

Monsanto

FROM NAME & LOCATION

S. H. Vogel WCK

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cc D. R. Dill
W. R. Benner
D. K. Lynch
J. F. Quinn

SUBJECT Chlorophenol Dioxin History

REFERENCE

TO : D. P. Roman

Following is a rough draft of a condensed summary on the history of my involvement on the chlorophenol dioxin problem, since its onset in 1970. The work described, for the most part, was carried out at the W.G.K. Plant by myself under the consultation and authorization of the Specialty Product Business Group R & D management (D. R. Dill, W. R. Richard). This summary is by no means "complete," since a more detailed discussion of this work will be presented in a final report which will be written and published in the near future.

This summary is being issued at this time to aid in decision making, with respect to future activities on the dioxin problem.

Work first began on the chlorophenol dioxin problem in early 1970. After analytical method development by Applied Science⁽¹⁾, a study was carried out with the following objectives:

- 1) measure the dioxin concentrations in all Penta/Santobrite process and product streams
- 2) measure concentrations in competitive Santobrite and Penta
- 3) define possible ways to reduce or eliminate the dioxins

The details of this study are reported in reference No. 2. In summary, the study revealed:

1) Higher chlorinated dioxins (hepta CDD and octa CDD) are present in Santobrite and Penta. OCDD is present in greatest amounts. These dioxins are primarily formed during the later stages of chlorination. They are also formed but at a much slower rate, during molten storage prior to prilling. Small amounts of HCDD and OCDD can also form in penta oil solutions (Cyclo-s if held at high temperature over a period of time. (MDL 50. ppm)

2) Lower chlorinated dioxin (tetra CDD) was not detected in finished Pen. However, levels of about 1 ppm TCDD were detected in chlorination mass at the early stages of chlorination. (MDL 0.5 ppm)

3) Santobrite contains somewhat lesser amounts of dioxins than Penta. Some of the dioxins are removed in the Santobrite process. They are removed as insolubles in the Cone settler and also possibly as sublimables in the drying process. The insolubles are currently being sewered.

4) Dioxins were not detected in any of the Penta or Santobrite scrubbing streams.

5) Competitive Penta and Santobrite are comparable in dioxin content to Monsanto's products.

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DIOXIN PRECURSOR STUDY

The most likely suspects for the unexplained CEF toxicity were believed to be polychlorodibenzofurans, or polychloro-2-hydroxydiphenylethers, (or both). We have no current way of quantitating DBF's. While analyzing Catomance Pent esters however, in 1973 (OR 210571-74) for dioxins, I observed that the sample increased in dioxin content when treated with morpholine and surmized, at that time, that morpholine was causing ring closure of dioxin precursors. I decided to look into this further, as a possible means of quantitating CHDPE's in Pen

Five Penta samples were morpholine treated (OR 256745), and after caustic clean-up were GC'd. This gives us a measure of dioxins and precursors. The amount of precursors can then be determined by difference from the original dioxin analyses (Al₂O₃ cleaned).

SAMPLE	Before Treatment		After Treatment	
	hepta CDD ppm	OCDD ppm	hepta CDD ppm	OC P
OR 212180-1-Plant Penta-Std. Conditions	96 160	1060	2624	62
OR 212180-7-Plant Penta-Amended Cond.	102 170	1090	2847	66
OR 211535-Lab Penta-Low Temp.	26 130	990	2658	82
KM-261-Plant Penta-Std. Cond.	25 290	1980	2934	86
OR-256338-Lab Penta-(Sulfur + Al Cat.)	69 110	870	2151	51

These were the same samples recently analyzed by Applied Science⁽¹⁷⁾. Hepta CDD and OCDD levels on the morpholine treated samples have increased dramatically in each case. Hexa CDD was not determined on the treated samples since large amounts of interfering dibenzofurans and phenylethers were not removed prior to morpholine treatment.

I also observed that Caustic (NaOH solution) would likewise, cause cyclization of the precursors to dioxins (256751).

The benzene extracts from the morpholine treated samples were submitted to Applied Science for low level dioxin analyses (particularly for hexa CDD and lower chlorinated dioxins). In the meantime, I developed a method that allows quantitation of Penta-CDD-OCDD precursors without the interferences in the envelope:

9/16 The Penta sample is dissolved in benzene, and chromatographed on alumina with excess benzene. All non-phenolics are eluted (this effluent can be GC'd to quantitate original dioxins present). The chlorophenols, which now include pentachlorophenol, tetrachlorophenol, other hydroxy Aromatic and the various dioxin precursors, are released from the alumina by MeOH washing. Morpholine .

