

F. 3. b. (Cont'd.)

the flaking period. There is little change in other dioxins from start to finish of flaking. The hepta CDD and OCDD values are inflated due to exposure to caustic during sample clean-up (See Section B. 2.).

c. Distilled Penta - Dow VS Monsanto (OR 256326)

A sample of Dow's commercially refined Penta was obtained in September, 1974. Comparative analyses to Monsanto lab distilled Penta is presented below.

	<u>Dow-Lot 09214M</u>	<u>Monsanto-Lot 214234</u>
Appearance	Slightly Off-White Prills	White Powder
Chem. Assay	101.26%	101.69%
MOI	< 0.1%	< 0.1%
MOT	98.0%	99.0%
Alk. Insols.	0.05%	0.04%
GLC: Tetra	7.6%	11.5%
Penta	91.9%	88.5%
H.B.	~0.5%*	< 0.1%
Dioxins:		<u>Duplicate Analyses</u>
<Hepta CDD	'Interfering Low Boilers	1.2 ppm, 0.1 ppm
Hepta CDD	12.8 ppm	0.6 ppm, 0.1 ppm
OCDD	9.9 ppm	0.6 ppm, 1.2 ppm

* Unknown which nearly co-elutes with tetrachlorophenol

There are a number of similarities as well as differences. Chemical assay, MOI, MOT, and Alkali Insols are comparable. Differences are as follows:

- 1) Appearance color of Monsanto material is noticeably lighter (due to our RT 53A stabilizer).
- 2) Tetrachlorophenol/Pentachlorophenol ratio is lower in the Dow sample.
- 3) There are a number of GLC "strangers" in the Dow sample - particularly low boilers.
- 4) Monsanto distilled material is lower in total dioxins.

GLC analysis was by internal marker method (OR 211759). Dioxin analysis was by Method No. 70-20. (Response factors described in previous section of this report.) Reproducibility of dioxin test is not particularly good as indicated by duplicate analysis on the Monsanto sample.

The Dow EC-7 sample was also examined for metals. Aluminum was the major metal present along with the usual trace amounts of other metals. This indicated the Penta was initially made by the phenol chlorination route and that refining does not remove all the aluminum catalyst.

F. 3. c. (Cont'd.)

(For detailed metal analysis, see Appendix E.2.)

Dow's recent distillation Pat. No. US 3816268 refers to the use of amine stabilizers.²² We suspected the unknown component, co-eluting with tetrachlorophenol might be such a compound. The Dow sample was individually spiked with the following amines which were mentioned in their patent. None matched the elution time of the unknown.

Triethylamine
Diphenylamine
Tetraethylenepentamine
Aniline
Triphenylamine

No other efforts were made to identify the unknown.

The wood treating industry has indicated there is a very severe caking and dust problem with Dow's EC-7 material. They also indicate Penta solvency compared to technical Penta in common wood treating oils is lower. There was one instance where the EC-7 material could not be used in their process because of low solvency.

No other producer, foreign or domestic, is commercially marketing a refined Penta. Vulcan Materials Co. however was recently issued a Patent (Reference No. 31) which describes batch distillation of Penta.

We have not studied the adaptability of our refined Penta in the wood treating industry. If we were to begin marketing refined Penta in a prilled form tomorrow, our product would likely have the same disadvantage as Dow's EC-7.

d. Santophen - 1

W.G.K. AR&D examined Santophen 1 for dioxins. None were found. MDL in their test was 0.1 to 0.5 ppm. Because of interferences however, chlorodioxins with less than 3 chlorine atoms could not be determined by their procedure. Their work is presented in W.G.K. AR&D Report No. 2448, "Dept. 239 - Santophen 1 - Analyses for Presence of Chlorodibenzo-p-dioxins in Product", 4-18-74, H. L. Campbell (Reference No. 44). (See more recent analyses pg. 67.)

e. Competitive Penta

The following Penta samples were received and analyzed for the various properties indicated.

	<u>Reichhold Lot 27874</u>	<u>Brazilian Chlorogil 8-27-74</u>	<u>Brazilian Chlorogil 10-4-74</u>	<u>Mexican Pentarin Lot 12731</u>	<u>WGK Typical</u>
Appearance	Brown Prills	Pulverized Flakes	Pulverized Flakes	Pulverized Flakes	Tan Prills
MOI	1.0%	2.0%	<0.1%	6.0%	<0.1%
MOT	32.0%	9.0%	34.5%	11.5%	55.0%
Chemical Assay	98.3%	98.3%	97.8%	95.6%	97.5%
GLC*					
Tetra	6.99%	10.8%	12.7%	4.4%	6.0%
Penta	85.69%	80.7%	78.4%	84.6%	86.5%
HB	7.32%	8.5%	8.9%	11.0%	7.5%
Dioxins:					
<Hepta**	3360 ppm	1108 ppm	1570 ppm	1601 ppm	700 ppm
Hepta	1337 "	675 "	1448 "	1632 "	1000 "
Pre-OCDD***	101 "	74 "	161 "	1143 "	370 "
OCDD	1272 "	1314 "	1555 "	3036 "	2700 "
TOTAL	6070 "	3171 "	4734 "	7403 "	4770 "

* Internal MKR. GLC Method (OR 211759).

** GLC Method (OR 212188) - Modified Method No. 70-20.

*** This compound is probably Octachlorodibenzofuran.⁴³

e. (Cont'd.)

Metal analyses were also run on the Mexican and Brazilian samples (See Appendix E, 2, for details). Dioxins were determined by Method 70-20. ^{29, 30} W.G.K. typical material is comparable or better quality compared to the competitive samples. There was no gross difference in dioxin content between any of the samples. Dioxin values (hepta CDD & OCDD) are inflated on all samples due to exposure to caustic in sample preparation (See Section B. 2. for details).

The Reichhold sample was later included in CEF studies. (See Section F-7).

f. Miscellaneous Samples

The following miscellaneous samples were also analyzed for dioxins by Method 70-20.

	<u><Hepta CDD</u>	<u>Hepta CDD</u>	<u>OCDD</u>
1) Dept. 236 Cone Tank Alkali Insolubles (OR 212171)	0.94%	0.59%	0.99%
2) Venturi Penta (OR 212192)	3.3 ppm	1.4 ppm	5.9 ppm

F. 3. f. (Cont'd.)

	<u><Hepta CDD</u>	<u>Hepta CDD</u>	<u>OCDD</u>
3) Dept. 237 Chloro-phenol Fractions cut (OR 212191)			
4) Overchlorinated Plant Penta-Ba, J-9 (OR 256342)	(Not determined - Sample Contained 4.65% Alk. Insols)		2.45%
5) Alkali Insolubles from Spent Central Fume Scrubber Liquor (OR 212171)	0.37%	0.31%	1.05%

Cone tank insolubles are from Santobrite solution prepared from a mixture of scrap Penta and Prill Fume Liquor. Venturi Penta is Penta from prill fumes. Chlorophenol Fractions is raw material chlorophenol for Penta (Dept. 236). The overchlorinated Penta is an end of batch chlorinator sample from a batch which was accidentally overchlorinated on Oct. 10, 1974. (Over chlorination resulted from faulty X-Pt. reading at end of batch.)

As of this writing, we have not analyzed the alkali insols (Samples 1 & 5) for those dioxins containing less than 7 chlorine atoms. We suspect though, copious amounts of the lower chlorinated dioxins, including TCDD, are present. We believe they are being generated through alkaline catalyzed cyclization of dioxin precursors. These insols, and the aqueous solutions associated with them, should be handled with extreme care.

4. Plant Demo - Low Temp. Chlorination

Bioassay tests (1973) on low temperature lab prepared Penta indicated a moderation of CEF activity.⁵⁷ This encouraged us to try low temperature chlorination in the Plant. Early in 1974, Amendment "F" to Dept. 236 SMPD (Reference No. 45) was prepared and approved to allow the tests. The following parameters were evaluated: 1) reduced temperature from 1.400 to 1.600 sp. gr., 2) increased catalyst level, and 3) reduced X-Pt./batch temperature spread during "rate of rise". Due to cooling limitations of the heat exchanger, low X-Pt./temp. spread could not be achieved without reducing the Cl₂ feed rate to a trickle. This extended chlorination time too much. Another amendment (Reference No. 46) was written to permit reduction of batch size to 50% of normal. This time the low spread was achieved without extending chlorination time.

In summary, the tests were carried out in seven segments, one of which was at standard conditions. Two to five batches were made at each set of conditions. Composite samples were made of each segment

F. 4. (Cont'd.)

and analyzed for higher chlorodioxins and other properties. Data from the tests are summarized on Table No. 1 (Page 41). Test results at this point indicated the following:

- (1) Low temperature from 1.400 to 1.600 sp. gr. gave a significant reduction in non-phenolic HB's eluting prior to hepta CDD. The reduction was comparable to that achieved in low temperature lab batches (211535 & 211525).
- (2) Increased catalyst level gave slightly lower total dioxins (We had not observed this in lab low temperature batches. In addition, Method No. 70-20 was used for analyses, and all values are no doubt inflated.)
- (3) HB's remained about the same level in all segments (internal marker method OR 211759).
- (4) From an operating standpoint, low temperature had a negligible effect on total batch time. Low spread was also easily maintained when batch size was cut in half. (A second heat exchanger would therefore be expected to give the same result on standard size batches.)
- (5) Average chlorine efficiency was increased about 4% when catalyst charge was doubled.
- (6) Normal quality characteristics remained essentially the same in all segments.

Batch temperature in the tests was primarily controlled by varying the chlorine feed rate while maintaining the same amount of cooling.

5. BioAssay On Low Temp. Plant Penta & Penta Oil Solutiona. CEF and Chloracne Response

The composite samples (OR 212180) from low temperature plant chlorination tests (References 45 & 46) were submitted for CEF and chloracne tests. A sample of Venturi Penta in AD-73 oil (48% wt.) was also submitted along with a sample of our current Penta additive mixture. The test results are summarized on Tables No. 2 & 3, (Pages 42 & 43).

Some of the plant low temperature samples showed a moderation in CEF activity (negative at 500 ppm), but none matched the moderation observed in low temperature lab Penta samples. The 48% Penta solution sample and the additive mixture were each void of CEF activity at the highest dietary level tested (1500 ppm). The chloracne responses on plant test samples were very confounding - best sample was the control material? ?

