Union Carbide's Agricultural Products Co., Inc., has proposed a tolerance of 0.3 ppm be established for combined residues of the insecticide-nematocide aldicarb and its cholinesterase-inhibiting metabolites aldicarb sulf oxide and aldicarb sulfone in/on the r.a.c., citrus (grapefruit, lemons and limes).

Presently, there is a tolerance of 0.3 ppm on the r.a.c. oranges (PP\# 6F1828/6(F5141), and a food additive tolerance of 0.6 ppm on dried citrus pulp (21 CFR 551.30). Tolerances of 0.002 ppm (milk) to 1 ppm (potatoes and sugar beet tops) are set on a number of other r.a.c.s (40 CFR 180.269).

Conclusion

1. The nature of the residue is adequately understood. Residues of concern are the parent, aldicarb, and its cholinesterase-inhibiting metabolites, aldicarb sulf oxide and aldicarb sulfone.

2. Adequate analytical methods are available for enforcement of the proposed tolerance.

3a. The submitted data will support the proposed tolerance of 0.3 ppm in/on the r.a.c. citrus (grapefruit, lemons, limes).

3b. The submitted citrus (limes and grapefruit) processing study supports the established tolerance of 0.6 ppm on dried citrus pulp. The residues in the other processed commodities will be covered by the r.a.c. tolerance of 0.3 ppm.

3c. Because lemon trees on the California coast flower continuously and the fruit is harvested many times per year, a revised label is necessary indicating a 30 day PHI for lemons.

4. The proposed use falls into Category 2 of Sec. 180.6(a) for meat and milk. Residues in meat and milk will be covered by established tolerances. No poultry feed items are involved here, therefore aldicarb and its anticholinesterase metabolite residues are not expected in poultry and eggs.
5. Presently, there is a general grazing restriction which reads, "Do not allow livestock to graze in treated areas before harvest." In our review of temporary PP# 6G1689 (M. J. Nelson, 1/8/76) for oranges, due to a lack of residue data on cover crops, a request was made to change the above grazing restriction to preclude all grazing in treated groves. This preclusion of all grazing was included in the petitioner's request for a permanent tolerance in/on oranges (PP# 6F1829, M. J. Nelson, 12/3/76).

Again, the general label restriction against preharvest grazing of treated areas must be expanded to preclude all grazing at any time from treated groves. Alternately, residue data for cover crops can be submitted and tolerance(s) proposed.

Recommendations

We recommend against establishment of the proposed tolerances until the deficiencies in Conclusions 3c and 5 are corrected.

Upon submission of the new label with a 30-day PHI for lemons, a grazing restriction at all times in treated groves, and TOX and BEE considerations permitting, we will be able to recommend for the proposed tolerance of 0.3 ppm in/on citrus fruits.

Detailed Considerations

Manufacture and Formulation

The products used are TRMIX 10G and TRMIX 15G. Inert ingredients are cleared for use under Sec. 190.1001.

The subject of nitrosamine contamination of technical aldicarb has been adequately addressed by Dr. R. J. Hummel (PP# 7F1995, 6/6/78).

Union Carbide has submitted an analysis of their starting material for aldicarb; however, N-nitrosamines were not analyzed. To make technical aldicarb, we see no problem with N-nitrosamine contamination from the above reaction. But the question of the presence or absence of N-nitrosamines in the starting material is still unanswered. However, because aldicarb does not fall into the two classes of compounds in which we are presently concerned with (see F. R. Vol. 42, #250, 12/29/77, p. 64531), we are not requesting additional analyses for N-nitrosamines for the
materials.

Proposed Use

For the control of citrus nematodes, use 10 lb. a.i./acre of TEMIK 15% Granular (TEMIK 15G) or 10 lb. a.i./acre of TEMIK 10% Granular (TEMIK 10G). The material is to be applied in a band along the dripline on both sides of the tree row by spreading the granules uniformly and immediately working into the soil (preferred method) or by shanking 2 to 3 inches deep using 4 to 6 inches on 12 inch centers. Band width should equal one-fourth tree row spacing.

