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

APR 15 1985

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: 85-MT-04105. Section 18 emergency exemption for the use of chlorpyrifos or permethrin on small grains. RCB #'s 705, 706. Accession #'s 146164 and 146165.

FROM: Sami Malak, Ph.D. Chemist
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

THRU: Edward Zager, Head
Special Registration Section II
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

TO: James A. Tompkins, PM#41
Emergency Response and Minor Use Section
Registration Division (TS-767)
and
Toxicology Branch
Hazard Evaluation Division (TS-769)

The Montana Department of Agriculture is requesting a Section 18 emergency exemption allowing use of the insecticide chlorpyrifos (Lorsban 4E), or permethrin (Pounce 3.2 EC or Ambush 2E) for control of army cutworms and pale western cutworms in small grains (oats, barley, wheat). Emergency exemptions were previously granted (82-84) to the state of Montana allowing use of chlorpyrifos and permethrin for insect control on small grains.

Permanent Tolerances

A. Chlorpyrifos

Permanent tolerances are currently established for the combined residues of the pesticide chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) and its metabolite 3,5,6,-trichloro-2-pyridinol in/on several raw agricultural commodities at levels of 0.05 to 15 ppm including 2.0 ppm for the meat, fat and meat byproducts of cattle; 1.0 ppm for the meat, fat and meat byproducts of goats, horses and sheep; 0.5 ppm for the meat, fat and meat byproducts of hogs and poultry including

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turkey; 0.1 ppm for eggs; and 0.5 ppm for milk fat, representing 0.02 ppm in whole milk (40 CFR 180.342). PP# 3F2947 proposing permanent tolerances for the combined residues of chlorpyrifos and its metabolite in/on wheat grain at 0.6 ppm (of which no more than 0.3 ppm is chlorpyrifos), in/on wheat straw at 6 ppm (of which no more than 2.5 ppm is chlorpyrifos), and a feed additive tolerance of 2 ppm under 21 CFR 561.98 (of which no more than 1 ppm is chlorpyrifos) in/on milling fractions of wheat except flour is currently in reject status (memo of V.F. Boyd, 1/20/84).

B. Permethrin

Permanent tolerances are currently established (a) for residues of the insecticide permethrin [(3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate)] in/on cottonseed at 0.5 ppm; (b) for residues of the insecticide permethrin [(3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate)] and its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid (DCVA) and (3-phenoxyphenyl) methanol (3-PBA) calculated as parent in/on several raw agricultural commodities at levels of 0.05 to 60 ppm including sweet corn at 0.1 ppm and corn forage and fodder at 60 ppm, each; and (c) for residues of permethrin and its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid (DCVA) and (3-phenoxyphenyl) methanol (3-PBA) and 3-phenoxybenzoic acid all calculated as parent, in/on several animal commodities as follows: 2.0 ppm for the fat, 0.15 ppm for the meat and 1.0 ppm for the meat byproducts of cattle, goats, hogs, horses and sheep; 0.05 ppm for the fat, meat and meat byproducts of poultry; 0.05 ppm for eggs; and 3.75 ppm for milk fat, representing 0.15 ppm in whole milk (40 CFR 180.378).

Proposed Use: The proposed use is either for chlorpyrifos or permethrin.

A. Chlorpyrifos

For insect control in small grains (wheat, barley and oats), chlorpyrifos (Lorsban 4E, Reg. No. 464-448) is to be applied once at 0.5-1.0 lb act/A in a minimum of 10 gallons of water/A by ground equipment or 2 gallons of water/A by aerial equipment. For this, the Montana Department of Agriculture is requesting 100,000 pounds of the active ingredient for use on 100,000 acres of small grains. The program is for the 1985 growing season. All applicable directions, restrictions and precautions on the registered label will be observed. There is a 28-day PHI. Treated fields will not be cut for hay or grazed within the preharvest interval.