TABLE NO. 1

DEPT. 236 - AMENDMENTS F & H DATA SUMMARY - AVERAGES

S. H. Vogel
5/15/74

	a	b	c	d	e	f	g	h										
Cl ₂ Assay (%)	1.400 Temp. (°C)	1.600 Temp. (°C)	Cat. Conc.	Final Spread (°C)	r.r. Heat History	<H ₇ CDD (ppm)	H ₇ CDD (ppm)	Pre- OCDD (ppm)	OCDD (ppm)	Total Dioxins (ppm)	H B (%)	MOI (%)	MOT (%)	Chem. Assay (%)	Total Time	Cl ₂ Eff. (%)	CONDITIONS	
OR 212180-1 CONTROLS (5)	94.75	94.8	106.9	0.073	7.0	16.5	713	1003	369	2716	4800	7.84	2.8	49.1	97.9	6'11"	81.9	CONTROL
OR 212180-2 Segment 1 (5)	93.6	79.3	114.4	0.074	6.7	16.4	689	1305	468	2929	5391	7.45	2.8	39.0	97.6	6'7"	83.6	80°C.
OR 212180-3 Segment 2 (5)	95.8	64.7	104.5	0.075	6.5	15.2	409	1170	522	2526	4627	7.09	1.7	57.0	98.3	7'52"	82.1	65°C.
OR 212180-4 Segment 3 (5)	96.0	64.4	102.5	0.124	6.5	14.8	389	942	544	1944	3819	7.13	3.7	44.0	98.2	8'31"	86.8	65°C 2x CAT.
OR 212180-5 Segment 4 (3)	95.0	63.1	104.4	0.066	3.1	41.1	397	850	334	2836	4417	7.53	3.3	32.0	98.4	14'7"	81.2	(Long r.r. Time) 65°C Low Spread
OR 212180-6 Segment 5 (4)	94.5	62.6	110.4	0.127	3.6	14.8	487	659	452	2696	4294	8.30	4.9	69.5	97.8	6'36"	---	1/2 Batch 65°C. Low Spread 2x CAT
OR 212180-7 Segment 6 (7)	94.0	64.4	110.1	0.093	2.8	18.0	332	559	314	2139	3344	7.50	4.0	66.8	98.2	6'58"	----	1/2 Batch 65°C. Low Spread
KM-261	90-95	~95	~110	~0.073	~7.0	~17	793	1092	120	3775	5780	~9.0						Plant Std. Lot
211535	100	80	~110	0.073	~3.0	< 10	321	523	< 50	3409	4303	7.45						Lab Reduced Temp.
211525	100	80	~110	0.073	< 1.0	< 10	337	504	291	3593	4725	7.22						Lab High Level Cl ₂
12938	100	~55	~70	~0.073	< 1.0	< 1.0	209	369	< 10	999	1577	5.30						Lab Min. Temp.
REICHOLD (6/6/73)---	---	---	---	---	---	---	190	647	< 10	2196	3033	8.28						
TOTAL PERICARDIAL FLUID (Survivors Only)																		Total Deaths
Sple.	Fluid																	
1	3.55						10											
2	3.15						15											
3	1.70						12											
4	2.15						12											
5	1.25						7											
6	1.65						6											
7	1.34						6											
COMMENTS																		
1. Individual batch conditions and analyses - Refer to Notebook Page No. OR 212180.																		
2. Last 5 entries are included for comparison purposes.																		
3. For details on compositing - See Notebook Page 212180.																		
a. Average batch temp. from 1.400 to 1.600 sp. gr. @70°C. (degrees C)																		
b. Average batch temp. from 1.600 sp. gr. to 130°C. batch temp.																		
c. Lbs. Aluminum catalyst per lb. mole ~phenol.																		
d. (mm) ² area between X Pt. & batch temp. from 130°C. batch temp. to end of batch (from strip chart).																		
e. H ₇ CDD ~ Hepta CDD																		
f. Probably Octachlorodibenzofuran - see Reference No. 43.																		
g. Total batch time from 1.400 sp. gr. to end of batch.																		
h. Determined by Gr. change of Scrubber Phenol.																		

TABLE NO. 2

CHICK EDEMA FACTOR BIOASSAY WITH
PLANT-PRODUCED PENTACHLOROPHENOL

42.

Project No. BTL-74-	Lot No.	Process Condition	ppm					ppm					Total Deaths
			0	150	500	1000	1500	0	150	500	1000	1500	
			Pericardial Fluid Volume (ml)					Mortality per 12 checks					
28	212180-1	Standard	0.10	0.12	0.15*	1.34*	1.20*	1	0	1	2	6	10
29	212180-2	80°C	do	0.10	0.12	1.24*	0.52*	do	2	2	2	8	15
30	212180-3	65°C	do	0.12	0.18*	1.06*	0.33*	do	0	2	2	7	12
31	212180-4	65°C 2x Catalyst	do	0.10	0.12	1.33*	0.86*	do	0	0	1	10	12
32	Low Spread 212180-5	65°C slow Cl ₂ rate	0.09	0.13	0.20*	0.38*	0.33*	0	0	0	4	3	7
33	" " 212180-6	65°C 2X catalyst reduced batch	do	0.13	0.46*	0.39*	0.60*	do	0	1	0	5	6
34	" " 212180-7	65°C reduced batch	do	0.12	0.15*	0.22*	0.69*	do	0	0	0	6	6
35	212180-9	Recovered Venturi	do	---	0.12	---	0.10	do	---	0	---	2	2
36	212180-8	Additive Mixture **	do	---	---	---	0.10	do	---	---	---	0	0

* indicates positive check edema factor activity.

** 15 ppm in diet equivalent to 1500 ppm pentachlorophenol addition.

TABLE NO. 3

Rabbit Ear Chloroene Bioassay with
Plant-Produced Pentachlorophenol *

Project No. CMU-74-41	Lot No.	Process Condition	Change in Ear Thickness (10-3 inch)	Visual Score	Microscopic Score
-----	-----	Ointment Control	<u>12.4</u>	<u>0.2</u>	<u>0.1</u>
A	212180-1	Standard Batch	16.0 ^a	1.0 ^a	0.9 ^a
B	212180-2	80°C.	22.9	2.0	1.3
C	212180-3	65°C.	23.6	1.9	1.5
D	212180-4	65°C 2x Catalyst	18.8	1.5	1.0 ^a
E	212180-5	65°C Slow Cl ₂ rate	18.5	1.6	1.3
F	212180-6	65°C 2x Catalyst reduced Batch	18.3	1.5	1.4
G	212180-7	65°C Reduced Batch	20.9	1.6	1.6

* Thirty applications of 0.5 g of an ointment containing 5% test material.

a. Indicates values that were NOT statistically different from control; all unmarked values are statistically greater than the control.

F. 5. b. Quantitative Evaluation of CEF Data

We next tried to evaluate the BioAssay data quantitatively to see how close we did come to matching the improvement seen in the low temp. lab batches. This evaluation is found in Appendix E (Item No. 3). In short, the "low spread" samples came within a few % of matching 211525 and 211535 material. The evaluation also predicts that if X-Pt/temp. spread is kept at 1°C or less during "rate of rise", we will match or surpass the CEF improvement obtained on the lab low temp. Penta. In addition, only three of 17 process parameters that were examined for relationship to CEF data gave confounding correlation to the predicted. Statistically, the low temperature from 1.400 to 1.600 Sp. Gr. was also quite important in moderating CEF activity.

6. Chlorination Studiesa. CAT. Impurities, Al/S Catalyst, Cat. Swamping Effect, and Penta Sulfur Analyses.

Additional chlorination studies were carried out in the 74-75 period. The studies were aimed at finding ways to suppress dioxin/HB formation. Areas studied were:

- (1) Alternate catalyst systems
- (2) Effect of catalyst impurities (Fe & Mn)
- (3) Effect when swamping with highly soluble catalysts (SbCl₃ & ZnCl₂).

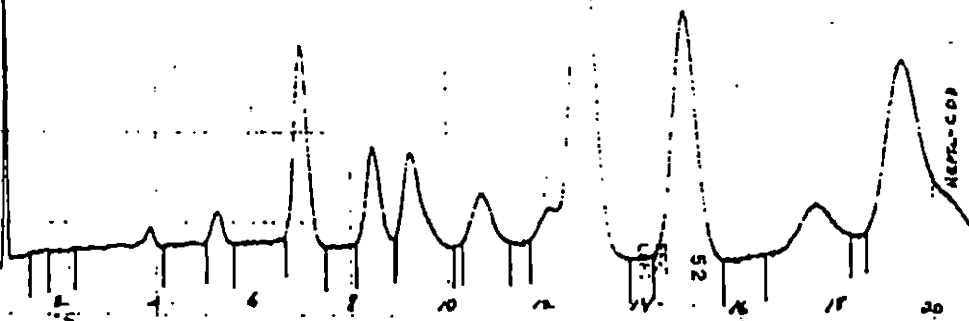
Data from this work is presented on Table No. 4 (Page 46). Only the Al/Te and Al/S alternate catalyst systems demonstrated a moderation in by-product formation. Chlorination selectivity was also enhanced as evidenced by higher than normal tri & tetrachlorophenol maximums. Reactivity was essentially unchanged as measured by chlorination time. One peculiarity of these systems is the obvious reduction/elimination of two non-phenolic components on the GC, believed to be hepta and octachlorodibenzofuran. (See Figure No. 1, Page 45.) Similar benefits were also observed over a large range of Al/S catalyst ratios. This implies there is some minimal amount of sulfur or tellurium required, and no benefit is gained when using quantities above the minimal amount. Other benefits are slightly increased chemical assay, markedly reduced alkali insolubles, and a significant reduction in < hepta CDD non-phenolics. Recently examined Reichhold Penta also has these characteristics. We looked for sulfur in their material: (256347)

	SULFUR	
		Avg.
Reichhold Lot No. 6-6-73	10 ppm & 5 ppm	8 ppm
Lab Prepared Al/S Cat.		
OR 256330	16 ppm & 13 ppm	15 ppm
OR 256347	5 ppm & 2 ppm	4 ppm

Figure No. 1

1-16-76
S.H. Vogel

LAB PENTA - LOT OR 257041
AL CATALYST
STD. PLANT CONDITIONS



257042
129005

LAB PENTA - LOT OR 257042
AL/S CATALYST
STD. MFG. TEMPERATURES

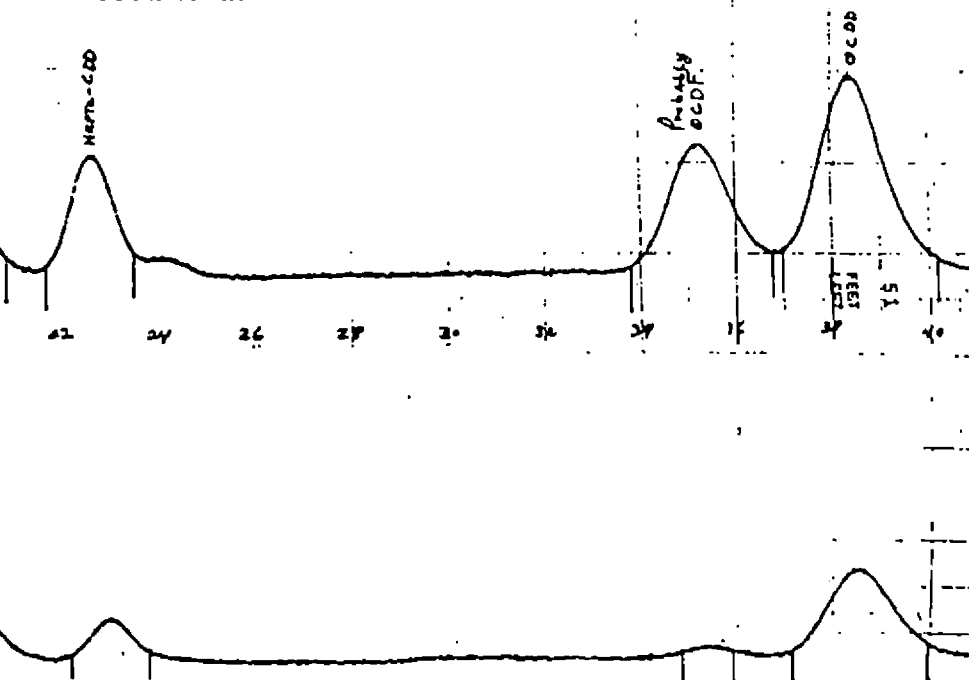


SPECTROSCOPY METHOD NO. 73-1 (MODIFIED)

1.0 GRAM PENTA IN 10 ML. BENZENE - CHROMATOGRAPHED OVER
40 ML. Al_2O_3 (5% H_2O DEACTIVATED), COMPOSITE 200 ML.
BENZENE ELUATE. 5.0 μ l OF 5000 x 1 DILUTION INJECTED.