For control of aphids, citrus rust mite, citrus red mite, and Texas citrus mite, rates of 4.45 to 10 lbs. a.i./acre of TEMIK 10G or TEMIK 15G are required. The pesticide is to be applied as above for citrus nematode control or by shanking in irrigation furrows using 2 shanks per furrow.

Only one application per year is recommended. Best control of indicated pests is attained when TEMIK is applied just prior to or during spring flush of foliage growth. General directions call for a 6-month crop restriction for soil treated with TEMIK and a livestock grazing restriction in treated areas.

Nature of the Residue

No additional metabolism studies were submitted with this petition. But labeled metabolism studies are available for plants (cotton, potatoes, spearmint, lettuce) and animals, and have been thoroughly discussed in previous petitions (R. S. Quick, PP# 8F0637, 11/29/67; R. S. Quick, PP# 9F0798, 4/1/69; D. V. Reed, PP# 2F1188, 6/13/72; M. J. Nelson, PP# 3F141A, 12/4/73).

More recent data on the metabolism of aldicarb sulfone, as Aldoxycarb (Standak) has been discussed in our memoranda by M. Nelson (PP# 9F2043/FAPP# 8H5178, 12/13/78 and PP# 9P2186, 7/19/79).

In summary, aldicarb is absorbed from soil and translocated in plants. Oxidation to aldicarb sulfoxide is followed by hydrolysis to the sulfoxide oxime and oxidation to aldicarb sulfone. Sulfoxides and sulfone oximes are also metabolized, in plants, to the corresponding nitriles, alcohols, amides and acids. The alcohols are conjugated to the respective water soluble glycosides. There is no evidence of free or conjugated hydroxymethyl derivatives of aldicarb, aldicarb sulfoxide or sulfone, or N-demethylated carbamate breakdown products in plants, and while present as minor metabolites in animals, are not of toxicological concern (G. E. Whitmore, PP# 2F1188, 3/20/72). The metabolism of aldicarb in animals appears to be essentially similar to that reported for plants.
The additional metabolism studies for aldicarb sulfone (aldoxycarb) review of M. Nelson (see references above) showed that methane sulfonic acid (MSA) is a significant metabolite and aldoxycarb amide is taken up in plants grown in treated soil and is present in rat urine. In both plants and animals, small amounts of the carbamate metabolite, N-hydroxymethyl aldoxycarb (aldoxycarb methylol) is detected.

Products of toxicological concern are the anti-cholinesterases aldicarb and its metabolites; aldicarb sulfoxide and sulfone. We consider the nature of the residue in plants and animals to be adequately defined.

Analytical Method

The analytical method used to determine aldicarb and aldicarb sulfoxide and sulfone is essentially the same as the enforcement method described in PAM II. Included were validation data indicating an average recovery of 88% for added aldicarb sulfoxide and sulfone.

The PAM II method consists of blending a 50g crop sample, add 200 ml of acetonitrile and 2.5 ml of 40% paractic acid. After 15 minutes, the mixture is filtered under vacuum, the dry filtered cake is blended for 5 minutes with 200 ml of fresh acetonitrile, filtered and the liquid extract divided into two equal parts. One part is discarded, the other part of the extract is evaporated at 40-50°C and 60-70 mm pressure. At room temperature, 30 ml of 10% sodium bicarbonate is added and the sample is partitioned with 35 ml dichloromethane and three 15 ml aliquots of chloroform. The combined extracts are concentrated to an oil residue of 3 ml. The oil residue is cleaned up using a Florisil column. After clean-up, 8 µl of sample is applied to a gas chromatograph packed with 5% carbonyl-20-M on 60/80 mesh Gas Chrom Q and aldicarb sulfone determined using a flame photometric detector.

For a confirmatory method, the non-polar 5% Apiezon-L Gas Chromatography column can be utilized.