B. Permethrin

For insect control in small grains (wheat, barley or oats) permethrin (Pounce 3.2 EC # 279-3014; or Ambush 2E # 10182-18) is to be applied at 0.1 lb act/A in a minimum of 10 gallons of water/A by ground equipment or 2 gallons of water/A by aerial equipment. For this, the Montana Department of Agriculture is requesting 10,000 pounds of the active ingredient for use on 100,000 acres of small grains. The program is for the 1985 growing season. All applicable directions, restrictions and precautions on the registered labels will be observed. Treated fields will not be cut for hay or grazed within a preharvest interval of 30 days.

Metabolism

A. Chlorpyrifos

The metabolism of chlorpyrifos in plants and animals has been discussed in several petitions and we concluded that the residue of concern in both plants and animals consists of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol or TCP (PP# 3F2947, memo of V.F. Boyd, 1/20/84).

B. Permethrin

The metabolism of permethrin in plants and animals has been reviewed several times. In plants, the nature of residues is discussed in previous reviews (PP# 7G1891, dated 3/10/77; PP# 8G2029 dated 12/27/78; PP# 8F2034 dated 3/14/78 by A. Rathman; and PP# 0F2389 dated 4/10/81 by J. Onley).

Data indicate that permethrin degrades slowly in plants, apparently via the hydrolysis at the ester site with conjugation of the resulting alcohol and acid to plant constituents. The significant components of plant residues are the parent compound, permethrin, and the metabolites (±)-cis, trans-3-(2,2 dichloroethenyl)-2,2-dimethylcyclopropane-carboxylic acid (DCVA) and (3-phenoxybenzyl) methanol (3-PBA).

The fate of permethrin in animals has been discussed in previous reviews (PP# 8F2034 dated 3/13/78 and PP# 8F2044 dated 4/24/78, both by A. Rathman). Metabolism studies on chickens, cows, goats, and rats showed that the significant components of residues in animals consisted of permethrin, DCVA and 3-PBA. The metabolites 3-phenoxybenzoic acid, 4'-hydroxy-3-phenoxybenzoic acid, and 4'-hydroxy-3-phenoxybenzyl alcohol were reported in the kidney and liver of the subject animals. The residues of concern in animals are permethrin, DCVA, 3-PBA and 3-phenoxybenzoic acid.

We conclude that the residues of concern are cis- and trans-permethrin, cis- and trans- DCVA (3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate), 3-phenoxybenzylalcohol (3-PBA) and 3-phenoxybenzoic acid (the latter is for meat, fat, meat byproducts, milk, poultry and eggs only).

Analytical Methodologies

A. Cholrpyrifos

The analytical methodology used to generate residue data for chlorpyrifos in/on wheat and wheat based products is that of Norton, E.J., 1980 "Residues of chlorpyrifos and 3,5,6-Trichloro-2-Pyridinol in Wheat Grain, Straw, and Milling and Baking Fractions." The method uses flame photometric detection for chlorpyrifos and electron capture detection for TCP. Method sensitivity for chlorpyrifos was reported at 0.01 ppm for grain and 0.05 ppm for forage, straw and milling and baking fractions; and that for TCP at 0.05 ppm for all fractions. The method is essentially the same as that listed in PAM II as method II (See PP# 3F2947, memo of V.F. Boyd, 1/20/84).

The analytical methodology for chlorpyrifos in milk and animal tissues is that of Claborn, H.V., et al., "Dursban Determination in Milk and Body Tissues of Cattle", JAOAC 51:1243-1245, 1968. The method is listed in PAM II as Method IV. Method sensitivity for chlorpyrifos is 0.1 ppm. The analytical methodology for 3,5,6-trifluoro-2-pyridinol, a metabolite of chlorpyrifos in beef fat is listed in PAM II as method V. Method sensitivity for TCP is 0.05 ppm.

We conclude that adequate analytical methodologies are available for enforcement. The methods are listed in PAM II as method II for plants that may be used for grain and grain-based products; and as method IV and V for animal commodities.

B. Permethrin

The analytical methodology used to determine residue data for permethrin in/on cottonseed and soybeans is listed in PAM II as method I. The method is recommended for all crops and may be extended to include grain and grain-based products. In this method, separate determinations are made of the cis- and trans-isomers of permethrin or as total permethrin using GLC with Coulson conductivity detection. Reported method sensitivity for permethrin is 0.05 ppm.

