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Stabilization of Thin Films of Pyrethrins and Allethrin

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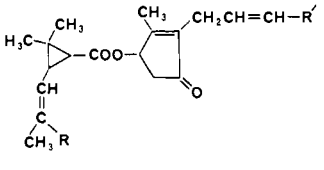
The combination of an antioxidant and an ultraviolet screening agent in a mineral oil formulation can significantly stabilize pyrethroids for at least 4 hr. Nonstabilized formulations show almost complete destruction in 4 hr.

Pyrethrins and analogous compounds have long been known as powerful insecticides, and are effective against a wide variety of arthropods. The term *pyrethroids* in this paper includes the natural insecticidal constituents of pyrethrin flowers, the pyrethrin, and the synthetic compound allethrin. For a review of the pyrethroids and their composition see Metcalf (1955) or Elliot (1969).



Most pyrethroids have the important practical aspect of a low order of toxicity to warm-blooded animals, and the advantage of a very low persistence of less than 4 hr. Low persistence is also disadvantageous—pyrethroids are highly unstable in the field; they rapidly convert to products having little insecticidal activity (Crowe *et al.*, 1961).

Their high instability when exposed to air and light (Stahl, 1960; Chen and Casida, 1969), as well as their high cost, have kept pyrethroids from finding much use in agriculture. Their primary use had been in the control of household pests, such as housefly, mosquito, and cockroach.

Many attempts have been made to stabilize pyrethroids and to prolong their effective life. The results evidently were not satisfactory, since they have not been commercially used. A few examples are the addition of trialkylphenols (Smith and Hill, 1947), the addition of 4-aminoazobenzene (Smith and Templin, 1956), and the addition of Food Yellow 10 (2,4-dihydroxyazobenzene) (Warner, 1963). Many other patents on stabilization are available, but none have been effective in the field, and are not used. The addition of Food Yellow 10 provides about 50% stabilization after exposure to sunlight for 4 hr, but has the undesirable feature of being a staining dye.

We have eliminated the use of staining dyes, and have discovered that the precise range of ultraviolet radiation that induces pyrethroid destruction is 290 to 320 nm. This range of photoreactivity in the near ultraviolet was found by measuring the transmittance of borosilicate glass and that of soft or window glass. Soft glass transmits radiation only above 300 nm, while borosilicate glass transmits radiation beginning at 290 nm. Pyrethroids were not destroyed when sunlight was filtered through soft glass, but were rapidly destroyed when exposed to sunlight filtered through borosilicate glass. Pyrethroids were not destroyed when exposed to the atmosphere in the dark, nor did any loss occur through evaporation. This difference explains the increased stability of pyrethrins in homes and greenhouses, and also corresponds to the erythermal spectra of sunlight (Das Gupta, 1962). Once this was realized we needed to find materials compatible with pyrethroids that would also be photostable and absorb in the 290 to 320 nm range.

The use of ultraviolet absorbers alone did not provide complete stability (Table II). Even more stabilization was provided by the use of certain oil-soluble antioxidants, although previous trials were not completely successful (Eddy, 1951; Head and Jones-Glynne, 1965; Bell and Kido, 1965).

METHODS AND MATERIALS

The primary materials tested were 20% purified pyrethrins (Fairfield Chemical Co., and the McLaughlin Gormley King Co.) and allethrin (City Chemical Co.). The stock solutions were refrigerated in dark brown bottles; they remained stable

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Table I. Percent of Cinerin I, Pyrethrin I, and Allethrin Found after Exposure to Sunlight for 4 Hr

Composition	Cinerin I	Pyrethrin I
1% pyrethrins in:		
Hexane	6	2
Kerosene	7	4
n-butyl phthalate	7	13
Mineral oil	67	59
Isopar 450	34	34
10% ethylene glycol monobutyl ether in Isopar M (Humble Oil)	6	2
10% ethylene glycol monobutyl ether in mineral oil	66	49
1% allethrin in:		
Hexane	4	

for more than a year. Diluted samples were made daily and discarded after use. Chemical composition was determined by gas–liquid chromatography using a $^1/_8$-in. o.d. glass column containing Chromosorb W 60/80 mesh coated with 5% S.E. 30 at a temperature of 190°C using an electron capture detector (Donegan *et al.*, 1962; Head, 1966). The test formulations were uniformly coated upon 2- × 8-in. glass slides using 1.0 ml total volume to apply 10 mg of pyrethroid. These slides were exposed to sunlight for 4 hr or until such times as most of the unstabilized pyrethroids had broken down. The light mineral oil we used is available under the trade name Klearol (Sonnenborn Co.).

The test formulations were made to contain 1% weight to volume of each of the additives, such as antioxidants, light absorbers, and pyrethroids.

After exposure, the residue was recovered by washing the slides with distilled *n*-hexane and diluting to volume so that

Table II. Percent of Cinerin I and Pyrethrin I Found in Combination of Pyrethrins and Additives after Exposure to Sunlight for 4 Hr. Pyrethrins, Antioxidants, and uv Screens Present in 1% Weight to Volume Concentration