GC CONDITIONS (MP-3750 - NICKEL 63 DETECTOR)

9 ft. x 1/8 in. GLASS COLUMN - 4E XE-60, 80/100 CHROM W HP
ISOTHERMAL 230°C.
HELIUM 60 ml/min.
PURGE 120 ml/min.
INJECTION TEMP. 230°C.
DETECTOR TEMP. 280°C.
ATTENUATION 1k x 1
RANGE 10 x 1
PULSE INTERVAL 150



1-14-76

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BATCH NO	CAT.	CAT. Conc.	% TETRA	% PENTA	% HB	PPM $\text{C}_{12}\text{H}_{10}\text{Cl}_2$	PPM H_7CDD	PPM C_{10}Cl_2	PPM C_{12}Cl_2	CHEM. ASSAY	COMMENTS
212197	Al/Ta	0.4/0.1	7.50	84.73	7.77	110	317	<10	2164	99.8	
256304	Al/Ta	0.4/0.05	6.32	87.14	6.54	93	496	<10	2174	99.9	
256322	Al/Ta	0.4/0.05	4.61	87.40	7.99	252	183	128	1827		Add Anhydrous Phenol dropwise during r.r.
256306	Al/ SnCl_2	0.4/29.2	4.00	88.9	7.09	885	1098	2727	1951	100.9	MOST SnCl_2 dissolved.
256313	Al/Sb	0.4/15.6	-	Sb	didn't dissolve	—	—	—	—	—	DISCONTINUE BATCH.
256310	Al/Zn	0.4/15.0	-	Zn	"	"	"	"	"	"	"
256320	Al/ ZnCl_2	0.4/32.0	-	ZnCl_2	"	"	"	"	"	"	"
256270	Al/Mn	0.4/0.1	5.32	86.71	7.97	299	847	195	2375	99.6	MOI 3.0%, MOT 10.5%
256317	Al/ FeCl_3	0.4/0.15	12.22	79.60	8.18	178	157	10	912		~100ppm Fe in Finished Penta-chlorinate
256383	Al/Zn	0.4/0.1	6.20	88.59	5.21	362	505	114	1752	99.0	MOI 2.0%, MOT 48.0%
256380	Al	0.40	8.07	84.85	7.08	329	1281	165	3101	99.7	CONTROL BATCH
256394	Al	0.44	6.98	87.49	5.53	748	128	Trace	1233		CONTROL BATCH
256392	Al	0.56	0.95	93.59	5.46	1254	228	143	2830		REPEAT OF OR211525
256396	Al	0.80	0.48	95.90	3.62	330	392	393	2272		" " " , MORE CAT + LOW Spn
											MOI MOT
256327	Al/S	0.4/0.97	2.12	92.04	7.84	101	189	<10	1891	99.8	8.0 10.0
256338	Al/S	0.4/0.05				367	233	<10	1395	101.0	<0.1 55.0 WITH ADDITIVES
			5.10	87.85	7.05					100.2	5.0 9.0 WITHOUT ADDITIVES
256344	Al/S	0.4/0.45				267	147	<10	1442	99.9	<0.1 69.0 WITH ADDITIVES - S during r.r.
			4.91	87.06	8.03					99.7	7.0 14.0 WITHOUT ADDITIVES.
256330	Al/S	0.4/0.1	7.54	86.01	6.45	201	232	<10	863	101.0	
256399	Al/S	0.8/0.2	<0.1	79.93	~20						OVERCHLORINATED - WOULDNT POINT.
256372	Al/ OSn	0.4/0.38	<5.0	20.71	~75					102.3	BATCH NEVER POINTED
256378	Al/ OSn	0.4/0.85	~20.0	~30	~50						DISCONTINUE - REPEAT OF 256372

CONDITIONS

1. FOUR MOLES - FRACTIONAL Phenol / BATCH
2. MULTI PINHOLE JET Cl_2 - NO AGITATION
3. 60°C, 1.400 → 1.600 SP. GV. @ 70°C
4. Jones Chem. REVMORIZED Cl_2
5. Reynolds - ALUMINUM TURNINGS
6. 2 LITR Ice Kettle - EXTERNAL HEAT - INTERNAL MANTLE COOLING COIL

- a. grams / 4.0 moles ~ 0.04
- b. INTERNAL MARKER GC - OR211759
- c. All nonphenolics lower boiling than hepta CDD
- d. H_7CDD ~ Hepta CDD, METHOD 70-20
- e. Probably OCTACHLORODIBENZOFURAN - See Ref. 4.
- f. r.r. = RATE OF RISE
- g. When XPT MEETS BATCH TEMP. @ 130°C.

- F. 6. a. The analyses were carried out by P. Jeannot of Physical Sciences Center. An oxyhydrogen combustion technique was used. (Notebook Page 772190) Although there is a wide variation in duplicate analyses, there is indication that Reichhold may be using sulfur in their system. Average sulfur content in their material is higher than our standard material. In addition, of the initial 94 ppm sulfur added to OR 256330, only 15 ppm remained at the end of chlorination. The same thing may have happened to the Reichhold sample during manufacture. A major assumption is made — that being, the sulfur analyses are not grossly in error.

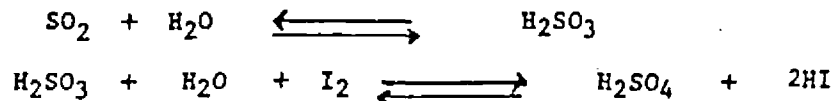
All Al/S runs on TABLE 4 were made at low temperature front-end (60°C. from 1.400 — 1.600 gr.). Some additional Al/S batches were made at standard manufacturing temperatures. Data from these runs are presented on TABLE No. 5. Only cursory dioxin analyses (Method 73-1) have been run on these samples to date. Compared to the control, non-phenolics in all Al/S runs are reduced about the same amount. We cannot explain the unusually high and variable HB content in the batches. Further evaluation might be done before Al/S system is tried in the plant.

Although we have not tested Al/Selenium system, it should exhibit the same effects as Al/Te or Al/S systems. Selenium is an analogue of Te and S. Use of Te or Se at this time was ruled out due to their toxic and cost disadvantages.

b. H₂O Content Before Catalyst Addition

Introduction of moisture to the chlorination mass via raw materials or other sources has traditionally been a concern. Presence of moisture after catalyst addition is known to moderate catalyst activity, or in severe cases, totally deactivate the catalyst. The detrimental effects of moisture in Cl₂ feed has been illustrated in a 1972 study by Neil Thompson.⁴⁷ Chemical assay and other quality characteristics are significantly harmed.

In lab chlorination studies, we have tried to minimize the moisture (in raw material phenol) problem by chlorinating for 30 to 60 minutes prior to catalyst addition. By-product HCl strips the moisture out. This is illustrated on Figure No. 2 (Moisture vs Level of Chlorination). Moisture content goes essentially to zero near the dichlor stage. Figure No. 2 also shows moisture profiles while chlorinating in the presence of sulfur as well as SO₂. The rate of H₂O disappearance was essentially the same on all three profiles. We had hoped S or SO₂ would facilitate titration of H₂O to H₂SO₄, analogous to K. F. titration:



LAB CHLORINATIONS
AL/S EVALUATION

TABLE NO. 5.

1-14-76
S.H. Vogel

CONDITIONS:

SAME AS TABLE 4 BATCHES -
EXCEPT STL. MFG. TEMPERATURES + 5 MOLE BATCHES.
(i.e., 100°C, 1.400 → 1.600 Sp.Gr.)

BATCH NO.	CAT.	a CAT. CONC.	TETRA	PENTA	HB	b ALK. INSOL.	CHEM ASSAY	BEFORE ADD.		AFTER ADD.		c HCB	COMMENTS
								MOI	MOT	MOI	MOT		
257041	AL	AI / S 0.15	7.77	82.74	9.48	0.050	97.8	2.0	39.0	<0.1	68.5	22.5	CONTROL
257042	AL/S	0.15/.0375	5.69	84.99	9.32	0.039	97.0	2.6	20.0	<0.1	50.5	12.7	
257044	AL/S	0.15/.075	8.51	81.87	9.62	0.038	97.7	4.2	31.0	<0.1	54.0	12.0	
257049	AL/S	0.15/.019	6.20	81.60	12.20							27.3	

a. grams / ~ mole of OOH

b. W.G.N. METHOD 10,017, EXCEPT EXTEND CAUSTIC
COOK PERIOD TO DELIBERATELY CYCLIZE PRECURSORS
TO DIOXINS. (OR 257048)

c. HEXACHLOROBENZENE - by GC OF BENZENE ELUATE FOR DIOXIN
ANALYSIS by METHOD NO-73-1 (APP. SC.) (OR 256740)

F. 6. b. (Cont'd.)

The difference being, Cl_2 would be the oxidizing agent instead of I_2 . Due to the high proton concentration in the mass, we suspect the equilibrium to sulfate was suppressed. This might be worth another try in the presence of barium ion which should force the equilibrium to the right by precipitating BaSO_3 and BaSO_4 .