The analytical methodologies used to determine residue data for permethrin metabolites, m-phenoxy benzyl alcohol (MPBA) and cis- and trans- dichlorovinyl acid (DCVA) in/on soybeans and soybean fractions are listed in PAM II as methods III and IIIA. The

methods are listed for all crops and may be extended to include grain and grain-based products. Reported method sensitivity for permethrin metabolites is 0.01 ppm.

Method II in PAM II determines individual isomers or total permethrin and is recommended for animal tissues and milk with a detection limit of 0.01 ppm.

Method IV in PAM II determines residues of the major metabolites of permethrin, m-phenoxybenzyl (MPB) alcohol, MPB acid, and dichlorovinyl acid (DCVA) in/on animal tissues and milk. The detection limit is reported at 0.05 ppm.

We conclude that adequate analytical methodologies are available for enforcement. The methods listed in PAM II as methods I, III and IIIA for all crops may be employed for grain and grain-based products; and method IV for animal commodities.

Residue Data

A. Chlorpyrifos

No data are included with this application. Data submitted in connection with PP# 3F2947 (memo of V.F. Boyd, 1/20/84) represent 13 studies from 9 wheat-growing states in which Lorsban 4E was applied to wheat at 0.5-1.0 lb act/A. Data were generated using Norton, E.J. (1980) method of analysis which is essentially the same procedure listed in PAM II as method II. The following is a summary of the residue data for chlorpyrifos in/on grain and grain-based products:

Substrate	Location	Method of Application	PHI (Days)	Residue Found (ppm) Chlorpyrifos	TCP	Combined
Grain	Oregon	Air	28	0.23	0.38	0.61
Straw	Oregon	Air	28	4.2	1.6	5.8
Forage	Texas	Ground	14	2.3	0.23	2.5
		Milling and Baking Fractions				
Grain	Illinois	Ground	14	0.55	0.25	0.80
Grain	Illinois	Ground	14	1.5	0.63	2.1
Straight Grade Flour	Illinois	Ground	14	0.08	0.06	0.14
Bran shorts	Illinois	Ground	14	1.0	0.42	1.4
Red shorts	Illinois	Ground	14	1.4	0.62	2.0
Red Dog	Illinois	Ground	14	0.47	0.15	0.62
Bread	Illinois	Ground	14	0.06	ND	0.06

Additional residue data reflecting applications to wheat are included in PP# 1G2438 also reviewed in connection with a Section 18 exemption for chlorpyrifos on small grains in Montana (memo of E. Zager, 8/28/81). Six residue studies were conducted in 5 states in which chlorpyrifos was applied three times at 0.5 lb act/A/ application with PHI's ranging from 14-17 days.

The time interval between applications ranged from 9 to 19 days; three studies used spring wheat and three studies used winter wheat (insecticide being applied in late spring or early summer) and both aerial and ground applications were made.

In the grain, maximum residues of chlorpyrifos ranged from 0.02 to 0.55 ppm and maximum residues of TCP ranged from ND (<0.05 ppm) to 0.25 ppm. In the straw, maximum residues of chlorpyrifos ranged from 0.08-1.7 ppm and maximum residues of TCP ranged from 0.06 to 0.92 ppm.

The residue study which was used to produce milling and baking fractions had the maximum residue levels in grain (0.55 ppm). The majority of the residue remained in the outer portion of the wheat berry while the endosperm had minimal residues.

Fraction	Chlorpyrifos (ppm)	TCP (ppm)
Bran	1.5	0.63
Flour	0.08	0.06
Break Shorts	1.0	0.42
Reduction Shorts	1.4	0.62
Red Dog	0.47	0.15
Bread	0.06	<0.05

Based on the available data we estimate that the combined residues of chlorpyrifos and its metabolite 3,5,6,-trichloro-2-pyridinol will not exceed 1 ppm in the grain, 6 ppm in the straw and 3 ppm in the milling fractions of wheat as a result of the proposed use.

