



PL 1111

MIC/TP&E/WGK PLANT PROCESS RESEARCH
(CO./DIV./DEPT./LOCATION)

FINAL
REPORT
(TYPE OF REPORT)

REPORT NO.: 3996

JOB/PROJECT NO.: 02-760.03 7311403

DATE: August 18, 1976

TITLE: Pentachlorophenol - Dioxin & Related Process Maintenance Studies.

AUTHORS: W. R. Bennet, T. R. Berner, D. R. Cova, D. R. Dill, O. Hicks, D. K. