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PP #2F1230. Chlorothalonil on various crops and in meat and milk. Evaluation of analytical methods and residue data.

Petitions Control Branch
and Toxicology Branch, PTD

The Diamond Shamrock Company proposes that tolerances for residues of the fungicide, chlorothalonil (also known as Daconil), tetrachloroisophthalonitrile*, and its 4-hydroxy metabolite be established as follows:

> 50 ppm in or on bean vines (lima and snap)
>
> 20 ppm in or on peanut vine hay, sugar beet tops, and sweet corn forage
>
> 15 ppm in or on lima beans (in pods)
>
> 0.2 ppm in or on sugar beets, in milk, and in the meat, fat, and meat byproducts of cattle, goats, hogs, horses, and sheep

Tolerances have been previously established for chlorothalonil as follows:

> 15 ppm in or on celery
>
> 5 ppm in or on broccoli, brussels sprouts, cabbage, cauliflower, cucumbers, melons, pumpkins, snap beans, squash (winter and summer), and tomatoes
>
> 1 ppm in or on carrots and sweet corn (kernels plus cob with husks removed)
>
> 0.3 ppm in or on peanuts
>
> 0.1 ppm in or on potatoes

Most of the newly proposed forage tolerances are submitted for the purpose of eliminating the need for label-imposed feeding restrictions for crops having established tolerances.

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*Note to PCB: We reiterate our previous statement made in connection with PP #1F1024 that the present regulation does not reflect the correct chemical names for this fungicide and its primary metabolite, i.e., tetrachloroisophthalonitrile and 4-hydroxytrichloroisophthalonitrile.

Conclusions:

1. The terminal residues of chlorothalonil have been adequately described. In or on plants, the parent compound is the principal component of concern. In milk and the tissues of animals, the 4-hydroxy metabolite is the component of concern.

2. Adequate methods of analysis are available for enforcement of the proposed tolerances. This conclusion is contingent upon the successful completion of method trials (for residues in meat and milk) currently underway.

3(a). The proposed tolerances for the vines of lima beans and snap beans are inadequate.

(b). The newly available data indicate that the established tolerance of 5 ppm for the raw agricultural commodity snap beans is inadequate.

(c). The proposed tolerances for milk and for the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep are not adequate.

(d). Residues of chlorothalonil on peanut vine hay, sugar beet tops, sweet corn forage, on lima beans, and in or on sugar beets will not exceed the proposed tolerances. However, to prevent a proliferation of tolerance levels, a tolerance of 0.3 ppm for sugar beets will be more appropriate.

4. The feed uses of crops treated with chlorothalonil fall into Category 1 of Section 180.6(a) with respect to meat and milk and into Category 3 with respect to poultry and eggs.

5. There will be no problem of followup residues as a result of the proposed or established uses of this fungicide. However, in view of the persistence of the 4-hydroxy metabolite in soils, we defer to PRD as to the need for a rotation restriction on followup crops.

Recommendations:

Because of Conclusions 3(a), (b), and (c), we recommend against establishing the proposed tolerances.

For further considerations of the proposed tolerances, we will need the following:

1. A more appropriate tolerance or a longer PHI for the vines of lima beans and snap beans. If the petitioner wishes to retain the PHI of 7 days, a tolerance of 100 ppm will be appropriate. If the petitioner should amend the proposed PHI from 7 to 14 days, the proposed tolerance of 50 ppm will be adequate.

2. A more appropriate tolerance for snap beans. This is necessary because the available data indicate the established tolerance of 5 ppm is inadequate. A common tolerance level (15 ppm) for snap beans and lima beans will be appropriate.

3. A more appropriate tolerance for meat and milk. A common tolerance level of 1 ppm for whole milk and for the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep will be appropriate.

4. To avoid a proliferation of tolerance levels, a tolerance of 0.3 ppm should be proposed for sugar beets.

5. To insure that residues of chlorothalonil on peanut hulls will be regulated, we will need a proposal from the petitioner to amend the established tolerance for peanuts to read "0.3 ppm in or on peanuts and peanut hulls."

Detailed Considerations

Formulation

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Chlorothalonil, tetrachloroisophthalonitrile, is formulated as a 75% wettable powder (Bravo W-75). The inerts consist of [redacted]

All the inerts are exempt under 180.1001(d).

Technical chlorothalonil is 95.6% (minimum) pure. The impurities are largely reaction byproducts with traces of other manufacturing impurities.

