006315

13 APR 1984

Date Out EFB:

TO: A. Castillo/Laird
Product Manager
Registration Division
TS-767

FROM: Samuel Creeger, Chief
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

Reg./File No.: 38906-RE

Chemical: .....Hydantoins

Type Product: Biocide

Product Name: Dantobrom RW

Company Name: Glyco Co.

Submission Purpose: Registration of new chemical for use in recirculating cooling towers

ZBB Code: Other

ACTION CODE: 160

Date in: 3/15/84

EFB # 4242

Date Completed: 4/11/84

TAIS (level II)	Days
61	3

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

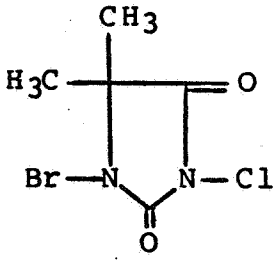
Glyco Inc. has submitted an application for registration of Dantobrom RW for control of bacterial, fungal and algal slimes in recirculating cooling tower systems.

The registrant notes there are currently 13 products registered with EPA which contain halogenated hydantoins as principle active ingredients; 6 of which are for use in industrial water systems, 2 for manufacturing use 2 for pulp and paper industry and 2 for spas and swimming pools.

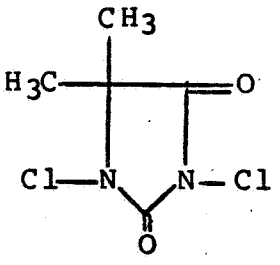
1.1 Dantobrom RW is a formulation containing the following as active ingredients:

1. 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)
2. 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) 028501
3. 1,3-dichloro-5-ethyl-5-methylhydantoin (DCMEH) 128826

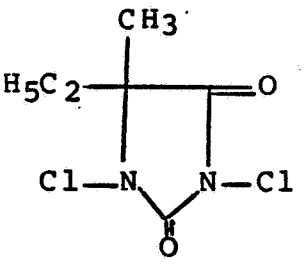
1.2 Chemical Structures



(1)



(2)



(3)

2.0 DIRECTIONS FOR USE

Use directions are appended to this review. Briefly, Dantobrom RW is added to water systems equivalent to 12 to 72-120 ppm concentration (0.1 to 1.0 lb. per 1,000 gallons water).

3.0 DISCUSSION OF DATA

Note: EAB has no file on any previously submitted studies which support current registration of halogenated hydantoins.

Studies reviewed here were submitted under EPA Accession No. 252642.

3.1 Hydrolysis

The active ingredients of Dantobrom RW were dissolved in distilled water at concentrations yielding the equivalent of 100 ppm. The solutions were maintained at 104°F at pH 7.0-7.5. After 30 minutes (dissolution) the samples were analyzed.

Analysis of dimethylhydantoin (DMH) and methylethylhydantoin (MEH) was by HPLC. Note: The analysis did not differeniate between monohalogenated and halogen free DMH or MEH as bisulfite was used during the extraction/analysis phase.

In a related study, Dantobrom RW and bromochlorodimethyl-hydantoin were added to a small scale "organic chlorine demand system" such that the rate of halogen (expressed as Cl_2 equivalent) never exceeded 2 ppm.

Note: Method of residue analysis for this small scale system was not reported.

Results

Equivalent recoveries were reported as ranging from 92 to 95%.

The registrant reports that hydrolysis resulted in 27 to 31% loss of hydantoin equivalents with 6-15% hydantoin equivalents recovered as imines (isopropyl- or butylimines) and 8-11% hydantoin equivalents recovered as ketones. See Table I.

The author reports that the results of the small "organic chlorine demand system" show that the hydantoin ring donates halogen without being split. "Hydantoin" recovery was 99.9 to 104%. "Hydantoin charge" ranged from 103 to 258 ppm. "Hydantoin recovery" ranged 97 to 250 ppm. No N-chloroimines were found. Small amounts of ketones were attributed to oxidation of organic substances present. See Table II.