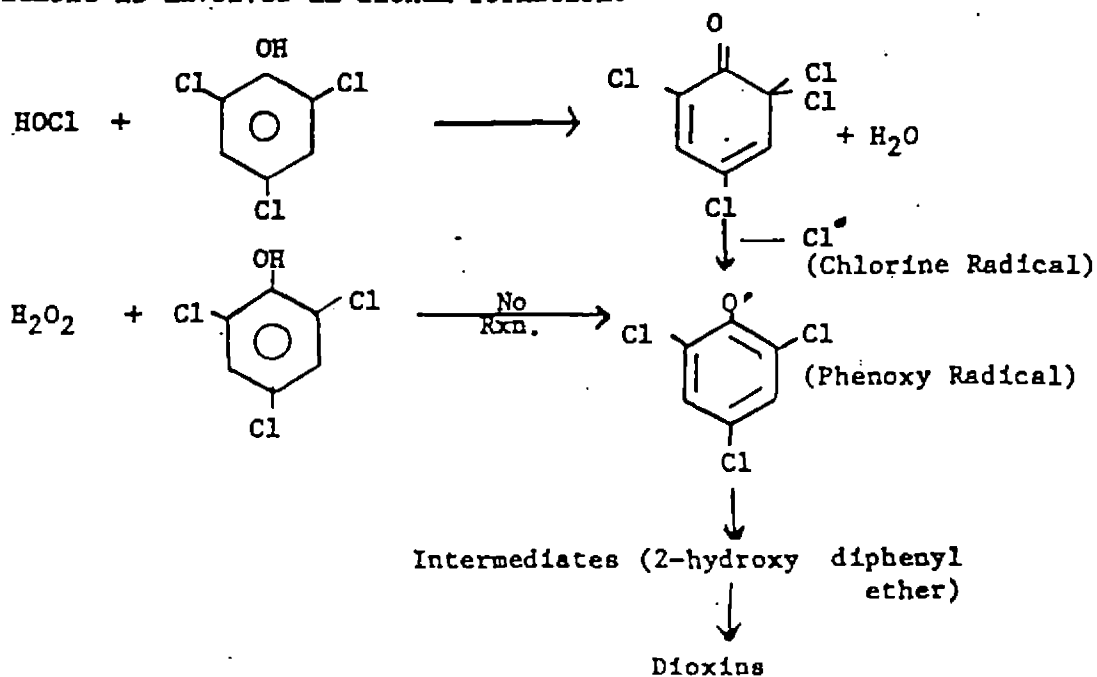
Aside from catalyst deactivation effects, moisture no doubt plays another detrimental role, in that hypochlorous acid is formed.



HOCl is a powerful oxidizing agent. Are dioxins generated when Penta is oxidized by HOCl? Or more importantly, is HOCl the principal reason for dioxin formation during chlorination?

A few milligrams of distilled Penta were introduced to a 25°C . basic solution of HOCl. Reaction was immediate. A yellow oil was first produced, which slowly became a tarry substance. Recovery of the oxidation products through hexane extraction + GC after phenolics removal showed a host of products, but OCDD and hepta CDD were present in large concentrations. The experiment was repeated in acidic HOCl solution. The reaction again proceeded but not as fast as in NaOCl, (256757).

We also tried Penta oxidation with aqueous Na_2O_2 . No reaction occurred. (The oxidation potentials for NaOCl and Na_2O_2 are very similar.) This leads us to be more convinced that a cyclohexadienone is involved in dioxin formation.



10 9.2 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0

$\frac{8}{3} \times \frac{3}{5}$

THANKS

Characterization of Phenol

Figure 10.3

49.4.

[illegible]

08256797

F. 6. b. (Cont'd.)

The overall detrimental effects of moisture in the chlorination, both before and after catalyst addition, are not clearly known. We don't know for example, at what level of chlorination a positive CEF on the mass first becomes apparent, and if it's related to moisture content.

7. Bioassay - CEF on parachlorophenol, 2, 4-dichlorophenol, Lab Penta Al/S and Al/Te catalyst, Reichhold Penta, and benzene chlorodioxin solutions of hexa-CDD and TCDD.

In December 1974, another series of chlorophenol samples were submitted for CEF evaluation.

BTL REPORT NO.	IDENTIFICATION	DIETARY LEVELS
BTL-74-104	p-chlorophenol-Still Residue	150,1500 ppm
BTL-74-105	Fractions phenol - 236 Feed	1500 ppm
BTL-74-106	Refined p-chlorophenol (PCP)	1500 ppm
BTL-74-107	Refined 2, 4-DCP	1500 ppm
BTL-74-108	Hexa CDD benzene solution	0.5,2,10,50,250 ppb
BTL-74-109	TCDD benzene solution	0.005,0.02,0.1,0.5,2.5 ppb
BTL-74-120	Reichhold Penta-256386	0,150,500,1000,1500 ppm
BTL-74-87	Lab Penta - 211535 (Low Temp.)	"
BTL-74-88	Lab Penta - Al/Te-256304	"
BTL-74-89	Lab Penta - Al/S -256330	"
BTL-74-90	Lab Penta - Al/S - 256338	"

Results of the tests are presented in TABLE No. 6. Page 52.

In summary, the following was indicated:

- (1) CEF activity was not observed in PCP still residue, fractions phenol, refined para, or refined 2, 4-DCP - at the highest level tested (1500 ppm).
- (2) Reichhold's Penta exhibited positive CEF activity - but not as severely as our commercial material. (Certain non-phenolic components (dibenzofurans?) are reduced or absent in the Reichhold sample; these same components are reduced or absent in our Al/S and Al/Te batches.) Reichhold has also indicated CEF activity on their Penta was negative on tests run at Hilltop Laboratories. REC studies were not made on this series of samples. Hence, we cannot say if REC toxicity is improved by the Al/S system or on Reichhold's sample.
- (3) Al/Te and Al/S prepared material shows negative or reduced CEF activity:
 - Al/Te-256304 - negative at 1500 ppm level
 - Al/S -256330 - " " 500 ppm level
 - Al/S- 256338 - " " 1000 ppm level

F. 7. (Cont'd.)

- (4) Low Temp. Lab Penta 211535 had negative CEF response at 1500 ppm level. This sample, when previously tested (BTL-73-28B), was positive at 1500 ppm level, but negative at 500 ppm level.
- (5) From the CEF data on HCDD and TCDD solutions, we could expect a positive CEF response with Pentachlorophenol containing at least 0.5 ppm TCDD or between 50 and 250 ppm HCDD.

8. Low Level Dioxin Analyses - Plant & Lab Penta

In early 1975, Applied Science's new sensitive gas chromatograph/mass spectrometry system became operational. Analyses of 5 selected Penta samples were carried out with the new system.⁴⁸ All of the samples had previously been studied for CEF activity.

SAMPLE IDENTIFICATION	ppm Dioxins				
	TCDD	Penta CDD	HexaCDD	HeptaCDD	OCDD
212180-1-Plant Std. Cond.	<0.01	0.01	8	160	1060
212180-7-Plant Low Temp.	<0.01	<0.01	8	170	1090
211535-Lab Low Temp.	<0.01	0.02	8	130	995
KM-261-Plant Std. Cond.	<0.01	0.04	15	290	1980
256338-Lab Al/S Catalyst	<0.01	0.03	5	110	870

None of the samples contained TCDD (M.D.L. 10 ppb). Concentration levels for other chlorodioxins are below the level of toxicological significance as indicated in BioTest studies on TCDD and hexaCDD solutions (BTL 74-108 & 109). There are insufficient dioxins present to account for the degrees of CEF activity observed. This suggests other "unknown" compounds are contributing to CEF activity.

These samples were not exposed to caustic in analytical preparation. Chlorophenols were removed by alumina treatment (Applied Science method 73-1). This series of samples represents our first "accurate" dioxin analyses of Penta.

9. Dioxin Precursors

a) Base Catalyzed Ring Closure to Dioxins

As just discussed in the preceeding section, dioxins alone do not account for the total CEF activity observed in technical Penta. It is apparent the activity is due to a combination of dioxins and other impurities in Penta. (Pure Penta does not elicit CEF activity.³⁷) Besides dioxins, there are four other major classes of impurities in Penta:

- Chlorobenzenes
- Chlorodiphenylethers
- Chlorohydroxy diphenyl ethers
- Chlorodibenzofurans

TABLE NO. 6

CHICK EDEMA FACTOR BIOASSAY WITH CHLOROPHENOLS

Project No.	Lot No.	PROCESS CONDITION (Identification)	PPM					PPM				
			0	150	500	1000	1500	0	150	500	1000	1500
BTL-74	OR-		Pericardial	Fluid	Volume	(ml)		Mortality per	12 chicks			
120	256386	Reichhold commercial Pentachlorophenol	0.05	0.08	0.33*	0.62*	0.66*	0	0	1	5	11
89	211535	75° Lab Batch	0.08	---	0.11	0.13	0.12	0	-	0	6	10
(73-28B)	211535	75°C. Lab Batch	0.10	0.10	0.10	----	0.48*	1	0	1	-	1
88	256304	60°C., Al, Te Catalyst	0.08	---	0.10	0.12	0.10	0	-	1	-	12
89	256330	60°C., Al, S Catalyst	do	---	0.13	0.60*	0.67*	do	-	1	5	8
90	256338	60°C., Al, S Catalyst	do	---	0.10	0.10	0.19*	do	-	1	4	6
104	256315-1	Chlorophenol Still Residue	0.05	0.06	----	----	0.10	0	0	-	-	0
105	256325-2	Pentachlorophenol Feed Stock	do	---	----	----	0.08	do	-	-	-	0
106	256315-4	CP 1327	do	---	----	----	0.04	do	-	-	-	0
107	256315-6	CP 3394	do	---	----	----	0.08	do	-	-	-	0
73-280		KH-261	0.10	---	----	----	1.842	-	-	-	-	-
74-28	Plant Penta	OR 212180-1	0.10	---	----	----	1.675	-	-	-	-	-
			0	2	10	50	250	0	2	10	50	250
108		CP 76171	0.05	0.11	0.08	0.11	2.20*	0	0	0	0	9
			0	0.02	0.1	0.5	2.5	0	0.02	0.1	0.5	2.5
109		CP 76172	0.05	0.08	0.09	0.20*	0.84*	0	0	0	0	7

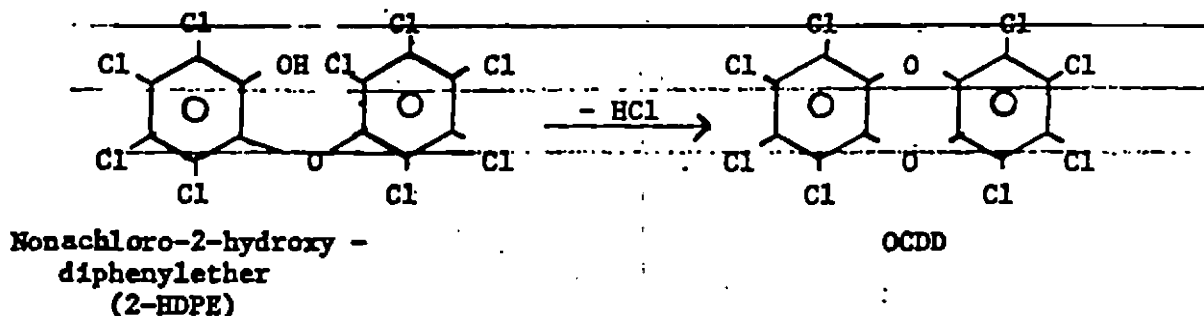
CP 1309 Pentachlorophenol
 CP 1327 para-Chlorophenol
 CP 3394 2, 4-dichlorophenol
 CP 76171 Hexachlorodibenzo-p-dioxin

* Indicates positive chick edema factor activity.