Established Uses (Beans, Corn, and Peanuts) and Proposed Uses (Lima Beans and Sugar Beets):

Beans (Lima & Snap) - Use 1.5 to 2.25 lbs act/A, starting at early bloom stage and repeat at weekly intervals or as necessary to maintain control. Do not apply within 7 days of harvest.

Corn (Sweet) - Use 1.1 to 1.5 lbs act/A. Begin applications when conditions favor disease development and repeat at 4 to 7 day intervals or as required to maintain control. Do not apply within 14 days of harvest.

Peanuts - Use 0.75 to 1.1 lbs act/A. Start applications when disease first appears and repeat at 10 to 14 day intervals or as necessary to maintain control. Do not apply within 14 days of harvest.

Sugar Beets - Use 1.1 to 1.5 lbs act/A. Begin applications when disease threatens and repeat at 10 to 14 day intervals or as necessary to maintain control. Do not apply within 14 days of harvest.

Nature of the Residue:

We have previously concluded (in PP #1F1024, see memo of W. S. Cox, 5/6/71) that the component of concern of residues in or on crops (forage, root, and vegetable) is the parent compound. Only at long intervals (over 30 days) after last treatment does the 4-hydroxy metabolite comprise any substantial part (up to 10%) of the total residues. However, by that time, total residues have dissipated to a marked degree. Residues of the parent compound are essentially all surface residues.

We reiterate our previous conclusion that the parent compound is the principal component of concern. However, since low level residues of the 4-hydroxy metabolite are present on crops, we have no objection to expressing the tolerance in terms of both compounds particularly since the metabolite is the component of concern in the residues in meat and milk.

For the nature of the residue in meat and milk, see below under "Residues in Meat, Milk, Poultry, and Eggs."

Analytical Methods:

The petitioner has accumulated residue data for the parent compound and the hydroxy metabolite on various crops from about 1963 until 1970. Up until 1968 or 1969, all residues (both compounds) were determined by an MCGC procedure after extraction and cleanup of the crop substrate. More recently, the petitioner has used an ECGC procedure and this method was tried out by AMS, CB on peanuts at 0.3 and 0.6 ppm and on broccoli at 2.5 and 5 ppm. (The tryout was for the parent compound only.)

Recoveries (reported by AMS) for peanuts ranged from 83 to 100% and for broccoli ranged from 80 to 100% (see memo of W. S. Cox, 9/18/71, PP #1F1024). We have concluded that adequate methods are available for enforcement of the established tolerances and we reiterate that conclusion with respect to the crop tolerances.

As to meat and milk, the petitioner has previously presented a GLC procedure using an MCGC detector and in the current petition he has presented milk and meat residue data by the same general procedure except that an EC detector was used. This procedure has been recommended for a method trial by AMS, CB, on the 4-hydroxy metabolite in milk and beef kidney and is now underway. Contingent upon successful completion of the method tryout, we conclude that adequate methods are available for enforcement of milk and meat tolerances. In accordance with established procedures, it is presumed that Meat and Poultry Inspection Programs, USDA, will be consulted also.

The petitioner has submitted adequate validation data for the various crops involved here, involving fortification with both parent and 4-hydroxy metabolite in all cases except for sweet corn and corn forage. We do not consider this deficiency important since the 4-hydroxy metabolite is not considered to be a component of concern in the terminal residues of plants and since there are other recovery data from which to translate.

Residue Data:

Lima Beans and the Vines of Lima Beans and Snap Beans:

The residue data for lima beans and lima bean vines are quite limited since they are comprised of only four studies, none of which reflect residues at the proposed 7-day PHI. In addition, only one study reports residues on the raw agricultural commodity, lima beans (in the pods). Finally, one of the four studies is of little value since "apparent" residues of the fungicide on untreated lima bean vines are reported in the range of 30 to 175 ppm. [This study is clearly aberrant and has been discarded from our considerations.]

The snap bean residue data (two studies) was originally reviewed in PP #7F0599 (see memo of Bernadette Malone, 8/28/67). At that time, the petitioner's label imposed a feeding restriction for snap bean vines, so no data were presented for the vines.

Despite the paucity of actual data for the vines of lima beans and snap beans, we believe that, by translation of the available data for peanut vine hay, a suitable estimate of residues on bean vines harvested at the proposed PHI is possible.

The peanut vine data indicate that, at 7 days, residues for vines would be of the order of 60 to 70 ppm. This is in fair agreement with the limited lima bean vine data which indicate that maximum residues at 7 days after last treatment would be of the order of 80 to 100 ppm.

Consequently, we conclude that the proposed tolerance of 50 ppm is inadequate in connection with a 7-day PHI. Thus the petitioner will either have to propose a more adequate tolerance (such as 100 ppm) or amend the label to impose a 14-day PHI in lieu of the proposed 7-day PHI.