No residue data are available for oats and barley. However, for the purpose of this Section 18 exemption, we are willing to translate data from wheat and estimate that residues of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol will not exceed 1 ppm in the grain, 6 ppm in the straws and 3 ppm in the milling fractions of barley, oats and wheat, reflecting the proposed PHI of 28 days.

B. Permethrin

No data are included with this application. Data submitted in connection with 82-MT-03 (memo of E. Zager, 3/22/82) reflect 4 studies conducted in MO, CO, NE and SD. Permethrin was applied to wheat either one or two times at the rate of 0.1-0.2 lb act/A.

Following two applications of 0.1 lb act/A residues of permethrin per se were non detectable (<0.02 ppm) in wheat grain and ranged from 0.57-2.2 ppm in wheat straw at a 21-day PHI. A single application of 0.2 lb act/A (2X) resulted in 0.02 ppm in the grain and 0.06 ppm in the staw at a 21 day PHI. Significantly higher residues resulted from two applications at 0.2 lb act/A (2X the proposed rate). Residues ranged from 0.21-1.1 ppm in the grain and 2.8-4.9 in the straw at a 28 day PHI.

No residue data are available for the metabolites of permethrin in small grains. However, residue data for the metabolites of permethrin in field corn were submitted with PP#2F2624. Following 1-6 applications of 0.1-0.2 lbs act/A no detectable residues of permethrin (<0.05 ppm) or its metabolites DCVA and 3-PBA (<0.01 ppm) were found in field corn kernels at PHI's of 0-89 days. Field corn cobs contained up to 0.21 ppm of permethrin per se but no detectable residues (<0.01 ppm) of the metabolites. Combined residues of the two metabolites DCVA and 3-PBA ranged up to ca 1 ppm (50% of residues of permethrin per se) in corn stover at PHI's of 28 days or more.

Based on the above data and translating the wheat residue data to oats and barley we estimate that residues of permethrin and its metabolites DCVA and 3-PBA will not exceed 0.3 ppm in the grains and 2 ppm in the straw of barley, oats and wheat.

Since no concentration of permethrin residues was observed in cottonseed processing fractions (A. Rathman, 4/24/78, PP#8F2044) no concentration of residues of permethrin is expected in the milled fractions of barley, oats and wheat.

Meat, Milk, Poultry and Eggs

A. Chlorpyrifos

Existing tolerances are 1.0 ppm for the meat, fat and meat byproducts of goats, horses and sheep; 0.5 ppm for the meat, fat and meat byproducts of hogs and poultry; 0.1 ppm for eggs; 2.0 ppm for the meat, fat and meat byproducts of cattle and 0.5 ppm in milk fat (representing 0.02 ppm in whole milk).

Cattle - In PP#3F1305, it was reported that no chlorpyrifos residues were found in whole milk after dairy cattle had been fed chlorpyrifos at levels of 1, 3 and 10 ppm in the diet for 14 days. Chlorpyrifos residues of 0.02 ppm were found in whole milk after a 30 ppm feeding level. At the 10 and 30 ppm feeding levels, the maximum chlorpyrifos residues in cream were 0.04 and 0.15 ppm, respectively. After withdrawl periods of 1-5 days, neither the milk nor the cream contained any detectable residues.

Beef cattle were fed chlorpyrifos in the daily diets at levels of 3, 10, 30 and 100 ppm for 30 days. The feeding level of 3 ppm gave maximum 0.16-0.23 ppm parent + TCP residues in liver, and the 10 ppm level gave maximum combined residues of 0.5 ppm in kidney. The 30 ppm level gave a maximum residue of 1.7 ppm in liver. At the 100 ppm level, a maximum of 5 ppm was found in beef fat; this decreased to 0.04 ppm 35 days after cessation of feeding. Apparently, residues of TCP were not analyzed for.

