

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: **JL 20 1981**

SUBJECT: PP#1E2510/FAP#1H5309. DDVP in or on figs. Evaluation of analytical methodology and residue data.

FROM: M. Nelson, Ph.D., Chemist  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)

*mjn*  
*7/17/81*

TO: Minor Uses Officer  
Registration Division (TS-767)  
and  
Toxicology Branch  
Hazard Evaluation Division (TS-769)

THRU: Charles L. Trichilo, Chief  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)



IR-4, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Station of California, proposes the establishment of tolerances for residues of the insecticide 2,2-dichlorovinyl dimethyl phosphate [aka DDVP; dichlorvos (ISO); Vapona®] in or on the r.a.c. figs at 0.1 ppm and the processed commodity dried figs at 0.5 ppm.

Tolerances are established (40 CFR 180.235; 21 CFR 193.140) for residues of DDVP in or on various commodities, including meat, milk, poultry, and eggs, at levels ranging from 0.02 to 2 ppm.

A letter of authorization from Shell permits use of registration files 201-125 (Technical Vapona® Insecticide) and 201-235 (Vaponite® 2 Emulsifiable Insecticide) in support of this present petition request.

DDVP is an RPAR chemical.

Conclusions

1. The nature of the residue is adequately understood.
2. Adequate analytical methodology exists to enforce the proposed tolerances.
3. The proposed tolerance levels are appropriate in conjunction with the proposed use pattern.
- 4a. There are no recognized animal feed items associated with figs. There is thus no reasonable likelihood of finding secondary residues in meat, milk, poultry, or eggs from this source.
- 4b. A restriction should be added to the proposed label text to preclude the possibility of grazing in treated fig orchards.
5. The IRL Status sheet is attached.

Recommendation

Contingent upon receipt of a suitably revised Section B (see Conclusion 4b), and provided TOX and EFB considerations permit, we recommend that the proposed tolerances on figs (@ 0.1 ppm) and dried figs (@ 0.5 ppm -- food additive) be established.

DETAILED CONSIDERATIONS

Manufacture and Formulation

DDVP is manufactured [redacted] The technical material contains a minimum of 96% DDVP, [redacted] (See EPA Reg. No. 201-125, Vapona® Insecticide.)

The formulation associated with the proposed use is Vaponite® 2 Emulsifiable Insecticide (EPA Reg. No. 201-235), which contains 2 lbs of DDVP as a.i. per gallon.

The most recent (11/23/77) confidential statement of formula indicates the composition of the Vaponite® 2 Emulsifiable Insecticide formulation to be: DDVP, 23.0%; related compounds, 1.7%; [redacted]

[redacted] The inerts are cleared for use under 40 CFR 180.1001.

Proposed Use

For controlling populations of Nitidulids (beetles) and Drosophila (flies) in fig orchards, apply Vaponite® 2 at the rate of 2 lbs a.i./A. (Use one gallon of formulation in 300-400 gallons of water per acre.)

Make full coverage application at beginning of harvest and repeat at 4-5 day intervals.

Do not make more than 5 applications. Do not apply within 5 days of harvest.

There is no grazing restriction included in the proposed directions for use. Information in our cultural practices file on figs would lead us to believe that there is little likelihood of a cover crop being present in a fig orchard (see 1/31/74 communique from the CA Fig Institute). In any case, it seems especially unlikely that any grazing would be allowed at the time of fig harvest (which is when applications are to be made) since some of the fruit would be on the ground. Nonetheless, as a precautionary measure--and for consistency in our policy re orchard grazing restrictions--we request a statement be added to the label to preclude grazing in treated fig orchards.

MANUFACTURING PROCESS AND INERT INGREDIENT INFORMATION ARE NOT INCLUDED

### Nature of the Residue

No metabolism information was provided with this petition, and the letter of authorization from Shell Chemical to access their DDVP files is too limited in nature to permit our use of their metabolism data for support purposes here.

Information is available, however, in the published literature (see Codex Monographs for 1965 and 1967).

DDVP is rapidly converted in plants (by hydrolysis) to dimethyl phosphoric acid and dichloroacetaldehyde. The latter is further degraded to dichloroethanol (by hydrolysis) and dichloroacetic acid (by oxidation).