F. 9. a) (Cont'd.)

Chlorobenzenes and chlorodiphenylethers are not known to be chloracnegenic, nor are they known to produce CEF activity. This leaves chlorodibenzofurans (DBF), and chlorohydroxy diphenylethers (HDPE) as the most likely suspects contributing to CEF activity. DBF's are known to be chloracnegenic.⁴⁹ CEF activity for DBF's is not known, but is estimated to be about 1/10 that of corresponding dioxins. This estimate is based on comparative acute toxicity responses between DBF's and dioxins.³

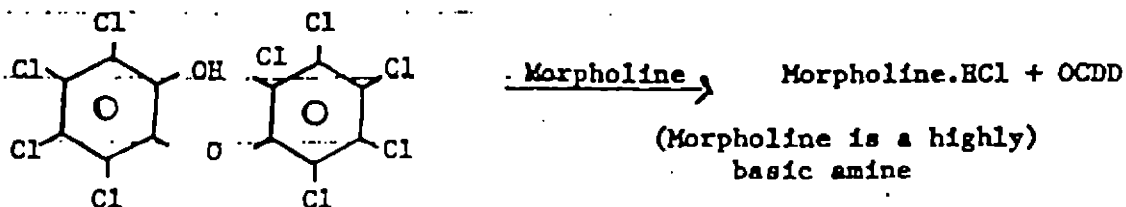
In mid-1975, we had no way of quantitating DBF's. (Method development for DBF analyses is currently going on at Applied Science at G.O.) Our interest then turned to HDPE's. Two types of HDPE's are found in Penta,⁵³ chlorinated 2-HDPE, and chlorinated 4-HDPE. 2-HDPE's are dioxin precursors, and are sometimes referred to as predioxins.



By loss of a molecule of HCl, the precursor is converted to a dioxin. Literature had indicated as much as 5% (wt) HDPE's are present in technical grade chlorophenol.⁵¹ The literature and our work had also indicated four conditions in which these precursors cyclize to dioxins:

- 1) Pyrolysis of sodium chlorophenate⁵²
- 2) Pyrolysis of HDPE under GC conditions⁵³
- 3) Photolysis⁵⁴
- 4) Chlorine radical initiation²²

While analyzing Catomance Penta esters in 1973, we had observed dioxins (hepa CDD & OCDD) increased dramatically when Penta samples were exposed to morpholine. This was our first indication the 2-HDPE's would also cyclize to dioxins under quite mild basic conditions (See Section E-7).



F. 9. a. (Cont'd.)

This phenomenon raised the question as to whether NaOH would also cause cyclization. This was indeed found to be true when a caustic solution of technical Penta was reportedly extracted with hexane. Dioxins were generated in the time intervals between extractions, and were repeatedly found in each hexane extract. Hexa CDD, hepta CDD, and OCDD were being formed. (OR 256751)

The base catalyzed cyclization reaction was also shown to be selective in that no additional precursors are generated during base exposure. Cooking distilled Penta in NaOH solution or in morpholine did not cause dioxins to increase (OR 256754). The increase in dioxins in "base exposed" technical Penta is due solely to cyclization of the precursors present in the Penta prior to base treatment.

b. Significance of Precursor Cyclization

Due to the ease of cyclization in the presence of bases, cyclization in biological systems may also be possible. Bases, such as amides in protein, may be basic enough to cause 2-HDPE's to be converted to dioxins. Thus, ingestion of 2-HDPE's may produce the same pathogenic effects as ingestion of dioxins themselves. Further, the concentration of 2-HDPE's plus dioxins in Penta is high enough to account for the degree of CEF activity observed on technical Penta. Attempts to cause cyclization with egg albumin were inconclusive. Accurate measurement of dioxins after exposure could not be made due to interferences from other compounds (OR 256763).

The second point of significance regarding the cyclization is that all dioxin analyses which had utilized a preliminary caustic clean-up step, no doubt gave erroneously high dioxin values. More dioxins were generated in the caustic clean-up step. All dioxin analyses which were run from 1970 up to April 1975, utilized a caustic clean-up and are therefore all erroneously high.

Thirdly, it seems somewhat unlikely that the concentration of hexa CDD found in "toxic fat" 10, 11 by Cantrell could have arisen solely from original hexa-CDD in the technical Penta, which had contaminated the fat. A more likely source of this concentration hexa-CDD, was probably heptachloro-2-HDPE in the Penta. Fatty amines catalyzed cyclization of this precursor to hexa CDD. (This precursor is present in concentrations as high as 320 ppm in technical Penta - See Page 57).

F. 9. b. (Cont'd.)

It is also apparent, even in the most recent literature on dioxins, that others have not recognized the near facile cyclization phenomenon. Dioxin analyses are still utilizing a caustic clean-up step.^{50, 51}

Dioxins are probably being generated in all Santobrite solutions in Dept. 227. The alkali insolubles associated with these solutions are no doubt extremely high in dioxin content. Production personnel have been alerted to handle these materials with caution.

c. Morpholine Treatment as Method of Analysis

Dioxin precursors in Penta can be measured indirectly by converting them to dioxins which can then be quantitated. The procedure is as follows:

Add 5 grams of Penta to a 250 ml flask and reflux in 50 ml morpholine (Fisher M-263) for two hours (extended period may be required - see Page 58). Cool and quantitatively transfer to a 100 ml volumetric flask. Rinse flask and dilute to volume with aqueous 1N NaOH. Cool to 25°C. and readjust volume if necessary. Acidify a 20 ml representative aliquot with 25 ml of 1:1 aqueous HCl. Cool, then extract twice with 10 ml portions of nanograde benzene. Combine the benzene extracts and wash twice with 25 ml portions in aqueous NaOH followed by 3-25 ml water washes. Prepare appropriate dilution in benzene and chromatograph on ECGC by conditions given in Method 70-20. Only Hepta CDD and OCDD can be quantitated. Hexa-CDD and lower chlorinated dioxins are masked by interfering compounds.

The following Penta samples were analyzed by the procedure. By subtracting original dioxins (before), hepta and octa CDD precursor concentrations are determined. Original dioxins determined by Method 73-1 (See Reference No. 42).

SAMPLES	ppm Hepta CDD			ppm Octa-CDD		
	Before	After	~ hepta Precursors	Before	After	~ octa Precursors
OR-212180-1 Plant Penta-Std.Cond.	160	2624	2464	1060	6237	5177
OR-212180-7 " " -Low Temp.	170	2847	2677	1090	6660	5570
OR-211535 Lab Penta -Low Temp.	130	2658	2528	995	8222	7227
KM-261 Plant Penta - Std.Cond.	290	2934	2644	1980	8648	6668
OR-256338 Lab Penta-Al/S Cat.	110	2151	2041	870	5164	4294
OR-256754 Lab Distilled Penta	0.1	N.D.	N.D.	1.3	0.6	N.D.
OR-256754 Lab Distilled Penta						
1N NaOH in place of Morpholine	0.1	N.D.	N.D.	1.3	0.3	N.D.
OR-256386 Reichhold Penta			2081*			4422*
OR-256304 Lab Penta- Al/Te Cat.			1884*			5080*

*Includes original dioxins.

Except for the distilled Penta samples, these were the same samples just analyzed by Applied Sciences. (See Section F-8) All of the samples had also been previously studied for CEF activity.

F. 9. c. (Cont'd.)

Large amounts of cyclizable hepta and octa CDD precursors are indicated in all the technical grade samples.

Lab Penta, prepared with Al/S or Al/Te catalyst, and the Reichhold sample all contain somewhat reduced amounts of these precursors.

Dioxins were not generated in the distilled Penta samples in either the caustic or morpholine treatment. Dioxins generated in the technical grade samples therefore came about solely from cyclization of the respective precursors.

The final benzene extracts from preparation of the samples were submitted to Applied Science for dioxin analyses by GC/mass spectroscopy in hopes of quantitating hexa-CDD and lower chlorinated dioxins. Their results were as follows:⁵⁵

Applied Science - Special Study S-75 - SS-17

SAMPLE

	Unknown			
	Chloro Aromatic	Penta CDD	Hexa CDD	Hepta CDD
OR-212180-1-Plant Penta-Std. Cond.	0.2 ppm	0.09 ppm	112 ppm	1940 ppm
OR-212180-7 " " -Low Temp.	0.3	0.10	102	1630
OR-211535 Lab Penta -Low Temp.	4.0	0.38	68	1270
KM-261 Plant Penta, Std. Cond.	0.3	0.36	35	1210
OR-256338- Lab Penta Al/S. Cat.	2.0	1.47	175	1490

The amount of individual dioxins present in the samples before morpholine has been subtracted from the listed values. Thus, the dioxin levels reported here represent original precursor concentrations. No dichlor or tri CDD was found in any of these samples with a detection limit of 0.1 ppm. The unknown chloro aromatic had a different GC retention time and mass spectrum from 2,3,7,8-tetra CDD. Its spectrum did contain 322 and 259 ions which would be expected from TCDD. The full mass spectrum however, contains ions foreign to TCDD. Because the spectrum was very weak, the possibility that this component is a tetra CDD, but not the 2,3,7,8 isomer, cannot be ruled out.

Penta-CDD, hexa-CDD, and hepta-CDD were found in concentrations roughly ten times that of the original levels before morpholine treatment. Hepta-CDD values were also, on the average, about 1000 ppm less than what our analyses had indicated (1500 vs 2500 ppm). Our higher hepta-CDD could be due to the inclusion of unresolved hepta dibenzofurans.