TABLE I

Hydrolysis of "Halohydantoins"

At 100 PPM In Distilled Water Solution

Compound		Hydantoin Charged, ppm		Hydantoin Recovered, ppm		Ketones Recovered,		N-chloroimines, ppm		Hydantoin Equivalent to Imines, ppm	Halo-forms, ppb	Hyd Acc abi
		DMH	MEH	DMH	MEH	ppm	Hydantoin Equiv. ppm	IPr	2-But.			
DBDMH	(I)	102	0	80	-	9.1	20	-	-	-	55	
DCDMH	(II)	98	0	69	-	3.5	8	10.9	-	15	33	
DCMEH	(III)	0	102	-	78	3.8	8	-	6.2	8	20	
BCDMH	(IV)	96	0	73	-	4.9	11	4.2	-	6		
BCMEH	(V)	0	103	-	89	2.7	5	-	3.3	4	32	
DantoBrom™	(VI)	86	18	74	18	3.4	8	5.9	n.d.	8	120	1

I 1,3-dibromo-5,5-dimethylhydantoin

II 1,3-dichloro-5,5-dimethylhydantoin

III 1,3-dichloro-5-ethyl-5-methylhydantoin

IV 1-bromo-3-chloro-5,5-dimethylhydantoin

V 1-bromo-3-chloro-5-ethyl-5-methylhydantoin

TABLE II

HYDROLYSIS OF DantoBrom™ RW
UNDER "CHLORINE DEMAND" CONDITIONS

Compound	Type of Demand	"Hydantoin" Charged, ppm		"Hydantoin" Recovered, ppm		Ketones Recovered		N-chloroimines, ppm		"Hydantoin" Equivalent to Imines, ppm	Haloforms	"Hydantoin" Account-ability, %	Halogen as Cl_2, Average	
		DMH	MEH	DMH	MEH	ppm	"Hydantoin" Equiv., ppm	IPr	2-But.		ppb		Free	Total
DantoBrom™ RW	Inorganic	258	46	250	53	<0.8	<2	N.D.	N.D.	-	N.A.	99.9	1.4	3.1
DantoBrom™ RW	Organic	105	18	104	18	2.2	5	N.D.	N.D.	-	1680	104	1.9	13.0
DantoBrom™ RW	Organic	105	19	104	19	1.9	4	N.D.	N.D.	-	2980	104	2.0	13.0
BCDMH*	Organic	103	0	97	-	1.9	4	N.D.	N.A.	-	2270	100	1.7	10.0
HOCl/HOBr	Organic	0	0	N.D.	N.D.	2.1	N.A.	N.D.	N.D.	N.A.	750	N.A.	2.2	9.0

* A commercially available spa disinfectant containing bromochlorodimethylhydantoin.

N.D. - Not detected

N.A. - Not applicable

The registrant concluded the data indicate that, at low concentrations of active halogen, haloimines are not formed.

Conclusion

The study is inadequate. EAB is unable to draw a conclusion as to the hydrolytic half-life of the hydantoins as active ingredients in Dantobrom RW. The study did not follow the Environmental Fate Guidelines. Some deficiencies include:

- Study was conducted at 1 pH range, not 3.
- Temperature was excessive.
- Was distilled water sterilized?
- Only one sampling was taken (after 30 minutes).
- Analysis should have included the monohalogenated degradation products.
- No half-life calculations could be determined.

The registrant should provide data on hydrolysis at "use" concentration. The registrant makes the statement that at "use" concentrations of 3 to 5 ppm of Br_2 (total free halogen expressed as Br_2) products formed were limited to the simple parent hydantoins stripped of halogen. Also, the registrant should relate this "use" concentration (of 3 to 5 ppm of Br_2) to the label directions which call for up 120 ppm formulation (1 lb. formulation per 1,000 gallons water). From the above statement, it would appear that the dehalogenated hydantoin ring would be the residue of concern in the environment (and not the imine or ketone fragments as reported of the 100 ppm concentrations).

3.2 Photolysis

Note: While this study is not required under the Guidelines, EAB does request this study in support of registration of pesticides for aquatic impact-indirect discharge uses.

A water/Dantobrom RW solution was prepared with sufficient product for a theoretical hydantoin concentration of 100 ppm. The solution was divided with one part exposed to sunlight for 30 days and the other kept in the dark.

Note: Method of residue analysis is not reported.

Results

The registrant reports "hydantoin accountability" was 93% and 92% in exposed and dark solutions, respectively. The same products as found in the hydrolysis study (hydantoins, choro-imines, ketones and free halogens) were found in both the exposed and dark solutions. See Table III.

