American Cyanamid Company proposes the establishment of tolerances for the combined residues of the herbicide pendimethalin \(N-(1\text{-ethylpropyl})-3,4\text{-dimethyl}-2,6\text{-dinitrobenzenamine}\) and its metabolite \(4-(\text{ethylpropyl}amino)-2\text{-methyl-3,5-dinitrobenzyl alcohol}\) in or on the raw agricultural commodities: sorghum fodder, sorghum forage and sorghum grain at 0.1 ppm.

A tolerance of 0.1 ppm \(40\text{ CFR 180.361}\) has been established for cottonseed, corn (grain, fodder and forage), and soybeans (forage and hay). A temporary tolerance \(PP\#6G1740\) for peanuts, peanut foliage, and peanut hay and hulls expires March 20, 1980. The temporary tolerance \(PP\#6G2040\) for sorghum grain, forage and fodder of 0.1 ppm expired August 24, 1979.

**Conclusions**

1. The formulation may contain as much \(1.5\%\) nitrosoamine. Based upon the minimum yield of sorghum grain per acre (Agricultural Statistics, 1977), the maximum calculated level of nitrosoamine on sorghum grain would \(\text{enough}\). We defer to TOX on the significance of this level.

2. The fate of pendimethalin is adequately delineated for the proposed use.

3. Adequate analytical methods are available to enforce the proposed tolerance.

4 (a) No detectable residues are expected in or on sorghum grain, fodder and forage. The proposed tolerance is appropriate. Since residues are non-detectable in sorghum grain, residues in the milled fractions are not expected to exceed that on the r.a.c. Therefore, a food additive tolerance is not needed.

4 (b) Residues of atrazine as a result of the application of the tank mix will not exceed the established tolerances for sorghum grain,
Sorghum and Forage.

5 (a). From feeding study data and the fact that residues in grain, forage and fodder are non-detectable, we conclude that the proposed use falls into category 3 of 122.6 (a).

5 (b). The established meat, milk, poultry, and eggs tolerances for atrazine will cover secondary residues in these commodities.

Recommendations

We recommend against the proposed tolerance for the reasons cited in conclusion 1. We defer to FON on the significance of the calculated nitrosoamine level in sorghum.

Detailed Considerations

Formulation

Pendimethalin is formulated as FRG7L (EPA Registration No. 241-243-2) an emulsifiable concentrate containing 44% active ingredient (5 lbs. a.i./gal). The inert, except for the nitrosoamine contaminant, are cleared for use under Section 180.1201 (4).

The manufacturing process for technical pendimethalin is described in our review of PPS71556 (memorandum: A. Smith, 5/8/73). The technical material contains 91-94% pendimethalin.

(According to the 1973 Agricultural Statistics, in 1977 the lowest yield per acre in a state was 16 bushels. With the average weight per bushel of 66 lbs., a minimum yield of 960 lbs. can be expected. We will defer to FON on the significance of these levels.

Proposed Use

To control most late season annual grasses and certain broadleaf weeds in grain sorghum, apply Frel at 0.5 to 1.5 lbs. a.i./A, broadcast, in 10 or more gallons/A by ground equipment. To further control velvetleaf and other broadleaf weeds, a tank mix of 0.75 to 1.5 lbs. a.i./A Frel and 1.25 lbs. a.i./A atrazine may be applied. The rate of Frel application is dependent on geographical area and soil type. The herbicide(s) is to be applied post-emergence when grain sorghum is 6 to 8 inches tall or after the last cultivation at least when grain sorghum is approximately 20 to 24-in tall. It should be thoroughly and uniformly incorporated into soil to a depth of 1 to 2 inches.

The established atrazine tolerances are 0.25 ppm for sorghum grain and 15 ppm for sorghum forage and fodder.