An alternative method for precursor determination, which permits quantitation of Penta-CDD through OCDD precursors without the diphenyl ether and furan interferences is as

F. 9. c. (Cont'd.)

A one gram Penta sample is dissolved in 10 ml nanograde benzene and chromatographed as described in Applied Science Method 73-1 (Ref. No. 42) with 200 ml nanograde benzene. All phenolic type compounds, which include dioxin precursors, are retained on the alumina. These are released and collected from the alumina by eluting 200 ml methanol over the alumina. The methanol eluent is collected in a 250 ml round bottom flask. 25 ml of morpholine is added. Equip the flask with a Snyder column and place in a steam bath. Methanol is boiled out, while morpholine causes dioxin precursors to cyclize to dioxins (extended cook period may be required to assure complete cyclization. See Page 58). The mixture is then cooled and acidified to pH <2.0 by addition of 1:1 aqueous HCl. After cooling, the mixture is extracted twice with 10 ml portions of nanograde benzene. The benzene extracts are combined, washed twice with 25 ml portions in aqueous NaOH, followed by three 25 ml water washes. Appropriate dilutions in benzene are prepared and ECGC'd. Alternatively, the benzene extract is concentrated by evaporation to 5 ml. A 1/2 ml aliquot is then chromatographed over 1 gram of Al₂O₃, (W-200 basic activity grade super 1 - from ICN Pharmaceuticals - 3440 Eschwege West Germany) contained in a 1 ml disposable pipet with 10 ml of 2% CH₂Cl₂:98% Hexane solution. This removes minute interferences remaining in the TCDD area. A second 10 ml fraction consisting of 50% (vol.) CH₂Cl₂ in hexane is collected. This fraction contains only the dioxins. An appropriate dilution is made and ECGC'd. The chromatograms are free of interferences in the Penta CDD and TCDD region allowing quantitation to 0.1 ppm and lower if desired. (The final chromatographing clean-up technique was developed by H. R. Buser of Switzerland. ⁵⁶)

Hexa CDD precursor content was determined in the following samples utilizing the method just described (without the final Al₂O₃ treatment).

Hexa-CDD Precursors in Penta

<u>SAMPLE</u>		<u>~ Hexa CDD</u>
OR 212180-1	Plant Penta - Std. Cond.	316 ppm
OR 212180-7	" " - Low Temp.	320
OR 211535	Lab Penta - Low Temp.	186
KM-261	Plant Penta - Std. Cond.	112
OR 256338	Lab Penta - Al/S Cat.	150
OR 256304	Lab Penta - Al/Te Cat.	175
OR 256386	Reichhold Penta	161
OR 214234	Lab Distilled Penta	< 0.1

Plant Batch - Sampled @ 130°C. during rate of rise > 200 ppm*

*This sample also contained >50 ppm of what was suspected to be Penta - CDD.

9. c. (Cont'd.)

Some of the samples are those which were analyzed for hexa-CDD by Applied Science as just discussed. Agreement between labs is not good. Most values reported here are higher. The precision, recoveries, etc. regarding the method have not been determined. There is some question about the completeness of cyclization of cyclizable precursors (see following section).

d. Cyclization in NaOH VS Morpholine

Initially we observed no difference in the amount of hepta and OCDD generated between 1 and 2 hour refluxing in morpholine. We therefore concluded that cyclization was complete within the two hour period. This may not have been true however, as indicated in the following comparison of cyclization in NaOH VS morpholine at ambient temperatures (OR 256753). Dioxin values given below include original dioxins present in addition to those generated in cyclization.

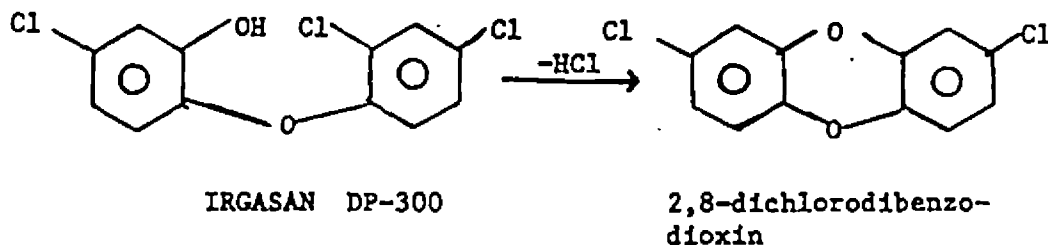
	<u>Moles Base/gram Penta</u>	<u>Hepta CDD</u>	<u>OCDD</u>
1.0 gram Penta, Lot KM-509 50 ml 1N NaOH, Stirred 18 hours @ 25°C.	0.050	5057 ppm	15,800 ppm
1.0 gram Penta, Lot KM-509 50 ml Morpholine, Stirred 18 hours @ 25°C.	0.574	5865 ppm	17,100 ppm
5.0 gram Penta KM-261 reflux in 50 ml Morpholine for 2 hours	0.115	2934 ppm	8,648 ppm

No firm conclusions can be made from the data. There is indication however, NaOH may be more effective when compared to equimolar amounts of morpholine. In addition, OCDD values are nearly double in the ambient runs compared to that on KM-261 in refluxed morpholine. The difference could be real; but more likely, KM-261 cyclization was probably incomplete.

e. Cyclization rate of Irgasan DP-300 VS dioxin precursors in Technical Penta

Irgasan DP-300 (2,4,4'-trichloro-2'-hydroxydiphenylether) is a commercial antimicrobial agent manufactured by CIBA-GEIGY. This compound also has the structure of a dioxin precursor:

F. 9. e. (Cont'd.)

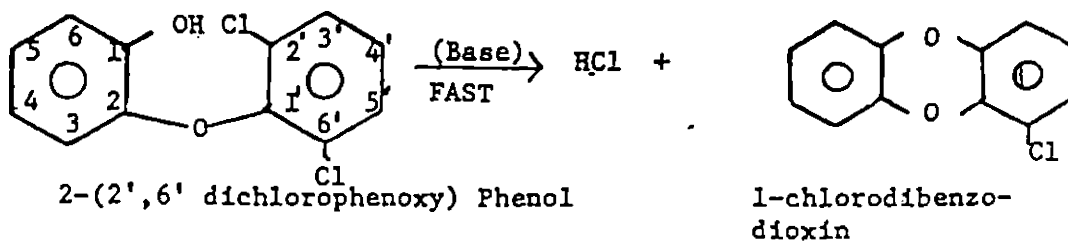


The rate of cyclization was observed in the following tests by monitoring HCl generation (AgNO_3 titration of Cl^-).

	ppm HCl Generated		
	96 hrs.	168 hrs.	456 hrs.
5.0 gram IRGASAN DP-300 50 ml Cl^- free Morpholine Cook @ 55°C. with stirring.	25.7	95.4	353.0
5.0 gram IRGASAN DP-300 50 ml Cl^- free xylene Cook @ 55°C. with stirring	25.7	25.7	39.0

The percent conversion to dioxin in the morpholine sample after 456 hrs. was only 0.27%. Cyclization is extremely slow. No conversion was apparent in the xylene solution which is not a basic solvent. (Confirmation of di-CDD by GC analyses not attempted.)

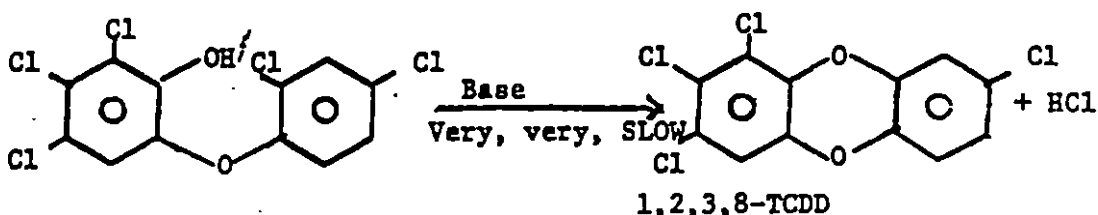
Since dioxins are generated very rapidly when Tech. Penta is cooked in morpholine, we can only conclude that position and number of chlorines in the precursor significantly affect the rate of cyclization to dioxins. The most likely explanation is that the precursor must have chlorines in each position ortho to the ether linkage before cyclization proceeds with ease:



F. 9. f. (Cont'd.)

Two isomers of Penta-CDD are generated depending on which chlorine atom is lost in the cyclization. The 1,2,3,7,8 isomer would be expected to be highly toxic based on Poland & Glover's toxicity studies on chlorodibenzodioxins.⁵⁷

A recent toxicity study on one dioxin precursor substantiates our prediction. Dr. McConnell (NIEHS), at the March 1976 Meeting of the Society of Toxicology, presented toxicological data (Paper No. 130) on 4,5,6-trichloro-2(2,4-dichloro-phenoxy) phenol. No deaths occurred among rats dosed with as high as 100 mg/kg body weight. Thus, this precursor did not produce demonstrable effects even at 50,000 times the LD50-30 of 2,3,7,8-TCDD.



This precursor is not the type that would be expected to cyclize easily. Therefore little or negligible cyclization would occur in the biological system. Consequently the precursor is not toxic because no dioxin forms in the biological system.

g. CEF Relation to Precursor Concentrations in Penta

Our data at this point shows no clear relationship between CEF activity and precursor concentration (See TABLE No. 6, Pg. 61 a)

10. Hexachlorobenzene In Penta

The presence of hexachlorobenzene (HCB) in technical Penta came to light in the 1973-75 period. Method of analysis developed by Applied Science and by Monsanto Australia R&D⁵⁸ was adapted to our ECGC (OR 256740). A few selected samples were analyzed yielding the following results.

SAMPLE	HEXACHLORO BENZENE	IDENTIFICATION
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 Mat.
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.

TABLE NO. 6

TECHNICAL PENTA CEF RESPONSE VS DIOXIN PRECURSOR CONTENT

<u>SAMPLE & DESCRIPTION</u>	<u>PENTA CDD PRECURSORS</u>	<u>~HEXA CDD PRECURSORS</u>	<u>~HEPTA CDD PRECURSORS</u>	<u>~OCTA CDD PRECURSORS</u>	<u>TOTAL PRECURSORS</u>	<u>TOTAL*</u>	<u>TOTAL*</u>
						<u>PERICARDIAL FLUID</u>	
OR-212180-1 Plant Penta - Std. Cond.	0.09 ppm	316. ppm	2464 ppm	5177 ppm	7957.ppm	3.55 ml	10
OR-212180-7 " " - Low Temp.	0.10	320.	2677	5570	8567.	1.34	6
OR-211535 Lab " - " "	0.38	186.	2528	7227	9941..	1.09	3
KM-261 Plant " - Std. Cond.	0.36	112.	2644	6668	9424.	3.60	10
OR-256338 Lab Penta - Al/S Cat.	1.47	150	2041	4294	6487.	0.39	11
OR-256386 Reichhold Penta	---	161	1800	4000	5961.	1.74	16

NOTE: Precision of these values is not known.
 The precursors were converted to dioxins by exposure to basic conditions, then dioxin concentrations were determined. Recoveries, and degree of conversion have not been determined, therefore these values may be erroneously low. The method of analysis is described on page 57 of this report

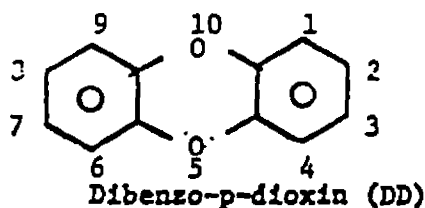
S. H. Vogel

*See Appendix E, Item 3.