However, the registrant reported loss of total chorine was higher in the exposed solution than in the dark solution. Both samples showed reduced levels of hydantoins and increased levels of N-chloroimines and ketones. As N-choroimines formed, they slowly hydrolyzed to the ketone.

Conclusion

This study was not conducted according to the Environmental Fate Guidelines. Some deficiencies are:

- Only one sample was taken (after 30 days).
- No half-life can be calculated.
- Formulated product, not separate active ingredients were used. However, only one active needs to be studied if the registrant can conclude that the other actives should degrade similarily. Most likely that would be the case here.

However, the results show that, with the exception of increased loss of free chlorine in exposed sample, the results of the exposed sample and the unexposed sample were essentially the same.

EAB concludes that, at the concentration used, exposure of Dantobrom RW active ingredients to sunlight has little affect on degradation of the active ingredients. However, EAB does not accept the study as satisfying the photo-degradation data requirement. A study must be submitted using a concentration approximating the actual use concentration since the data in the hydrolyis study suggest the simple hydantoin is stable at "use" concentrations.

7 8

Table III

Photodegradation of Dan Brom™ BW

	Expected Composition Initial Dissolution Mixture[1]	Final Composition Sample Not Exposed to Sunlight	Final Composition Sample Exposed to Sunlight
DMH (ppm)	71	46	42
MEH (ppm)	15	16	12
N-chloroisopropylimine (ppm)	6.1	7.8	5.3
N-chloro-2-butylimine (ppm)	ND[2]	ND	ND
Ketones (ppm)	3.6	9.2	13.9
Free Halogen (ppm as Cl_2)	10	7	0.0
Total Halogen (ppm as Cl_2)	27	20	1.5
Hydantoin Accountability[3]	-	93	92

1. Based on earlier dissolution experiments
2. Not Detected.
3. The percent of the hydantoin charged that is accounted for as DMH, MEH, ketone, and N-chloroisopropylimine.

3.3 Biodegradability

The registrant submitted an abbreviated report on a study of a water treatment plant discharge of holding waters from the Glyco halohydantoin plant.

Results showed that analysis of water initially containing 3,000 ppm dimethylhydantoin concentration contained 15-45 and <1 to 4 ppm of dimethylhydantoin and methylethylhydantoin in the primary effluent, respectively. Less than 1 ppm of either was found in the final discharge before chlorination.

4.0 EXECUTIVE SUMMARY

While the hydrolysis study does not satisfy the data requirements to support registration, some generalizations may be made. It appears that the degradation of the active ingredients in distilled water (at high concentrations) occurs under different mechanisms than that in actual use (at low concentrations). The author reports that, in absence of halogen demand, both active halogen and hydantoin is lost from the Dantobrom RW active ingredients. Degradation products were monochlorohydantoins, N-chloroimines, ketones, carbon dioxide, nitrogen and chlorine ion. In presence of halogen demand, the hydantoin ring is dehalogenated but remains intact.

Also, there appears to be little affect of photolytic degradation of Dantobrom RW active ingredients at high concentrations. With the exception of a greater loss of total halogen, there were no significant differences between the solution exposed and dark control. The same degradation products were found in the exposed solution as were found in the hydrolysis experiment.

5.0 RECOMMENDATION

5.1 EAB concludes that the data are not adequate to satisfy the hydrolysis and photolysis data requirements. Certain deficiences in each of the studies preclude a determination of the hydrolytic or photolytic degradation of the active ingredients of Dantobrom RW. See Sections 3.1 and 3.2, above, for specific deficiencies. The registrant should be informed of these deficiencies.

9 10

5.2 The registrant should submit a hydrolysis and photolysis study conducted at use concentrations. The registrant should consult the Environmental Fate Guidelines for information on conducting these studies.

EAB suggests that the registrant submit protocols for review before initiating these studies. The protocols should describe fully how the registrant intends to conduct the study.

5.3 The registrant should clarify the statement that at "use" concentrations of 3 to 5 ppm of Br_2 (total free halogen expressed as Br_2) products formed were limited to the simple parent hydantoins stripped of halogen. From the above statement, it would appear that the dehalogenated hydantoin ring would be the residue of concern in the environment.

5.4 The registrant should relate this "use" concentration (of 3 to 5 ppm of Br_2) to the label directions which call for up to 120 ppm formulation concentration in water.

Clinton Fletcher
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

10 11