



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

PymSD/JSB

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

JUN 8 1989

MEMORANDUM

SUBJECT: PP# 9F3713, Amendment 1  
Guthion (Azinphos-Methyl) in or on Almond  
Nutmeats and Hulls; Revised label and the Analytical  
Chemistry Laboratory Report on Method Validation.

FROM: H. Fonouni, Ph.D., Chemist *H. E. Fonouni*  
Dietary Exposure Branch  
Health Effects Division (H7509)

THRU: Richard D. Schmitt, Ph.D., Acting Chief  
Dietary Exposure Branch  
Health Effects Division (H7509) *Richard D. Schmitt*

TO: D. Edwards, PM 12  
Insecticide-Rodenticide Branch  
Registration Division (H7505)

and

Insecticide-Rodenticide Support  
Toxicology Branch  
Health Effects Division (H7509)

The petitioner, Mobay Corporation, in a previous submission (pp# 9F3713) requested that the Agency amend 40 CFR 180.154 by increasing the current tolerance for the residues of O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3-(4H)-yl)methyl]-phosphorodithioate in/on almond hulls from 10.0 to 20.0 ppm. In addition, a revised use pattern whereby the preharvest interval is reduced from 60 to 28 days was proposed.

### CONCLUSIONS

1. A revised label has been submitted in which grazing of livestock in the treated fields within 21 days of the last treatment is prohibited.
2. The method, Mobay No. 69523, Addendum I, Section I. B. Oil Seed Crops, has undergone successful method validation, for quantification of the residues of guthion per se in/on almond nutmeats and hulls, by the Analytical Chemistry Branch using the modifications suggested by Mobay in a phone communication (refer to the Detailed Considerations, Modifications a-c). A revised method incorporating the subject modifications must be submitted expeditiously for inclusion in PAM II.
3. The Analytical Chemistry Branch (ACB) and DEB have noted two discrepancies between the information transmitted by telephone and the written communication provided recently by Mobay (letter of April 17, 1989) on the subject modifications. These include the volume of solvent used in separating guthion from its oxygen analog and the more efficient gas chromatographic column/conditions proposed in the recent communication (refer to the Detailed Considerations, DEB Comment No. 2, Deficiency No. 2).
4. DEB recommends inclusion of the gas chromatographic column/conditions reflected in the letter of April 17, 1989 as an alternative to those used for the method validation in the requested revised enforcement methodology (refer to conclusion 2). However, to assure a lack of decomposition/loss of guthion as a result of the higher temperatures used representative recovery data for guthion (almond nutmeats or hulls) as well as chromatograms (controls, standards, treated samples) reflecting use of the more recent column/conditions must be included in the revised method.

### RECOMMENDATIONS

DEB has no objection to the revised use pattern contingent upon submission of the modified analytical methodology reflected in aforementioned conclusions 2 and 4. It should be noted that, an increase in tolerance for the residues of O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3-(4H)-yl)methyl]phosphorodithioate in/on almond hulls is not required.

### NOTE TO PM

DEB recommends that, this memorandum be forwarded to the petitioner.

DETAILED CONSIDERATIONS

The pertinent deficiencies (conclusions) raised in DEB memorandum of 12/27/88 are followed by the petitioners's current response and DEB comments. The numbers used correspond to those in the previous memorandum.

Deficiency #1

DEB agrees with the revised use pattern contingent upon a label restriction prohibiting grazing of livestock in the treated fields within 21 days of the last treatment but, presently, recommends against raising the tolerance for the residues of O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3-(4H)yl)methyl]-phosphorodithioate in/on almond hulls from 10.0 to 20.0 ppm.

Mobay Response:

A revised label has been submitted in which grazing of livestock in the treated fields within 21 days of the last treatment is prohibited.

DEB Comment(s):

Deficiency 1 is satisfactorily addressed. It should be noted that, the deficiencies raised in the Residue Chemistry Chapter of Guthion Registration Standard (4/4/1986) are not pertinent to this revised registration. However, should the Agency alter the tolerance expression as a result of the registrant's response to the deficiencies raised in the Registration Standard, additional information/data might be required.

Deficiency #2

Since the current colorimetric enforcement method for plant commodities, Method II, PAM II, is not specific for the residue of concern, the petitioner should submit a nonconfidential copy of the new gas chromatographic methodology, Method 69523 with Addendum I, to be forwarded to the Agency's Analytical Chemistry Branch for validation and possible inclusion in PAM II. If the GLC method undergoes successful method validation, revision of tolerance for almond hulls would not be required.

Mobay Response:

2. The petitioner submitted a copy of Gas Chromatographic Method for Determination of Guthion<sup>R</sup> Residues in Plant Material, Mobay Method No. 69523, for method validation.

DEB submitted the method to the Analytical Chemistry Laboratory (ACL) requesting an expeditious method validation for the residues of guthion per se in/on almond nutmeats and hulls (memorandums of 3/6/89 by H. Fonouni).