As to lima beans (in the pods), the combined data for lima beans and snap beans indicate that the proposed tolerance of 15 ppm for lima beans is adequate. However, based on the presently available data, we conclude that the established tolerance of 5 ppm for snap beans is not adequate and that the petitioner should be asked to propose a more adequate (higher) tolerance for snap beans. We believe a common tolerance for snap beans and lima beans set at 15 ppm would be appropriate.

Peanut Vine Hay:

The label imposes a 14-day PHI for peanuts. We have concluded immediately above that a 14-day PHI is necessary for bean vines if the proposed tolerance of 50 ppm for bean vines is to be considered adequate. However, peanut vines are not consumed as such, but are converted to peanut vine hay by air-drying of the harvested peanuts and vines for three to six weeks after harvest, i.e., removal of the peanuts per se from the soil. Thus, there would actually be a 5 to 8 week interval between "harvest" of the vine hay and last treatment. Thus, there will be a material reduction of residues between the harvest of the peanuts (for air-drying) and the "harvest" of the peanut vine hay. While we have no data reflecting such a drying period, we have adequate decline curve data to support a conclusion that residues of the fungicide on peanut vines will be well below 20 ppm. Since it will not affect our conclusions concerning meat and milk, we see no objection to a recommendation for the proposed tolerance. On this basis and considering the available data, (even though limited), we can conclude that the proposed tolerance of 20 ppm is adequate for peanut vine hay.

In the previous petition (PP #1F1024), we failed to consider the need for a tolerance for peanut hulls, the byproduct of the shelling of peanuts.

Peanut hulls are largely fiber in content and have less value as a feed than do the straws of the various grains. Nevertheless, it can be fed as a substitute for straw at times.

While we have no residue data for peanut hulls per se, the residue data for the root crops (potatoes and sugar beets) definitely show that residues of chlorothalonil do not translocate from the foliar parts of the plants to the roots. Then, we can conclude that, even at harvest, there would be only trace contaminative residues of chlorothalonil on the peanut shells. There residues would be further dissipated during the long (3 to 6 week) period of the field drying of the pulled peanuts.

On this basis, we conclude that for peanut hulls the use on peanuts would be essentially a no-residue situation and the established tolerance for peanuts (the nut meats) of 0.3 ppm is adequate for both peanuts and peanut hulls. We will ask the petitioner to propose that the established tolerance for peanuts be amended to read "peanuts and peanut hulls."

This change will not affect any of our considerations with respect to meat, milk, poultry or eggs.

Sugar Beet Tops:

The petitioner is proposing a 14-day PHI. The sugar beet top data are somewhat limited (only one study at the proposed PHI) but when combined with the residue data for the bean vines, peanut vine hay and celery (reviewed in PP #1F1024), we conclude that the proposed tolerance of 20 ppm is adequate if the proposed PHI is observed. 14 day

Sugar Beets:

There are no data for samples taken at the proposed 14-day PHI. However, there are data from studies involving a 2X application rate, a 23-day PHI and five applications. The maximum residue reported is 0.09 ppm. Taken in conjunction with the data for carrots and potatoes in PPs #7F0599 and 1F1024, we conclude that the data are adequate to conclude that residues on treated sugar beets will not exceed the proposed tolerance of 0.2 ppm. However, to prevent the proliferation of tolerance levels, we believe the tolerance for sugar beets should be set at 0.3 ppm.

Sugar Beet Byproducts:

The use on sugar beets (roots) is essentially a "negligible residue" situation. Since the petitioner shows that washing of crops with water materially reduces surface residues and since roots are washed prior to processing, we conclude that there will be no concentration of residues in sugar beet pulp or molasses. Consequently, no data are needed for these commodities nor will food additive tolerances be needed.

Corn Forage (Sweet):

A 14-day PHI is proposed. The data are very limited (only one value from one study); this datum was derived from 14 applications at 3/4 the recommended rate but at the recommended PHI. The one value is <10 ppm on the husk portion of the corn ears. However, the available data for the aerial parts of other plants (such as celery and sugar beet tops) give ample support to the conclusion that a tolerance of 20 ppm is adequate for corn forage, providing the proposed PHI is observed.

In PP #1F1024, we raised the question as to whether the ensiling of corn forage and fodder could result in the microbial conversion of chlorothalonil to its hydroxy metabolite. The petitioner has conducted a laboratory experiment which demonstrates that chlorothalonil is degraded during the fermentation process associated with ensiling, but that the hydroxy metabolite is not formed to any significant extent.