Losses of DDVP residues in plants also occur (from the plant surface) by volatilization.

We consider the nature of the residue in figs to be adequately defined, based on translation of the plant metabolism information contained in the referenced sources.

### Analytical Methodology

Residue data were obtained from field trials conducted in 1976, 1978, and 1979. The most extensive study was that conducted in 1979, and the methodology used for the residue analyses in that study was identified as Method RM-3G-3 (2/23/73): "Analysis of Naled and DDVP Residues", Chevron Chemical Company.

That method, which was reportedly modified to be applicable for the quantitative residue analysis of DDVP in or on figs at a method sensitivity level of 0.005 ppm, consists in brief of: solvent extraction of acidified crop tissue; liquid-liquid partitioning clean-ups; and, determination of the DDVP present by AFID-GLC.

Recovery studies by the methodology were made by fortifying control fig macerates (prior to extraction) at the level of method sensitivity (0.005 ppm), and at 5X (0.025 ppm) and 50X (0.25 ppm) that level with DDVP. Recoveries ranged 80-88%. Control values were <0.005 ppm.

A frozen storage fortification study run at those same levels for ca 6 weeks yielded recoveries of 80-100% by the methodology. (Field-treated samples were actually frozen stored 3-8 months prior to extraction and analysis.)

Fig samples from the 1978 field trial were analyzed by a procedure utilizing a flame photometric detector, as reported in Volume VI, Gas Chromatographic Analysis Analytical Methods for Pesticides and Plant Growth Regulators, edited by G. Zweig, Academic Press, pp.537-538 (year not given).

A few of those samples were also analyzed by the Shell procedure (discussed above) for comparison purposes of the two methodologies; the levels of residues obtained were reportedly the same, regardless of methodology used.

No specific information was provided as to the analytical procedure utilized for DDVP residue determinations in the 1976 field trial, other than to mention it was a GLC method. We note that the sensitivity level of the procedure was  $\leq 0.01$  ppm.

PAM II also contains a GLC procedure (microcoulometric detector) suitable for residue analysis (and enforcement purposes) of DDVP residues. That procedure, however, is 10X less sensitive (i.e., sensitivity is reportedly 0.05 ppm) than the AFID-GLC procedure (Method RM-3G-3) discussed herein.

Methodology is also available to distinguish DDVP from Naled, in the event it is needed for specificity purposes (microcoulometric GLC; JAOAC 48, 748 (1965)).

We conclude that adequate analytical methodology exists to enforce the proposed tolerances.

#### Residue Data

Residue data for DDVP residues in or on figs (fresh, air-dried/ground-dried, and dehydrated/commercially dried) are submitted from field trials conducted in CA in 1976, 1978, and 1979. (Note: CA produces more than 99% of the USA fig crop according to information in our Cultural Practices File.)

1979. The 1979 tests were conducted to show the magnitude of DDVP residues in fresh figs (the r.a.c.), air-dried (ground-dried) figs, and commercially dried figs following multiple applications at dosage rates of 2 lbs a.i./A (1X rate) and 4 lbs a.i./A (2X rate). For the 1X dosage, Vaponite® 2 was applied to fig trees at the rate of one gallon of Vaponite® 2 in 300 gallons of water per acre. Five applications were made at 5-day intervals and samples of fresh figs were harvested 5 days after each application, i.e., immediately before the next application. A portion of each harvest sample was allowed to air-dry (ground-dry) for a few days (which is the standard practice) and then rinsed and commercially dried (48 hours at 120°F). Samples of the fresh figs, the ground-dried figs, and the commercially dried figs were taken after each application for residue determinations. The procedure was the same for the 2X dosage rate.

The results show that residues of DDVP on fresh figs five days after application of the insecticide at the 1X rate do not exceed 0.02 ppm after multiple (5) applications at 5-day intervals. Even at the 2X dosage rate, residues do not exceed 0.05 ppm after multiple applications.

The results also show that residues of DDVP on air-dried (ground-dried) figs from the 1X dosage rate do not exceed 0.25 ppm after multiple (5) applications. At the 2X dosage rate, residues do not exceed 0.53 ppm after multiple applications.