A MTO has been performed using this method for cottonseed. Fortification levels were 0.05 ppm aldicarb, aldicarb sulfoxide and aldicarb sulfone, respectively. Recoveries averaged 97% (68-112%) for the three fortified pesticides (R. S. Quick MTO memorandum, 5/13/69).

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

Residue Data

Residue data was submitted for aldicarb, and its metabolites of concern (reported as aldicarb), in/on limes, lemons and grapefruit. Areas represented are the major citrus-growing states of California, Texas, and Florida. A citrus processing study on limes and grapefruit was also submitted. Storage stability studies in citrus performed up to 13 months at -10°F indicated satisfactory recovery (89-140%).
Lemons

At an application rate of 10 lbs. a.i./acre, residues of 4.62 and 0.85 ppm were reported with PHI's of 31 and 150 days, respectively. Data was only reported from the major lemon producing State of California.

Because residue data, submitted for aldicarb and its sulfoxide and sulfone metabolites in/on lemons, had PHI's of <30 days and because lemon trees on the California coast continuously flower and the fruit is harvested many times per year, a revised label (Section 3) is necessary to indicate a 30-day PHI for this use of aldicarb on lemons.

Limes

The highest levels of residue were reported for applications of aldicarb 34 days after treatment. Levels of application were 5, 10 and 20 lbs. a.i./acre with maximum residues observed at 0.95, 0.85 and 0.26 ppm, respectively.

Data was reported from Florida. This is satisfactory, as limes are grown commercially only in Florida.

Grapefruit

Studies of aldicarb residues and its metabolites of concern (reported as aldicarb) were submitted from California, Texas and Florida. Maximum residues of aldicarb for application rates of 5, 10 and 20 lbs. a.i./acre were reported to be 0.67 (31 days), 0.22 (61 days) and 0.34 (64 days) ppm, respectively. The proposed tolerance was exceeded at 0.34 ppm (61 days) and 0.22 ppm (97 days), but the application rate in these studies was 20 lbs. a.i./acre or twice the maximum use pattern.

The above residue studies plus the residue studies submitted in PPs 85-1682 and 6P1829 (oranges) suffice to indicate that the proposed tolerance of 0.3 ppm for citrus fruits group is satisfactory.

Processed By-Products

One processing study each for limes and grapefruit was submitted. Processed products of interest were unwashed fruit, dried citrus pulp, citrus oil, citrus juice and molasses. At 2X the maximum recommended use pattern, none of the processed products for limes or grapefruit, showed residues greater than 0.47 ppm aldicarb. The maximum residue of 0.47 ppm was reported in dried citrus pulp processed from grapefruit. Dried citrus pulp from processed limes contained 0.37 ppm at 2X the maximum recommended use pattern. The remaining processed products of concern did not exceed the proposed tolerance of 0.3 ppm when aldicarb was used at X and 2X the maximum recommended application rate. The established food additive tolerance of 0.6 ppm in dried citrus pulp will be satisfactory to cover the ca.1.75-2 fold concerning of aldicarb residues therein.
Residues in Meat, Milk, Poultry and Eggs

This topic has been adequately addressed by M. J. Nelson in our review of FFD 6F1829, 12/3/76. In summary, there are no poultry feed items involved here; therefore, there is no reasonable expectation of secondary residues in poultry tissues and eggs.

Meat and milk have established negligible residue tolerances of 0.01 ppm and 0.002 ppm for aldicarb and its metabolites of concern. These tolerances were established from lactating cow feeding studies where the diet was 1 ppm total aldicarb carbamates. Because these and other established uses will not produce animal feed items (e.g., dried citrus pulp, culled citrus fruits, citrus molasses, etc.) which will bear residues greater than 1 ppm in the diet, there should be no transfer of residues to meat and milk exceeding the established negligible residue tolerances. This is, therefore, a 40 CFR 180.6(a)(2) classification with respect to secondary residues in meat and milk.

No data was submitted for cover crops in treated areas; therefore, the general grazing restriction of livestock on treated areas should continue.