Pigs - Pigs were fed chlorpyrifos in the daily diets at 0.3, 1, 3 and 10 ppm for 30 days. Residues (parent plus TCP) were not detected in any tissues at the 1 ppm feeding level. The 3 and 10 ppm levels gave maximum residue values of 0.08 and 0.3 ppm respectively in liver. No residues were found in any tissues 21 days after cessation of feeding.

Barley grain may be fed to cattle at up to 80% of the diet equivalent to 0.8 ppm chlorpyrifos and TCP, while wheat grain may be fed to finishing swine at up to 90% of the diet equivalent to 0.9 ppm chlorpyrifos and TCP. Straws in general are not fed at more than 10% of livestock's diet, equivalent to 0.6 ppm. Wheat bran may be fed to cattle at 25% of the diet, equivalent to 0.75 ppm of chlorpyrifos and TCP in the diet.

Based on the feeding studies we find the above meat and milk tolerances adequate to cover residues resulting from the proposed use.

Poultry - Existing tolerances are 0.1 ppm for eggs and 0.5 ppm for the meat fat and meat byproducts of poultry including turkeys.

Possible poultry feed items are grains at up to 70% of the diet, equivalent to 0.7 ppm chlorpyrifos and TCP; and wheat bran, 10% of the diet equivalent to 0.3 ppm chlorpyrifos and TCP. Thus maximum residues in poultry diets could approach 1 ppm. According to the available poultry feeding study, no detectable residues (<0.01 ppm) were found in eggs at dietary levels of up to 10 ppm. While no residues (<0.01 ppm) were detected in poultry tissues at 0.3 ppm in the diet, 1 ppm in the diet gave residue levels of 0.1 ppm in poultry tissues.

According to PP#3F1306 (ED. R. Gee 3/1/73), maximum residue levels in turkey tissues from the registered pen. treatments were expected to be 0.17 ppm, for which a tolerance level of 0.2 ppm was previously established. The current level of 0.5 ppm is obviously sufficient to include residues expected from the additional feed uses as wheat grain alone may comprise 70% of the diet of turkeys.

Thus we estimate that residues of chlorpyrifos and its metabolite TCP will be less than 0.5 ppm in the meat, fat and meat byproducts of poultry including turkey as a result of the proposed use.

The existing 0.1 ppm tolerance will be adequate to cover residues in eggs likely to occur from the proposed use.

B. Permethrin

This section was reviewed in connection with our memo of 82-MT-03 (E. Zager, 3/22/82).

Barley grain may be fed to cattle at up to 80% of the diet equivalent to 0.25 ppm permethrin and its metabolites in the diet, while wheat grain maybe fed to finishing swine at up to 90% of the diet equivalent to 0.3 ppm. Straws in general are not fed at more than 10% of livestock's diet equivalent to 0.2 ppm.

Grains may be fed at up to 70% of poultry's diet equivalent to ca 0.2 ppm of permethrin and its metabolites.

A cattle feeding study was submitted in connection with PP#8F2099. Groups of 3 cows were fed permethrin at levels of 0.2, 1.0, 10 and 50 ppm for 28-31 days.

At the 0.2 and 1 ppm levels all samples of milk contained <0.01 ppm permethrin; the maximum value from the 10 ppm feeding level was 0.06 ppm (no metabolite results reported). At the 50 ppm feeding level, the maximum value for permethrin was 0.2 ppm; the residue level for each metabolite (DCVA, 3-PB Alcohol and 3-PB Acid) was reported as <0.01 ppm.

Permethrin residues in tissues from the 0.2 ppm feeding level were all <0.01 ppm except for one sample of peritoneal fat which contained 0.04 ppm permethrin. At the 1 ppm feeding level peritoneal fat again was the only tissue to contain permethrin with a maximum of 0.02 ppm. DCVA, 3-PB Alcohol and 3-PB Acid residues in liver, kidney and muscle samples from the 1.0 ppm feeding levels were all ≤0.01 ppm.