F. 10. (Cont'd.)

Mechanism of formation of hexachlorobenzene is speculated to arise from HCl cleavage of polychlorodiphenylethers. Lower chlorinated benzenes are also reported to be present. ⁵⁶ There is some evidence the Al/S or the Al/Te catalyst system suppresses HCB formation to a moderate extent.

The principal concern for hexachlorobenzene is its slow degradation rate in the environment.

G. CHLORINATED DIBENZODIOXINS: COMPARATIVE TOXICOLOGY

To show appreciable toxicity: ⁵⁷

1. At least three of the 2,3,7,8 positions must be halogenated,
AND
2. At least one of the eight carbons must be unsubstituted.

THUS, DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, 1,2,3,4-TCDD, and OCDD (Octa-) show little biological activity at levels tested.

2,3,7,8-TCDD is one of the most toxic substances known, as LD₅₀ for male guinea pig is 0.6 micrograms kg. body weight; LD₅₀ for rabbit is 0.115 mg/kg. It is a potent acnegen, is positive cause of chick edema at 1 μg/kg/day feed, is teratogenic and it is mutagenic to certain bacteria.

HCDD (Hexachloro, mixed isomers) is active in chick edema and acnegenicity testing at about ten times the level of 2,3,7,8-TCDD. It is far less lethal.

Data on Penta-CDD and Hepta-CDD are not available except that Hepta-CDD impurity in OCDD at 15% level appears to have no adverse effects.

H. PENTA TREATED WOOD - DIOXIN ANALYSES

Wood borings supplied to Monsanto by Koppers Inc., were analyzed for hepta CDD and OCDD content by Applied Science of G.O. (Ref. No. 58) in March 1975.

Pentachlorophenol and hepta- and octa-chlorodibenzodioxins were found in each of three treated woods examined. The lower chlorinated dibenzodioxins could not be determined due to interferences. The data are shown in the following table.

I. BIOASSAY - CEF & REC DATA SUMMARY (Cont'd.)

<u>BTL. NO.</u>	<u>DESCRIPTION</u>	<u>CEF RESPONSE</u>
73-28A	Lab Penta - Solvent chlorination	Negative @ 1500 ppm
73-28B	Lab Penta - Low Temp. OR211535	Slight @ 1500, Neg. @ 500
74-87	Repeat of 73-28B	Neg. @ 1500, Neg. @ 500
73-28C	Lab Penta-high level chlorination	Slight @ 1500, Neg. @ 500
74-35	48% Penta in AD-73 Oil Prill fumes	Negative @ 1500
74-88	Lab Penta - Al/Te Cat.	Negative @ 1500
74-90	Lab Penta Al/S Cat.	Slight @ 1500, Neg. @ 500

Low temperature chlorination, paralleling OR 211535 condition, was plant-trialed (BTL-74-28 through 74-34). Although CEF improvement was indicated, the improvement did not match OR 211535. Note however that all the "low spread" samples showed the most improvement. A semi-quantitative assessment of this data is found in Appendix E-3. This assessment predicts a negative CEF response if spread is 1°C or less. This might be accomplished in the plant by better heat removal during rate of rise. Lowest spread achieved during the low temperature plant runs was about 3°C.

CEF response of WCK Penta VS Reichhold is essentially equivalent (72-49 vs 74-120).

Prill fume Penta (74-35) did not elicit CEF activity indicating its purity. It is essentially sublimed Penta.

The use of low temperature - low spread chlorination, coupled with a catalyst change to Al/Sulfur or Al/Tellurium presents the best opportunity for a lower by-product Penta. Further evaluation in the lab of the Al/S catalyst system may be necessary before plant trial. (See Section F. 6-a for further discussion regarding Al/S Cat. System.)

All chlorophenol process streams in para-chlorophenol and 2, 4-dichlorophenol manufacture gave negative CEF responses at the 1500 ppm level (74-104 through 74-107).

No firm conclusions can be made regarding the CMU chloracne data. A detailed description of CMU's method is found in their reports accompanying the test results on each sample. Solution containing the test material is applied to a rabbit's ear and skin irritation is observed over a certain period of time. The test results on all samples were confusing, to say the least. A copy of their report No. CMU-74-41A through G is found in Appendix E-4.

TABLE No 7

Chlorophenol Bioassay DATA SUMMARY
 CHICK EDGEM FASTER (C) + RABBIT EAR CHLORACNE (RCL)

508-76
 S.H. Vogel

APPLIC. SCIENCE METHOD NO. 73-1
 READ FOR BIOID ANALYSIS.

Smoothly Feeding Cep. Larvae										APPLIED SCIENCE METHOD NO. 73-1 read For Dieldrin Analysis.									
BTL NO.	REFERENCE NO.	DESCRIPTION	As Percentage of Total Volume (ml)						TOTAL	CAU NO.	Dieldrin (ppm)	Dieldrin (ppm)	Dieldrin (ppm)	Dieldrin (ppm)	TOTAL	COMMENTS			
			0	50	150	500	1000	1500									0	50	150
72-48		Growth Phase - Pure	0.11	0.11	0.10	0.13		0.11	4										
72-49	KM-261	Plant Phase - Std. Conditions	0.14	0.11	0.11	0.48		0.75	14										
73-28A	OR-210597	Chlorinated in Parachlorophenol	0.10	0.08	0.07	0.20		0.11	5	73-27	6.4	0.07	0.14	0.04	15	290	1980	3285	in Cap Response of Smoothly Feeding
73-28B	OR-211535	Lab Phase - Low Temp. chlorinated	0.10	0.11	0.10	0.10		0.48	3	73-27A	13.4	1.75	1.92	0.02	5	180	995	1180	TLDD Control
73-28C	OR-211525	Lab Phase - High Level	0.08	0.09	0.10	0.11		0.17	4	73-27B	14.1	1.20	1.28	0.02	5	180	995	1180	can be used at All Levels
73-28D	OR-211544	KM-261 - Plant Phase	0.08	0.10	0.10	0.44		1.87	10	73-27C	13.3	1.48	1.28	0.04	15	290	1980	3285	TLDD Control
73-28E	OR-211544	Doc 20-7 - Lab Sample	0.11	0.12	0.09	0.28		0.09	2	73-27D	21.3	2.03	2.80	0.04	15	290	1980	3285	TLDD Control
73-28F	OR-211544	Monsieur - Lab distilled	0.11	0.09	0.11	0.11		0.11	5	73-27E	10.5	0.37	0.14	0.04	15	290	1980	3285	can be used at All Levels
74-28	OR-212180-1	Pl. Phase - Std. Cond.	0.10		0.12	0.15	1.24	1.20	10	73-27F	8.0	0.46	0.15	0.04	15	290	1980	3285	TLDD Control
74-29	OR-212180-2	" " - 80%	0.10		0.10	0.12	1.24	0.32	15	74-41	13.4	0.2	0.1	0.01	8	160	1061	1228	TLDD Control
74-30	OR-212180-3	" " - 65%	0.10		0.10	0.12	1.04	0.25	12	74-41A	16.0	1.0	0.9	0.01	8	160	1061	1228	TLDD Control
74-31	OR-212180-4	" " - 60%, 2X CAT.	0.10		0.10	0.12	1.23	0.2	12	74-41B	22.9	2.0	1.8	0.01	8	160	1061	1228	TLDD Control
74-32	OR-212180-5	" " - 65%, Low Spent - Slow	0.09		0.12	0.20	0.32	0.32	7	74-41C	23.6	1.1	1.5	0.01	8	160	1061	1228	TLDD Control
74-33	OR-212180-6	" " - 65%, " " - 1X CAT.	0.09		0.13	0.42	0.37	0.60	6	74-41D	18.2	1.5	1.0	0.01	8	160	1061	1228	TLDD Control
74-34	OR-212180-7	" " - 60%, " " - 1X CAT.	0.09		0.12	0.15	0.22	0.15	6	74-41E	18.5	1.6	1.4	0.01	8	160	1061	1228	TLDD Control
74-35	OR-212180-9	18% on Air Phase Phase in 40-73 0/L	0.09			0.12		0.10	2	74-41F	20.9	1.6	1.6	0.01	8	160	1061	1228	TLDD Control
74-36	OR-212180-8	Allyl Mixture (Pine, TFF, RT33A)	0.09					0.10	2	74-41G	20.9	1.6	1.6	0.01	8	160	1061	1228	TLDD Control
74-120	OR-256306	Rabbit Ear Phase, Lot. 7A874	0.05		0.08	0.33	0.62	0.66	17										
74-87	OR-211535	Lab Phase - Low Temp. chlor.	0.08			0.11	0.13	0.12	16										
74-88	OR-256304	" " - AL/T2 CAT.	0.08			0.10	0.12	0.10	13										
74-89	OR-256330	" " - AL/S CAT.	0.08			0.13	0.67	0.67	14										
74-90	OR-256339	" " - AL/S. CAT.	0.08			0.10	0.10	0.17	11										
74-104	OR-256315-1	Chlorophenol with residue	0.05		0.06			0.10	0										
74-105	OR-256315-2	Fructose From Parachlorophenol	0.05					0.08	0										
74-106	OR-256315-4	Parachlorophenol	0.05					0.04	0										
74-107	OR-256315-6	" 2,4-dichlorophenol	0.05					0.08	0										
74-108		has CO2 28% X Pure	0.05	0.08	0.09	0.20		0.11	0.08	0.11	220								
74-109		Tetrachloro 28% Pure	0.05	0.08	0.09	0.20		0.11	0.08	0.11	220								

J. "ACCURATE" DIOXIN AND DIBENZOFURAN ANALYSES - Data Summary

Table No. 8, page 67, summarizes all of our "accurate" dioxin/furan analyses on chlorophenols generated in the past few months. Sample preparation for all analyses listed utilized an alumina clean-up step. Thus problems of precursor cyclization to dioxins due to caustic exposure is avoided. Previous analyses had utilized a caustic clean-up step.

Typical levels of dioxin and furan found in Penta are as follows:

	<u>Dibenzodioxins</u>	<u>Dibenzofurans</u>
Tetrachloro	<0.1 ppm	<0.1 ppm
Penta "	<0.1	<0.5
hexa "	5 - 20	30 - 90
hepta "	200 - 300	250 - 450
octa "	400 - 1000	150-- 600

Trace amounts of these impurities, but lower chlorinated, are also found in parachlorophenol, 2, 4-dichlorophenol, and Santophen 1. The presence of the highly toxic 2,3,7,8 TCDD has not been confirmed in any WGK produced chlorophenols. (One parachlorophenol sample showed a TCDD level of 0.1 ppm, but is a questionable value due to interferences.)

Reichhold Penta has somewhat lower amounts of furans and dioxins compared to typical WGK Penta.