Livestock can graze or be fed forage from Frel treated grain sorghum. If the tank mix is used, then livestock can graze or be fed forage 21 days following application.
Restrictions are not to use Proclaim plus atrazine on coarse textured soils and not to apply Proclaim preplant incorporated or preemergence to grain sorghum, when wind velocity favors drift and post emergence prior to the 4-inch growth stage of grain sorghum.

Nature of Residue

No metabolism studies were submitted with this petition, but were discussed in our reviews of PP50G1739, PP40G1740, PP50G1580 and PP50F1556 (memoranda: A. Smith, 6/22/76, 5/19/76, 3/31/75, and 5/5/75). Radionabeled C-pendimethalin is absorbed, translocated and metabolized by sweet corn, cotton, bean, potato, peanut and soybean plants. The plant residue consisted primarily of the parent and the benzo alcohol metabolite with other minor metabolites which were dependent on the type of plant. These other constituents were not characterized in most cases because of their low levels or high polarity.

The fate of pendimethalin is adequately delineated for the proposed use. The residues of concern are the parent and its benzo alcohol metabolite.

In rats, approximately 90% of the administered radioactivity (PP50F1556, memorandum: A. Smith) was excreted within 24 hours, primarily as the parent (PP50G1551, K. L. Gunderson, 3/27/74). Upon isolation and characterization, the metabolites indicated oxidative degradation. At least 26 metabolites have been identified. Seven metabolites from urine and tissues have been identified. Five have a carboxylic acid function and the remainder were uncharacterized. The major component excreted in the feces was the parent.

In feeding studies, cows and goats extensively metabolized and excreted pendimethalin. Two goat urine metabolite was the benzo alcohol. In the feces, at least eight metabolites were present and unidentified and the major component was the parent. No detectable residues (less than the method of sensitivity) were observed in the milk of goats and cows fed 20 ppm and 1 ppm pendimethalin respectively. In tissues, some deposition does occur but there is apparently no tendency to concentrate.

The animal metabolism of pendimethalin is adequately characterized for the proposed use.

Analytical Method

Pendimethalin is determined in sorghum forage and fodder by grinding, extracting with aqueous/acidic methanol, filtering, acidifying and then partitioning the residue into hexane. The combined hexane layers are concentrated and the residue is cleaned-up on a Florisil column eluted with hexane/benzene. After concentrating, pendimethalin is quantitated by gas chromatography with an electron capture detector to determine pendimethalin in sorghum grain, the finely ground sorghum grain sample is extracted with methanol/chloroform. After filtering and concentration, the residue is cleaned-up on a Florisil column and the procedure becomes as previously described.

Apparent residues in untreated grain ranged from <0.031 to 0.05 ppm or below the reported level of detection, 0.05 ppm. In silage and stover, these residues ranged from <0.001 to 0.06 ppm with one aberrant sample having apparent residues as high as 0.18 ppm. We are disregarding this sample.
No detectable residues, <0.05 ppm were observed in untreated samples of sorghum grain, fodder and forage in the previous submission, PP530940 (memorandum: A. Smith, 6/5/73). Recoveries ranged from 73 to 128% at fortification levels of 0.05 to 5.0 ppm for grain, fodder and forage.

The benzylic alcohol metabolite is quantitated in sorghum forage and fodder by extraction with aqueous acidic methanol and then partitioning into chloroform. After reaction with acetic anhydride to obtain the acetate derivative, the residue is quantitated by electron capture gas chromatography. In grain the initial extraction is performed with chloroform methanol and the residue reacted with acetic anhydride directly after concentration. The procedure is then similar to the forage and fodder method.

Apparent residues in untreated samples ranged from <0.002 to 0.05 ppm for grain and <0.002 to 0.02 ppm for silage and stover. Apparent residues for grain and forage were non-detectable in the previous submission, <0.05 ppm. Recoveries ranged 63 to 134% at fortification levels of 0.05 to 5.0 ppm for grain, fodder and forage.