The commercially dried (dehydrated) figs showed substantially lower residues of DDVP than the air-dried figs, as would be expected since the commercial dehydration takes place after the figs have been air-dried on the ground for several days before being harvested. Even at the 2X dosage rate, the maximum DDVP residue found was 0.054 ppm on a sample of figs that received 5 applications at the 2X dosage rate.

A degradation study on fresh figs was also conducted during these 1979 trials. Vaponite® 2 was applied at 2 lbs. a.i./A and samples taken at 1, 2, 4, 6, and 10 days after application. Residues of DDVP shortly after application (0-day) showed 0.72 ppm. These residues declined to less than 0.1 ppm within 2 days and to less than 0.005 ppm within 6 days.

1978. One phase of the 1978 tests was conducted to determine the magnitude of DDVP residues in dried figs following a single application of Vaponite® 2 at a dosage rate of 2 lbs a.i./A. Samples were collected immediately after application (0-days) and at intervals of 1, 3, 5, 7, and 10 days after application. After collecting the samples, they were washed and then dried at 120°F for 48 hours. These dried samples showed only 0.12 ppm DDVP residues at 0 days and only trace residues (0.01 to 0.04 ppm) at other sampling intervals.

The other phase of the 1978 tests was conducted to determine the magnitude of DDVP residues in dried figs following multiple applications of Vaponite® 2 at 2 and 4 lbs. a.i./A. Four applications were made at 5 day intervals for each dosage. Residue samples were taken 5 days after each application and immediately prior to the 2nd, 3rd, and 4th treatments. Each harvest sample showed only trace levels of DDVP in each sample of dried figs, ranging between 0.01 and 0.05 ppm.

1976. In the 1976 tests, five applications of Vaponite® 2 were made at 5-day intervals to growing figs at a dosage rate of 2 lbs. a.i./A (1X rate) and 4 lbs a.i./A (2X rate) and samples taken for residue analysis after the first, third, and fifth applications. The samples collected after the first and third applications consisted of figs taken directly from the trees; i.e., fresh. The samples collected after the fifth application were taken from the ground and represented ground-dried (air-dried) figs. For the first two sampling periods, samples of figs were taken shortly after application (0-days) and at intervals of 1, 2, and 3 days after application. The data show that residues of DDVP dissipate rapidly from fresh figs and become negligible (<0.01 ppm) within 48 to 72 hours. The data also show that residues found after 3 applications at 5-day intervals show no higher residues than those found after a single application.

The samples taken after the fifth application represented typical harvest samples of figs that have fallen from the trees and allowed to air-dry before being mechanically harvested. These air-dried (ground-dried) figs show higher residues of DDVP. In these 1976 trials, the air-dried samples show that residues declined to about 1 ppm within 48 hours and to about 0.2 ppm (1X rate) to about 0.5 ppm (2X rate) after 72 hours. After 7 days, residues had declined to 0.03 ppm.

Comments. These residue data are adequate to support the proposed tolerance levels of 0.1 ppm for figs (fresh) and 0.5 ppm for dried figs (food additive) in conjunction with the proposed use pattern.

#### Residues in Meat, Milk, Poultry, and Eggs

There are no recognized animal feed items associated with figs. Accordingly, there is no reasonable likelihood of finding secondary residues in meat, milk, poultry, or eggs from this source. A label restriction (which we are requesting) will preclude any possibility of grazing in treated orchards.

#### Other Considerations

An International Residue Limit (IRL) Status sheet is attached. According to it, there are no relevant Canadian or Mexican tolerances; there is a Codex Proposal (step 9) for DDVP residues in or on "fruit" at 0.1 ppm. The tolerance proposed in this present petition for DDVP residues in or on figs (fresh--the r.a.c.) at 0.1 ppm is consistent with this.

Attachment

TS-769:RCB:M. Nelson:gs:X77324:CM#2:RM810:7/12/81  
cc: RF, Circ.(3), Nelson, Watts, FDA, TOX, EEB, EFB, PP#1E2510/FAP#1H5309  
RDI: Quick, 7/9/81: Schmitt, 7/10/81