A chicken feeding study was submitted in connection with PP#8F2034. Laying hens were fed permethrin at levels of 0, 0.4, 3.4 and 33 ppm. Permethrin residues in the egg whites at all feeding levels were less than 0.02 ppm. At the 3.4 and 33 ppm feeding levels, residues in the yolk ranged up to 0.5 and 0.64 ppm, respectively. Permethrin residues in all liver samples at all feeding levels were less than 0.01 ppm at the 0.4 and 3.4 ppm feeding levels. Residue data for the metabolites of permethrin for those chickens that received 33 ppm permethrin in their diet were submitted with PP#8F2099. Except for one muscle and tissue composite which had 0.02 ppm DCVA, the metabolites (DCVA, 3 PB Acid and 3-PB Alcohol) did not exceed 0.01 ppm

in the tissues. Except for one liver sample which had 0.02 ppm 3-PB Acid residue values for the metabolites did not exceed 0.01 ppm in liver tissues. In whole egg samples, the maximum DCVA, 3-PB Alcohol and 3-PB Acid residues were 0.03, 0 .03 and <0.01 ppm, respectively.

Based on the above data we estimate that secondary residues of permethrin and its metabolites: DCVA, 3-PBAcid and 3-PBAlcohol in milk, eggs and in the meat, fat and meat byproducts of cattle, goats hogs, horses, poultry and sheep will not exceed the established tolerances as a result of the proposed use.

Conclusions

A. Chlorpyrifos

1. For the purpose of this Section 18 exemption, we consider the residue of concern for chlorpyrifos in plants and animals to be the parent compound, chlorpyrifos per se, and its metabolite 3,5,6-trichloro-2-pyridinol (TCP).

2. Adequate analytical methods are available for enforcement. The methods are listed in PAM II as method II for plants which may be employed for grain and grain-based products, and as method IV and V for animal commodities.

3. Residues of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol will not exceed 1 ppm in the grains, 6 ppm in the straw and 3 ppm in the milling fractions of barley, oats and wheat, reflecting the proposed use and a PHI of 28 days.

4. Secondary residues of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol will not exceed currently established tolerances of 2.0 ppm for the meat, fat and meat byproducts of cattle; 1.0 ppm for the meat, fat and meat byproducts of goats, horses and sheep; 0.5 ppm for the meat, fat, and meat byproducts of hogs and poultry, including turkey; 0.1 ppm for eggs; and 0.5 ppm for milk fat, representing 0.02 ppm in whole milk.

5. A reference standard for chlorpyrifos is available from the U.S. EPA Pesticide and Industrial Chemicals Repository.

B. Permethrin

1. For the purpose of this Section 18 exemption, we consider the residue of concern for permethrin to be cis- and trans-permethrin; cis- and trans- DCVA (3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate); 3-phenoxybenzylalcohol (3-PBA) and 3-phenoxybenzoic acid (the latter is for meat, fat, meat byproducts, milk, poultry and eggs only).

2. Adequate analytical methodologies are available for enforcement. The methods listed in PAM II as method I, method III and IIIA for plants may be used for grain and grain-based products; and method II and IV for animal commodities.

3. Residues of permethrin and its metabolites DCVA and 3-PBA will not exceed 0.3 ppm in the grains and 2 ppm in the straw of barley, oats and wheat as a result of the proposed use, reflecting a PHI of 30 days.

4. Secondary residues of permethrin and its metabolites DCVA and 3-PBA, will not exceed currently established tolerances of 2.0 ppm for the fat, 0.15 ppm for the meat and 1.0 ppm for the meat byproducts of cattle, goats, hogs, horses, and sheep; 0.05 ppm for the fat, meat, and meat byproducts of poultry; 0.05 ppm for eggs; and 3.75 ppm for milk fat, representing 0.15 ppm in whole milk.

5. A reference standard for permethrin is available from the U.S. EPA Pesticide and Industrial Chemicals Repository.

Recommendation

TOX considerations permitting, we have no objection to the proposed Section 18 exemption. An agreement should be made with FDA regarding the legal status of the treated commodities in commerce.

cc: R.F.,Circur,Reviewer;chlorpyrifos S.F.,permethrin S.F.; Section 18 S.F.(chlorpyrifos and permethrin).

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