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is added to the methanol effluent and placed on a steam bath (round bott flask equipped with Snyder Columbe). The methanol is boiled out while t morpholine causes cyclization of the precursors to dioxins. The solutio is cooled, and acidified to pH<2.0 by addition of 1:1 aqueous Hcl. The released chlorophenols and dioxins are taken up in benzene. The benzene solution is washed twice with aqueous caustic and 3 times with distilled water. Appropriate dilutions in benzene are prepared and subsequently EC The chromatogram is clean of interferences in the Penta CDD and Hexa CDD region allowing ready quantitation of these dioxins (OR256760).

A comparison of dioxin values obtained on the morpholine treated benzene extr sent to Applied Science⁽¹⁹⁾ against the values I obtained by the method just de is presented below (OR256774).

	Concentration (ppm)					
	Unknown Chloro		Penta CDD		Hexa CDD	
	Aromatic	G.W.M.	G.W.M.	S.H.V.	Hepta CDD	S
212180-1 Control Plant	0.2	0.1	120	316	2100	21
212180-7 Plant Low Temp.	0.3	0.1	110	320	1800	21
211535 Low Temp. Lab	4	0.4	73	186	1400	21
KM-261 Control Plant	0.3	0.4	50	112	1500	21
256338 Al/S Lab	2	1.5	180	150	1600	21
256304 Al/Te Lab	-	-	-	175	-	1
256386, Reichhold	-	-	-	161	-	2
214234, Mon. distilled	-	-	-	N.D.	-	N
130°C Batch Sample from Plant	(Not determined)					
>50 ppm Penta CDD (SHV)	"-" Indicates not determined					

G.W.M. analyses are the sum of original dioxins present plus the dioxins generated in morpholine treatment: S.H.V. hexa CDD values represent on dioxins formed during morpholine treatment, and can be considered equivalent to the precursor concentrations in the untreated samples. All hepta and values are sums of precursors plus original dioxins.

What do the analyses tell us? Does the ease of cyclization of the precursor to dioxins have any significance?

1) First, and most importantly, a similar mechanism of cyclization could conceivably occur in biological systems, due to the catalytic effect of amides in protein and nucleic acids. The sum of the precursors plus diox in Penta is high enough concentration to account for the degree of CEF Toxic observed. Attempts to cause cyclization with egg albumin were inconclusive (256763). (Toxic fur had 13.3, 54.7 Hexa CDD - by 1/2/76 to J. H. G.)

2) The values given should not be taken as absolute. Method refinement is needed to determine a number of factors, such as, completeness of cycliza recoveries, etc. Agreement between labs is not good, particularly on hexa values.

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14) Chloracne response as measured by Rabbit Ear test at CMU, also show no clear relation to the precursor concentrations.

LITERATURE REVIEW (Aug 75) - Compared. - 11.1/11.1

Following the discovery of base catalysis of dioxin precursors to dioxins, a thorough review of all dioxin literature, on hand and an up-dated search on new literature, was made. Two questions were in mind.

1) Is anyone studying dioxin precursors as a source of CEF or REC activity in chlorophenols?

2) Has anyone else recognized base catalyzed cyclization of these precursors?

The answer to each of these questions is still "no." The 2nd is evidenced even in the most recent literature (1/75) where caustic is still being used for phenolic extraction in sample preparations. (21)(22)(23)

HEXACHLOROBENZENE

Presence of hexachlorobenzenes in Penta chlorophenol also came to light in the last year or so. The same benzene extract obtained for dioxin analyses can be GC'd for HCB. Method developed by Applied Science and adapted on my GC, gave the following results on a few selected samples.

<u>SAMPLE</u>	<u>HEXACHLOROBENZENE</u>	<u>IDENTIFICATION</u>
OR 212180-1	39.7 ppm	Plant Penta - Std. Conditions
OR 212180-7	31.5	Plant Penta - Amended Cond.
OR 211535	27.7	Lab Penta - Low Temp.
KM-261	56.4	Plant Penta - Std. Cond.
OR 256338	13.0	Lab Penta - Al + Sulfur Cat.
OR 214234-Refined	53.4	Plant Penta-Lab Distilled
Reichhold Lot No. 72874	28.8	Reichhold's Improved Material
Dow EC-7 Lot No. 09214M	106.	Dow's Refined Material
Monsanto Australia Ba No. 73346026	15.3	
OR 256399	999.6	Lab - overchlorinated batch
OR 256304	30.6	Lab, Al/Te cat

Hexachlorobenzene probably comes about through Hcl ether cleavage of dioxin precursors to generate HCB and catechols. Lower chlorinated benzenes are probably also present. There is also indication that Al/S system may suppress HCB formation to some extent.

S. H. Vogel
WGK Plant Process Tech.

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