Based on these data, we now conclude that residues transferred to meat and milk by ensiled corn fodder and forage will be essentially the same as those resulting from the foraging of corn.

Residues in Meat and Milk:

In the feeding study evaluated in PP #1F1024, the petitioner fed lactating cows a mixture of chlorothalonil and its hydroxy metabolite in a ratio of 125:1 at levels of 25, 75, and 250 ppm parent compound. Since residues in meat and milk were comprised solely of the hydroxy metabolite, we were unable to make any *a priori* conclusions as to the transfer of residues of the parent compound to meat and milk.

In the current petition, there is presented an additional study wherein one cow was fed the parent compound at 250 ppm, a second cow was fed 2 ppm of the hydroxy metabolite and a third served as a control. The two cows were fed the chemicals for 44 days with milk samples taken at intervals of 2 to 6 days (average 3.1 days) and during a 15-day withdrawal period.

The second milk-out study shows that the parent compound has relatively little tendency to transfer to milk--0.2% of the ingested fungicide appeared in the milk as the hydroxy metabolite. Maximum residues of 1.3 ppm appeared in the milk as a result of ingesting 250 ppm in the daily ration. The results for feeding of the parent compound are in strong contrast to those for the hydroxy metabolite--the transfer rate for the metabolite is over 100X that for the parent. From a daily feeding of 2.0 ppm of hydroxy-chlorothalonil, maximum residues of 1.54 ppm of the hydroxy metabolite are reported in the milk.

There is no particular pattern to the reported residues--however, a plateau was reached at 18 to 26 days from the feeding of each compound. During the first week of the withdrawal periods, there was little decline in residue levels in milk. Detectable residues were found in the last milk-out sample taken (15 days after last feeding).

Overall, the proposed feed uses of Daconil-treated crops are categorized in (a)(1) of Section 180.6 since the hydroxy metabolite (even though a minor component of the residues) transfers to milk and meat even at very low levels (i.e., <0.1 ppm in the diet).

As to potential residue levels in milk, we need consider the highest tolerance on a major feed item--in this case, bean vines could occasionally comprise essentially 100% of the diet. Above, we have concluded that a 100 ppm tolerance would be necessary for lima bean vines--of this 100 ppm, we would expect the hydroxy metabolite to comprise, at most, 1 ppm. In the earlier milk-out study, cows were fed parent compound and hydroxy metabolite in a ratio of 125:1. At the maximum level of 250 ppm parent and 2.0 ppm metabolite, maximum residues of 1.34 ppm (hydroxy metabolite) were found. Based on the latter study, residues in milk from lima bean vines containing 99 ppm parent and 1 ppm metabolite would be about 0.7 ppm. Consequently, we believe a tolerance of 1.0 ppm will be quite adequate to cover total residues in milk. The meat data indicate that the hydroxy metabolite shows no tendency to store selectively in fat, thus we believe that the milk tolerance should be established on a "whole milk" basis.

As to meat, we believe the data from the first feeding study wherein chlorothalonil and its hydroxy metabolite were fed simultaneously is also appropriate. Based on this study, maximum residues of 1.0 ppm could occur in tissues although it is not likely that <u>meat</u> animals would be fed a 100% vine diet. However, in the absence of other data and to prevent the proliferation of tolerance levels, we believe that a common tolerance of 1.0 ppm for residues of the hydroxy metabolite in meat and whole milk is appropriate.

<u>Residues in Poultry and Eggs</u>:

Peanut meal, the residue of shelled peanuts processed for oil, is a component of poultry rations (up to 30%). However, the available data show that residues of chlorothalonil on peanuts occur <u>only</u> on the aerial parts (i.e., the vines). Thus, this use on peanuts is essentially a "no-residue" situation for peanuts in the shell. [Note: The 0.3 ppm tolerance was set due to limitations of the residue method which showed "apparent residues" of 0.2 ppm on untreated peanuts.] Consequently, we can place the poultry feed use of peanuts in Category 3 of Section 180.6(a) and we need not concern ourselves with tolerances for poultry and eggs in connection with the use on peanuts since there are no other poultry feed items involved in the proposed uses.

<u>Soil Persistence</u>:

Soil persistence studies previously submitted in PP #1F1024 show that Daconil is rapidly degraded in soil to the hydroxy metabolite, but that these residues are tightly bound to the soil. We reiterate our previous conclusion that followup residues will be no problem in connection with the proposed uses. However, we defer to PRD as to the need for rotation restrictions on followup crops.

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WSCox:jrf 5/24/72
RD/I - RSQuick 5/8/72
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