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

JAN 29 1985

RCB # 22

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Reg. No. 7969-60. Dazomet as "temporary soil sterilant" for raising food crops. Accession Number 253681.

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and

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The Agricultural Chemicals Group, BASF Wyandotte Corporation has requested an amended registration for Dazomet Technical (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione, BASAMID GRANULAR®, EPA Reg. No. 7969-60) to be used as an impermanent sterilant for soil intended for raising food crops.

Dazomet Technical is federally registered for use in formulating soil fumigants and technical microbicides (EPA File No. 7969-AN, W. Anthony memo of 8-27-82). Current uses include use in seed beds for tobacco, turf, and ornamentals as a preplanting treatment. Precautions include exclusion from foodstuffs and drainage (into lakes, streams, ponds, or public water). The product is toxic to fish.

MITC

No food crop tolerances exist for this product.

The petitioner has submitted supplementary, apparently foreign data on BASAMID GRANULAR® that in volume 2 of 3 includes: "(A.) Behavior in Soil; (B.) Residues in Soil and Transplanted Crops; (C.) Behavior in Water; and (D.) Leaching Behavior." In the accompanying letter (Technical Leaflet/Directions for Use) Donald M. Yoder states, "In as much as each formulator has his own specific procedure and desired concentrations in compounding soil fumigants or microcidal agents, no specific concentration recommendations can be given." This "use" is not acceptable; a label will be required that details specific directions for use.

Two greenhouse studies in this submission relate to the fate of the product in crops. In the first, uptake of ^{14}C-residues by several crops from ring-labeled ^{14}C-Dazomet treated Japanese soils, "Jppa and Shiga" was studied. Soil was treated with ^{14}C-Dazomet at a rate of 50 g/m^2. Twelve days after treatment seedlings of melons, cucumbers, lettuce, and tomatoes were planted; radishes were seeded. Neither Dazomet nor methyl isothiocyanate (MITC) could be found in any of the mature plants. (MITC is considered by the Company to be the primary residue of concern; however, no data has been provided to verify this contention.) However, multicomponential (uncharacterizable /unidentifiable) residues were detected. These polar, methanol extracts represented, in most cases, >50% of total radioactive residues. Total $^{14}CO_2$ in combusted solid plant materials ranged from 0.04 to 2.20 mg/kg "^{14}C-equivalents" (petitioner's terminology). This term is consistently used throughout the submitted study. In two companion studies, radioactive residues are consistently reported in parent compound equivalents. Thus, the "^{14}C-equivalents" may be ^{14}C-Dazomet equivalents. However, RCB cannot conclude that is so on the basis of this submission. Translocation was also examined in cucumbers, melons, and tomatoes. Lower, middle, and upper plant parts were sampled. Radioactivity was detected in all plant parts; however, lower plant parts contained the majority of the activity. Crops did absorb activity from treated soil; this activity was translocated to all plant parts.

In the second study, the uptake of ring-labeled ^{14}C-Dazomet into Chinese cabbage from treated sandy loam soil was studied. Soil was treated with 100 mg/kg ^{14}C-Dazomet and aged 30, 120, and 365 days. The total radioactive residues as the parent compound calculated from $^{14}CO_2$ analyses, were: 9.90, 7.26, and 4.81 mg/kg soil, after the respective aging periods. Four-leaf stage cabbage was transplanted into treated, aged soil and grown to maturity (105 days). The activity as parent in

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harvested plants were: 0.20, 0.07, and 0.08 mg/kg, respectively. As in the first study, the radioactive, polar methanol extracts were not identified; neither parent nor MITC were detectable. Similar residues were also detected in cabbage grown on treated soils that had been preplant-aged for periods up to 365 days.

The soil data submitted indicates that residues do persist. Labeled studies and a citation to a Mylone (a compound similar to Dazomet) degradation study suggest that MITC (the postulated degradate) is the persisting residue. The fact that MITC, per se, was not detectable in this submission, may reflect on the inadequacy of the analytical methods submitted. Since approximately half of the radioactivity (i.e., residues) was not identified, RCB cannot conclude their significance relative to residues in crops. Nevertheless, the finding of detectable residues in plants in the above studies confirms that the proposed use of Basamid Granular® as an impermanent sterilant for soil intended for raising food crops is a food use requiring tolerances.