ACB Response (Method Validation):

In a telephone conversation, C. Stafford (ACB) raised several questions concerning the methodology including a need for substituting benzene, a carcinogen, by an alternative solvent. As requested by RD (P. Jenkins) the issues raised were relayed by the reviewer (H. Fonouni) to Mobay Corporation (F. Sandie), and the petitioner's responses were transmitted by phone to ACB. The petitioner subsequently provided responses to the issues raised in a written format (letter of April 17, 1989). DEB submitted the correspondence to ACB for evaluation and requested that comments on the subject matter be included in the method validation report (memorandum of 5/10/89 by H. Fonouni).

The method, Mobay No. 69523, Addendum I, Section I. B. Oil Seed Crops, has undergone method validation by the Analytical Chemistry Branch with the following modifications as suggested by Mobay in a telephone communication (Memorandum of 5/15/89 by C. Stafford).

Modifications -

a. Toluene was substituted for benzene in the procedure.

b. Silica Gel Column for Separation of Guthion (PS) and Oxygen Analog (PO):

Step 2. Silica gel 100-200 mesh, Fisher Cat. No. 5-679 was utilized.

Step 3. 1/2 inch of anhydrous sodium sulfate was used instead of "superbrite beads".

Step 5. The column was rinsed with 150 ml toluene instead of 250 ml of benzene.

Step 6. Guthion was eluted with 100 ml toluene and 300 ml 2% acetonitrile in toluene instead of 250 ml 2% acetonitrile in benzene.

Step 7. Guthion oxygen analog was eluted with 300 ml 20% acetonitrile in toluene instead of 250 ml 20% acetonitrile in benzene (this step is not pertinent to this method validation).

It should be noted that, since toluene was substituted for benzene a higher temperature, 58 degrees C, was employed to remove the solvent (Step III.8.).

c. Since the gas chromatographic column reflected in the method was not commercially available, the following column/conditions were utilized.

Column:

J & W DB-608 megabore capillary column, 30 m X 0.55 mm i.d. X 0.83 micron (film thickness) with a direct flash evaporation injector liner.

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Conditions:

Carrier Gas - Nitrogen, 30 ml/min  
Injector T - 200 Degrees C  
Column T - 230 Degrees C  
Detector T - 200 Degrees C

The following information/data were provided by ACL (memorandum of 5/15/89 by C. Stafford).

Retention Time:

Guthion (PS) - 16 Min

Limit of Detection:

Almond nutmeats and Hulls - 0.05 ppm each

Average Recovery: (Calculated from the data provided by ACL)  
Almond nutmeats - 71.8% (range 65.7-75.7), for fortifications of 0.2 and 0.4 ppm.  
Almond Hulls - 97.1 (range 96.0-98.0) for fortifications of 10 and 19 ppm.

Time Required for Analysis:

Two days for a set of four samples.

DEB Comment(s):

1. The method, Mobay No. 69523, Addendum I, Section I. B. Oil Seed Crops, has undergone successful method validation, for quantification of the residues of guthion per se in/on almond nutmeats and hulls, by the Analytical Chemistry Branch using the aforementioned modifications, a-c. A revised method incorporating the subject modifications must be submitted expeditiously for inclusion in PAM II.

2. The Analytical Chemistry Branch (memorandum of 5/30/89) and DEB have noted two discrepancies between the information transmitted by telephone and the written communication provided recently by Mobay (letter of April 17, 1989) which include:

a. Silica Gel Column for Separation of Guthion (PS) and Oxygen Analog (PO):

Step 6. Use of 300 ml of 2% acetonitrile in toluene instead of 250 ml (a potential discrepancy).

b. Gas Chromatographic Measurement of Guthion and its Oxygen Analog

The proposed use of a more efficient gas chromatographic column/conditions instead of those indicated in the phone

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conversation and reflected in the aforementioned Modification C.

**Column:**

DB-1, 15 meter X 0.53 mm i.d. column having a 1.5 micrometer film thickness (J & W Scientific) with a direct flash injector liner.

**Conditions:**

Carrier Gas - Helium, 10 ml/min

Injector T - 260 Degrees C

Column T - 230 Degrees C

Detector T - 275 Degrees C

**Retention Times: (Reported by the Petitioner)**

Guthion - 5.0 Min.

Guthion Oxygen Analog - 3.8 Min

3. DEB recommends inclusion of the more efficient gas chromatographic column/conditions reflected in the preceding comment as an alternative to those used for the method validation in the requested revised enforcement methodology (refer to Comment 1). However, to assure a lack of decomposition/loss of guthion as a result of the higher temperatures used representative recovery data for guthion (almond nutmeats or hulls) as well as chromatograms (controls, standards, treated samples) reflecting use of the more recent column/conditions must be included in the revised method.

cc: Reading File, Circulation, Reviewer (H. Fonouni), PP# 9F3713, ISB/PMSD (E. Eldredge).

H7509:DEB:Reviewer(HF):CM#2,Rm803:557-7561:typist(hf): 6/7/1989.

RDI:Section Head:D. Edwards:6/7/1989:R.Loranger:6/7/89

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