These methods have undergone a successful method trial on cottonseed (PP531156, Memorandum: W. J. Boodoo, 3/26/76). At fortification levels of 0.05 and 0.1 ppm of either pendimethalin or its benzylic alcohol metabolite, recoveries ranged from 76 to 92%.

Considering the successful method trial, we conclude that adequate methods are available to enforce the proposed tolerances.

Residues of atrazine were determined in sorghum silage, stover, and grain by a modified version of the method in FAP II, the enforcement method. Residues in or on untreated samples were <0.03 ppm for sorghum silage and stover and <0.004 ppm for sorghum grain. Recoveries ranged from 33 to 96% at fortification levels of 0.05 to 0.5 ppm of sorghum grain and from 96 to 105% at fortification levels of 0.5 to 2.0 ppm of sorghum silage and stover. The petitioner has demonstrated a capacity to adequately measure atrazine residues.

Residue Data

Residue data was collected from Virginia (1), Arkansas (1), Nebraska (2), Texas (3), New Mexico (1), and Colorado (1) for sorghum grain, silage and stover. Pendimethalin was applied at 2.75 to 1.5 lbs. a.i./A. The tank mix was applied at 3.75 lb. pendimethalin and 1.0 lb. a.i./A atrazine at four sites. PHI's ranged from 41 to 111 days.

Residues of either pendimethalin or its benzylic alcohol metabolite were <0.05 ppm in or on sorghum grain, stover or silage, the method's sensitivity except for one stover sample which was 0.06 ppm. However, other samples in that set had residues less than the reported level of sensitivity. Residues of atrazine were <0.05 in or on grain and < 0.05 in or on stover and silage.

Additional data is contained in PP530940. No residues of pendimethalin or its metabolite (<0.0 ppm) were detected in sorghum grain, fodder, silage or forage in studies performed in Texas, Kansas and Colorado at rates of 1-3 lbs. a.i./A alone or at the lower rates in combination with atrazine.
0.5-1.0 lb. a.i./A) or propazine (0.5-1.9 lb. a.i./A) at PHI's of
56-144 days. Residues of atrazine in sorghum silage (1 sample), grain (1)
and forage (3) were <0.05 ppm.

We anticipate that residues of pendimethalin and its benzal alcohol
metabolite in or on sorghum grain, fodder and forage will be non-detectable
and will not exceed the proposed tolerance. Since residues are non-detectable
in grain, residues in sorghum milling fractions will probably be non-detectable
and not exceed that of grain. Consequently, a food additive tolerance is
not needed.

Residues of atrazine in or on grain and fodder and forage are not expected
to exceed the established tolerances of 0.25 ppm and 15 ppm respectively.

**Meat, Milk, Poultry and Eggs**

The feed items of concern are sorghum grain (livestock and poultry) and
sorghum fodder and silage (livestock only).

In feeding studies, residues in milk of dairy cows fed an equivalent of
1 ppm pendimethalin were less than 0.01 ppm, the sensitivity of the method.

No detectable residues were observed in the milk of goats fed an equivalent
of 0.5 and 1.5 ppm pendimethalin containing radiolabeled pendimethalin. (However,
detectable radioactivity was found at the 20 ppm feeding level which was equivalent
to 0.01 ppm). In goat tissues, the maximum residues of pendimethalin and its
benzal alcohol metabolite was 0.04 ppm at the 1.5 ppm feeding level. These
feeding levels are 10X or 15X the proposed tolerance and the feeding level if
the total diet were sorghum grain, fodder and forage. Consequently, we antici-
pate that secondary residues in meat and milk will be non-detectable or a category
3 situation of 180.6 (a).

Since the residues are non-detectable in sorghum grain, the poultry feed
item, and considering the aforementioned feeding studies, we expect no detectable
residues in poultry or eggs from the proposed use or a category 3 situation of
180.6 (a).

The established meat, milk, poultry and egg tolerances for atrazine will
cover secondary residues in these commodities.