storage did not show any difference in the residue levels. Samples were always frozen whole before storage and homogenized deep-frozen before analysis in order to eliminate decomposition of the residues. The Meeting noted that this information provided on propineb residues was consistent with the results of frozen storage stability studies on mancozeb reported under that heading. It was also considered likely that the results of frozen storage stability studies on ETU would apply to PTU.

No information was reported on PTU levels in food moving in commerce or at consumption.

Residue analytical methods are available to determine propineb residues as CS<sub>2</sub>, using colorimetric or GLC detection, and PTU residues by HPLC. These methods are suitable for regulatory purposes with limits of determination of 0.1-0.2 mg/kg for CS<sub>2</sub> and 0.05 mg/kg for PTU. The propineb residues can be qualitatively distinguished from the other dithiocarbamates by converting them to propylenediamine which can be determined by gas chromatography after derivatization.

## RECOMMENDATIONS

On the basis of data on residues from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits. Since the origin of CS<sub>2</sub> cannot be identified, the maximum residue levels estimated for the dithiocarbamate group have to be taken into account.

Definition of the residue: propineb: CS<sub>2</sub>  
PTU: propylenethiourea

Commodity		Recommended MRL (mg/kg)					PHI (days)
		New			Previous		
		CS <sub>2</sub>	CS <sub>2</sub> <sup>1</sup>	PTU	CS <sub>2</sub> <sup>2</sup>	PTU	
FP 0226	Apple	3	(2)	0.1	3	0.1	21
VR 0578	Celeriac			w		0.05	
FS 0243	Cherry, sour			w	1	0.1	
FB 0269	Grapes	5	(2)	0.1	5	0.1	56
VC 0046	Melons	0.1*					7
VA 0385	Onion, bulb	0.2*		0.02*			7
FS 0247	Peach			w	3	0.05	
FP 0230	Pear	3	(2)	0.1	3	0.1	21
FS 0014	Plums (including Prunes)			w	1	0.1	
VR 0589	Potato	0.1*		0.02*	0.1	0.02	7
VO 0448	Tomato	3	(1)	0.05	3	0.1	7

<sup>1</sup> MRLs based on the current residue data from supervised trials.

<sup>2</sup> Codex MRLs for the group of dithiocarbamates (propineb was not included).

\* At or about the limit of determination.

## FURTHER WORK OR INFORMATION

### Desirable

1. Residue data from supervised trials on bell peppers.
2. Freezer storage stability studies on propineb and PTU residues in representative commodities.
3. Metabolism study on farm animals.
4. Residue transfer study on farm animals.
5. Monitoring data on PTU in food in commerce and at consumption.

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