Composition	Cinerin I	Pyrethrin I
Pyrethrins with:		
Amyl para-dimethylaminobenzoate in hexane	47	31
Amyl para-dimethylaminobenzoate in mineral oil	77	65
Glyceryl para-aminobenzoate in hexane	43	20
Ethyl cinnamate in hexane	10	16
Ethyl cinnamate in 10% ethylene glycol monobutyl ether in mineral oil	62	59
Ethyl cinnamate in mineral oil	93	72
Benzyl cinnamate in 10% ethylene glycol monobutyl ether in mineral oil	79	68
Benzyl cinnamate in mineral oil	80	71
Isobutyl cinnamate in kerosene	10	16
Isobutyl cinnamate in *n*-butyl phthalate	15	31
Isobutyl cinnamate in 10% ethylene glycol monobutyl ether in mineral oil	68	60
Isobutyl cinnamate in mineral oil	77	65
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone in kerosene	42	35
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone in *n*-butyl phthalate	11	28
Isobutyl cinnamate + 2,6-dioctadecyl para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	72	66
Isobutyl cinnamate + 2,6-dioctadecyl para-cresol in mineral oil	88	66
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl para-cresol in 10% dibutyl phthalate in mineral oil	90	94
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	95	96
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl para-cresol in 10% ethylene glycol	96	62
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl para-cresol in 10% ethylene glycol monobutyl ether in isoparaffin—450	67	82
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl para-cresol in hexyl alcohol	81	71
2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid + 2,6-dioctadecyl para-cresol in 1% ethylene glycol monobutyl ether in mineral oil	90	85
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone in 10% ethylene glycol monobutyl ether in mineral oil	93	77
2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid in *n*-butyl phthalate	8	27
2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid in 10% ethylene glycol monobutyl ether in mineral oil	96	34
2,6-Di-*tert*-butyl-4-methylphenol in hexane	14	55
2,6-Dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	76	63
2,6-Dioctadecyl-para-cresol in mineral oil	94	78
Amyl para-dimethylaminobenzoate + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	80	58
Amyl para-dimethylaminobenzoate + 2,6-dioctadecyl-para-cresol in mineral oil	102	83
Ethyl cinnamate + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	79	78
Ethyl cinnamate + 2,6-dioctadecyl-para-cresol in mineral oil	97	80
Benzyl cinnamate + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	93	90
Benzyl cinnamate + 2,6-dioctadecyl-para-cresol in mineral oil	103	92

5 μl contained approximately 50 ng. The pyrethrins were quantized by using a disc integrator and the cinerin I and the pyrethrin I peaks from previously prepared calibration samples. Cinerin II and pyrethrin II peaks were not quantized. Tables I–IV showing the results of the additives therefore are characterized by the larger cinerin I and pyrethrin I peaks; allethrin is characterized by a single major peak.

Tables I–IV do not include the large number of antioxidants and light absorbers that did not show adequate stabilization, although they met the criteria of being antioxidants or uv screens in the critical 290 to 320 nm range.

DISCUSSION

The mechanism for photodecomposition of pyrethroids has not been elucidated completely by Chen and Casida (1969), however, they state that the acid portion of the molecule is oxidized stepwise to yield esters of *trans*-caronic acid. This mechanism is preferred over that proposed by Sasaki *et al.* (1968) for methyl *trans*-chrysanthemumate. Chen and Casida did not find *cis*-chrysanthemumic acid or *meso,cis*-caronic acid. Since oxidation occurs in the acid, the use of an antioxidant and a photoscreen seemed desirable to preserve pyrethroids.

For optimum stabilization of pyrethroids, a combination of antioxidants, solvent, and ultraviolet absorbant should be used. Many combinations of antioxidants and uv absorbers will provide enough stability (Table II), but not if each agent is used singly. The solvent selected is an equally important agent. In these tests, mineral oil was the preferred solvent for stability. It may be that a saturated paraffin is quite nonreactive and does not produce peroxides as do ketones or ethers.

The most useful of the uv screening agents are: first, the aromatic ketones in which two aromatic nuclei are attached directly to an oxogroup, *e.g.*, the derivates of benzophenone; and second, the esters of aromatic acids, *e.g.*, the esters of substituted benzoic acids. When antioxidants were incorporated into mixtures of pyrethroid toxicants and uv screening agents, we observed the greatest stabilization with those possessing an hydroxyl group attached directly to an aromatic nucleus and having 14 or more carbon atoms, *e.g.*, 4-methyl-2,6-di-*tert*-butylphenol or 2,6-dioctadecyl-para-cresol. Table IV shows the effect of sunlight on the toxicity of formulation with and without stabilization additives. It can also be seen that sun exposure readily destroys the toxic action of pyrethrins.

Stabilization of allethrin does not use mineral oil as a solvent (Table III). But if the other work with pyrethrins is comparable, stability should greatly improve with mineral oil as a solvent.

Combinations of 2,6-dioctadecyl-para-cresol and 2-hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone with pyrethrins have been field-tested. In 1969, applications of this formulation gave good control of hemlock looper (Mason, 1970). In the summer of 1970, the Canadian Department of Forestry and Fisheries obtained satisfactory control of spruce budworm (*Choristoneura fumiferana*), a major defoliator of eastern forests (Fettes, 1971).

Table III. Percent of Allethrin Remaining after 4 Hr Exposure to Sunlight. Allethrin, Antioxidant, and uv Absorber Present in 1% Weight to Volume Concentration

Composition	Allethrin
Allethrin + 2-hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone in 10% ethylene glycol monobutyl ether in isopar "M"	66
Allethrin + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in isopar "M"	42
Allethrin + 2-hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone in 1% ethylene glycol ether in isopar "M"	84

Table IV. Effect of 4 Hr of Sunlight Exposure on Toxicity of Pyrethrins Formulation to Western Spruce Budworm. Pyrethrins, Antioxidants, and uv Absorber Present in 1% Weight to Volume Concentration

Composition	Percent dead after 7 days	
	Unexposed	Exposed
Pyrethrins in combination with:		
Hexane (control)	100	10
2-Hydroxy-4-(2-hydroxy-3-methacrylyloxy)propoxybenzophenone + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl in mineral oil	100	100
Amyl para-dimethylaminobenzoate + 2,6-dioctadecyl-para-cresol in 10% ethylene glycol monobutyl ether in mineral oil	100	100

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