Monsanto distilled, as well as Dow's EC 7 refined Penta, contain only trace amounts of dioxins. Furans in refined Penta have not been determined.

Alkali insolubles associated with Santobrite solutions (cone tank mud) contain gross levels of dioxins. TCDD (0.10 ppm) was also detected in 30% aqueous Santobrite solution. Production of this material (SPS-30) has been discontinued. Use of a weaker solution (21%) as feed to Penta/oil solution is continuing.

Method 73-1, coupled with mass spectroscopy, was used for all dioxin analyses presented on TABLE 8.

K. AR&D SPECIAL STUDY - PLANT PENTA DIOXINS & "COOKED" ALKALI INSOLUBLES ANALYSES

In April 1976, WGK AR&D group analyzed a series of plant produced Penta samples for dioxins and alkali insolubles by a modified procedure supplied by PPT group. Method No. 73-1 clean-up procedure, followed by simple ECGC, was used for dioxin analyses. The "cooked" alkali insolubles method (OR 257048) is essentially the same as our routine Method No. 10,017 except for the following changes:

TABLE NO. 8

Plant Process Technology
S. H. Vogel 7/15/76

1976 - "ACCURATE" CHLOROPHENOL DIOXIN & DIBENZOFURAN ANALYSES

DATA SUMMARY (OR 257051) Method 73-1 Applied Sciences Analyzes

SAMPLE DESCRIPTION	DIOXINS (ppm)								DIBENZOFURANS (ppm)					COMMENTS
	Cl	Cl ₂	Cl ₃	Cl ₄	Cl ₅	Cl ₆	Cl ₇	Cl ₈	Cl ₄	Cl ₅	Cl ₆	Cl ₇	Cl ₈	
Santophen-1, KE-08-41	N.D.	9.1	< 0.9	< 0.03	}									Values may be inflated due to interferences.
Santophen-1, KE-03-15	N.D.	26.2	26.2	< 0.9										
p-Chlorophenol KE-10-5069	0.8	< 0.04	< 0.02	< 0.01										*Possible interference.
p-Chlorophenol KE-01-5003	17.3*	6.5*	2.1*	0.1*										
2,4-Dichlorophenol, KE-06-1009	0.8	< 0.02	< 0.04	< 0.01										
2,4- " " , Tk.2, 1-15-74	0.3	< 0.02	< 0.03	< 0.01										
2,4- " " , 93% (257059)	< 0.18	0.23	0.3	< 0.09										
Penta-60 KD-4				< 0.01	< 0.2	9	90	130						
Penta-60 KD-2				< 0.01	< 0.25	11	100	150						
Santobrite SPS-30 (257051)				0.11	1.3	2.3	17	12	} Na Penta basis					Scrap + Prill Fumes Scrap + Prill Fumes.
Santobrite SPS-21 (Penta Sol'n Feed)				0.06	0.5	1.3	11	7.5						
Cone Tank Alkali Insolubles				< 13	< 177	< 352	1.8%	12%	(Dry basis)					Santobrite Mud
Pentachlorophenol KE 06-56				< 0.01	< 0.05	11	220	440	0.6	0.36	49	276	172	Very dark material.
" " " KE 07-74				< 0.01	< 0.17	12.6	306	761						
" " " KE 08-84				< 0.03	< 0.08	9.6	220	521						
" " " KE 08-89				< 0.01	< 0.03	18	270	800	0.08	0.26	87	445	140	
" " " KE 10-111				< 0.01	< 0.12	10.2	256	717						
" " " KE 11-135				< 0.02	< 0.07	10	333	921						
" " " KE 12-147				< 0.01	< 0.17	15.5	538	1983						
" " " KE 12-157				< 0.01	< 0.07	9.9	305	826						
" " " OR 212180-1				< 0.01	< 0.01	8	160	1060						
" " " OR 212180-1				< 0.01	< 0.07	9.6	181		< 0.01	< 0.02	32	230	610	
" " " OR 212180-7				< 0.01	< 0.01	8	170	1090						
" " " OR 212180-7				< 0.02	< 0.11	6.8	160							
Reichhold Penta (OR 256386)				< 0.01	< 0.05	13	123	380	< 0.4	< 1.7	37	90	57	Lot 72874
Dow Refined Penta-09214M-EC7				< 0.01	< 0.02	< 0.02	0.3	0.2						Commercial Plant Penta-Lab Refined.
Monsanto - Lab Refined (OR 214234)				< 0.01	< 0.02	< 0.01	< 0.06	0.05						
Lab Penta - OR 211535				< 0.01	0.02	5	130	995						Low Temperature
" " " - " "				< 0.01	< 0.03	< 4.0	93							" "
" " " - OR 256338				< 0.01	0.03	5	110	870						Al/S Catalyst
" " " - " "				< 0.03	< 0.09	< 3.4	90							

K. AR&D SPECIAL STUDY - PLANT PENTA DIOXINS & "COOKED" ALKALI INSOLUBLES ANALYSES (Cont'd.)

Cook with stirring at 80°C. for 2-1/2 hours. Add 10 ml of NaCl saturated H₂O. Adjust pH to 9.0 - 9.5 while still warm with 1:1 HCl. Cool and filter in normal manner. (The cooking procedure causes cyclization of dioxin precursors to dioxins.)

A summary of the results is found in Appendix E-5. Conclusions from the study were as follows:

1. There is no dioxin build-up during the first 4 hours of molten hold period prior to prilling. Our additives are apparently stabilizing the material.
2. There is no clear relation between total dioxin level and cooked alk-insol. content. Additives also interfere in the cooked alkali-insol. test causing inflated values. "Cooked" alk-insol values on the average are about double compared to the routine method.

One sample (Chlor. Batch C-22) was also analyzed by Applied Science at G.O. Agreement between labs was good.

L. APPLIED SCIENCE DIOXIN METHODS OF ANALYSES 1970 - 1976

A copy of each dioxin method of analysis developed by Applied Science from 1970 to 1976 is found in Appendix E-6 and E-7.

M. PENTA BIODEGRADATION STUDY - PURDUE UNIVERSITY

Penta industry sponsored biodegradation studies were carried out by E. J. Kirsch et al at Purdue University in the period 1972 through 1975. Their studies are published in Reference No. 59. One major finding was that refined Penta degrades more easily than technical grade Penta. 60

DESCRIPTION OF RECOMMENDED PROCESS

Process for Engineering Design, Report No. P-1729, describes a distillation process for Penta refining. (See Reference No. 38.)

Amendments F and H to Dept. 236 SMPD were also issued for plant trial of low temperature chlorination. (See References No. 45 and 46.)

ANALYTICAL PROCEDURES

Analytical procedures associated with the work detailed in this report are described or referenced throughout the "Results and Discussion" section. The dioxin GLC methods developed by Applied Science and PPT are also found in Appendix E-6 and E-7.

TOXICITY AND HAZARDS

Chlorodibenzodioxins and chloro-dibenzofurans are known to be extremely toxic substances. Caution should be exercised when handling Penta impurities, as well as dioxin/furan analytical standards.

ATMOSPHERIC AND STREAM POLLUTION

The alkali insolubles associated with Santobrite [®] solutions are currently sewered. Since they contain high levels of dioxins, another means of disposal should be found. Incineration is recommended. Processes for the disposition of Venturi and Central fume scrubber wastes are described in another report (Reference No. 34).

The importance of good housekeeping and adequate ventilation in chlorophenol production departments to minimize worker exposure to toxic impurities, as well as to chlorophenols themselves, cannot be over emphasized.

ACKNOWLEDGEMENTS

Dioxin methods of analyses and related special studies were carried out by J. P. Mieure, M. W. Dietrich, G. W. Mappes, O. E. Kinast, O. Hicks, and others in the Applied Science section at G.O.

Distillation studies and subsequent PED Report No. P-1729 for Penta refining were the efforts of D. R. Cova and J. E. White of MIC Engineering Specialties.

Process cost estimates on various approaches to Penta refining were made by D. A. Novac of CED.

Coordination of bioassay testing was handled by P. L. Wright, Dept. of Medicine and Environmental Health at G.O.

Successful demonstration of low temperature chlorination in the plant were the efforts of R. R. Sorrell, J. Starzyk, and the chlorinator operators R. Steele, F. Falconer, K. Wilcox, and C. Robinson.

Acknowledgement is also given to WGK control lab Section I personnel for providing numerous dioxin related analyses in support of plant and lab chlorination studies as well as routine monitoring of competitive Penta and Santobrite.

Special thanks is also given to R. D. McEntire and B. Soehlin for their excellent work in providing non-routine analyses associated with plant low temperature chlorination studies.

INTRODUCTION

A special Safety Audit Committee was established by D. E. Munie to make a comprehensive safety audit of the DCA/PCA manufacturing facilities at Luling and the Chlorophenols manufacturing facilities at W. G. Krummrich. The committee completed the safety audit of the DCA/PCA facility and the findings and recommendations were issued in a report issued February 24, 1977.

The committee(1) for the safety audit of the Chlorophenols manufacturing facility consists of the following:

- B. W. Eley, Senior Industrial Hygienist
- G. F. Fort, Manager Environmental Affairs, MIC
- D. J. Metherd, Operating Superintendent
- D. P. Roman, Research Group Leader, R&D, MIC D&P
- W. W. Russell, Principal Safety Specialist, S&PP
- R. L. Liss, Manager R&D, MIC D&P (Chairman)

This committee carried out its Safety Audit of the Chlorophenols manufacturing facility at the W. G. Krummrich plant primarily to determine if any function, practice or condition of the entire process and products could have a significant impact on the safety of the personnel, property, or environment. A significant impact is defined as a potential "incident" which might lead to a) major disabling injury or loss of life of personnel; b) an impact on the environment or the community which could lead to company liability or adverse publicity in maintaining our role as good citizens; c) major loss of property or market.

FINDINGS

1. Overchlorination of pentachlorophenol provides a potential for major process accidents and formation of highly toxic materials. An earlier major incident at WCK and a very recent incident at NUFARM in Australia from overchlorination results in unstable product subject to exothermic decomposition and eruption.
2. Since 1975 approximately 40% of the personnel who work continuously in Pentachlorophenol (Dept. 236) show visible evidence of chloracne with one to seven people requiring medical treatment semi-annually. The observed chloracne has been comedones or blackheads on the face, primarily around the eyes and on the cheekbones and temples.
3. Monitoring of Pentachlorophenol (in air) conducted by the plant environmental control group indicates that at times, exposure levels associated with specific work functions (e.g. block pouring, sawing 1000 pound molds, and sampling the Penta chlorinator) exceed the established OSHA time-weighted-average and short-term exposure limits established by the American Conference of Governmental Industrial Hygienists (ACGIH).

SUBJECT: ...

(1) J. D. Lunn, Industrial Hygienist, assisted in one phase of the program.