Analytical methods abound in this submission. Reported are nine methods, with "detectability in the ppb range", for the parent Basamid/Dazomet and four possible degradants/ metabolites: MITC, 1,3,5-trimethylhexahydrotriazine thione (THTT), N-methylthiourea (MTU), and N,N'-dimethylthiourea (DMTU).

In the 1st method (BASF No. 161, Basamid HPLC determination in Soil), samples are extracted with dichloromethane (DCM), because the parent is soluble in this organic solvent. The extracts are cleaned up by silica gel column chromatography, and analyzed by HPLC using a UV detector at 280 nm. Dazomet separation from interfering biological material is effected by elution with DCM/n-hexane (90/10). This method has a detection limit of 0.05 mg/kg and a recovery range of 36.2-84.7% at fortifications of 0.05-100 mg/kg.

In the 2nd method (No. 162, GC determination of MITC), soil samples are admixed with H_2O/n-hexane (30/1); MITC is insoluble in H_2O, but soluble in alcohol and ether. After a 40-min. continuous distillation, the aqueous phase is separated using a "trituriumm", and salted with NaCl. The separated hexane phase is analyzed by GC. This method has a detection limit of 0.01 ppm and a recovery of 83.2% at 0.125 ppm fortification.

The 3rd method (No. 163) is actually 2 separate methods: A. "Method of analysis (Dazomet)" and B. "Method of MITC residual analysis". Method B. is essentially the same as No. 162. In method A, samples are extracted with an "homogenized reagent",

methanol, and n-hexane; treated with $SnCl_2$ and $CHCl_3$; refluxed 1 hr. with HCl; and the resulting CS_2 absorbed with EtOH. The ethanol is analyzed by GC, and Dazomet equivalents calculated therefrom. This method has a detection limit of 0.004 ppm and a recovery range of 73.5-94.0% at a fortification of 40 "Mg of dazomet". Whereas, in method B. samples are admixed with "homogenized reagent", n-hexane, and water, and continuously extracted via heating for 40-min. The aqueous phase is separated, salted (NaCl), and the hexane phase analyzed by GC. Method B., as in No. 162, has a detection limit of 0.01 ppm and a recovery range of 82.8-83.6% at 0.125 ppm fortification.

The 4th method (No. 164, GC determination of Dazomet) is essentially the same as No. 163 A. "Homogenized samples" are extracted with methanol, partitioned with n-hexane, extracted with chloroform, rehydrated with water, treated with stannous chloride, charged with HCl, and refluxed for 1 hour. The resultant CS_2 is absorbed in ethanol, analyzed by GC, and Dazomet equivalents calculated therefrom. This method, as in No. 163 A, has a detection limit of 0.004 ppm and a recovery range of 73.5-94.0% at a fortification of 40 micrograms.

The 5th method (No. 165, A method for determination of Dazomet residues in crops by high performance liquid chromatography), was developed for analyzing Dazomet residues in cabbage, cucumber, and tomato. Crops are homogenized with silver diethyl dithiocarbamate (DDTC-Ag), adjusted to pH 7.0 with NaOH (required for tomato samples), and extracted with DCM. The extract is dried and cleaned up on a Florisil column. The concentrated DCM eluate is analyzed by HPLC using a Nucreosil 5 CN (cyanopropyl phase) column and a 2,2,4-trimethylpentane - ethyl acetate solvent system. Dazomet was detected by UV adsorption (285 nm); 0.5 ng is detectable. This method has detection limits of: 0.005 ppm (cucumber and tomato), and 0.01 (cabbage); and a recovery range of 78-95% at "0.05 ppm level".

In the 6th method (No. 139, Methyl isothiocyanate GC determination in soil, water, and potatoes), samples are hydrated with water, distilled into chloroform, $NaHCO_3$, and sarcosine ethyl ester HCl, and refluxed 1-hr. The aqueous phase is saturated with NaCl, acidified with HCl to pH 2-3, extracted with chloroform, dried, dissolved in acetone and analyzed by GC using a N-resp. S-detector (FID). The determination of MITC in potatoes and soil has, respectively, detection limits of 0.1 and 0.05 mg/kg and recoveries of 61 and 74%.

In the 7th method (No. 170, HPLC determination of 1,3,5-trimethylhexahydrotriazine thione (THTT) in soil), samples are extracted with methanol, cleaned up by water/chloroform partitioning, and analyzed by HPLC using a silica gel column and a DCM/MeOH (97/3) solvent system. THTT was detected by UV adsorption (250 nm). This method has a recovery range of 45-81% at a fortification of 0.05-10 mg/kg. No detection limit is given.

And in the 8th method (No. 157, HPLC determination of monomethylthiourea (MTU) and dimethylthiourea (DMTU) in potatoes and soil), samples are macerated with methanol (and sodium ascorbate for potatoes), cleaned up by column chromatgraphy on aluminum oxide/silica gel with a methanol/methylene chloride solvent system, and analyzed by HPLC at 240 nm. This method has a detection limit of 0.05 mg/kg (for both) at respective recovery ranges of 51-93 and 54-100%.

In summary: four of the methods (Nos. 161, 163 A, 164, & 165) are for determining the parent (i.e., Dazomet). Only the fourth (165) is detailed. Of the three methods (Nos. 162, 163 B, & 139) for determining MITC, the first two are essentially the same, and lack required details. The accuracy of the third (139) varies with the type of sample being analyzed, and thus is inadequate. The last two methods (Nos. 170 & 157) are for determining residues, possible Dazomet degradates. All were developed abroad and lack sufficient detail required for evaluation. Therefore, none of the methods, as submitted, are adequate as enforcement procedures. The petitioner will have to provide a detailed, validated analytical method for Dazomet. In addition, methods may be required for additional residues of concern.

The residue data submitted in this petition was derived from 18 foreign (Canada, F.R.G., Netherlands, Japan, and Denmark) studies, viz., 2 soil residue; 15 transplanted crop-soil; 1 transplanted crop-hydroponic. Four soil types and 10 RACs were used. The registrant reported that, "using these methods no parent and/or degradant could be found in the harvested crops". However, residues of the compounds in question were detected in soil in both of the 2 soil residue studies (both in W. Ger); as well as in cabbage in 1 (Japan) of the 15 transplanted crop studies.

One day after application of product (59 g a.i.)/m^2 of clayey loam, residues of DMTU (0.45) and THTT (0.11 ppm) were detected. At 29 days post application, the respective values were 0.053 and 0.05 ppm; 0.05 detection limit. Corresponding values in humus sandy loam were 0.16 and 0.23 ppm after 1 day and <0.05 and 0.06 ppm after 29 days. Moreover, cabbage on Shiga soil treated with Basamid Granular (20 kg/10a) had MITC residues of 0.03 and <0.01 ppm (control = 0.01) at 63 and 120 days after setting, respectively. Corresponding values of 0.04 and 0.05 ppm MITC were detected, respectively, at 63 and 120 days after setting; with the "2x" treatment (i.e., 40 kg/10a). Thus, residues do persist in treated soil, and are taken up by transplanted crops.

Leaching and water data are also available in this submission. However, RCB defers to EAB for their evaluation.

Summary and Conclusions

1) The use of Dazomet as a preplant soil sterilant will result in detectable residues in soil and crops up to one year after treatment. We consider this a food use requiring tolerances.

2) The submitted data are not adequate to make a determination as to the residue(s) of concern.

3) When the Company identifies the residue(s) of concern, additional analytical methods may be required to determine these residues.

4) No specific use of the product has been detailed. Complete labeling must be submitted. Residue data will be required for crops to be treated along with appropriate tolerance proposals. These data must reflect the maximum proposed use rate with the minimum PHI requested.

Recommendation

We recommend against registration of this product for the reasons cited above (1-4). For further consideration the requested data must be submitted. We defer to EAB as to the nature of the soil residues and leaching behavior of Basamid Granular.

cc: R.F., Circu, Reviewer, Subject file, Amended use file, EAB
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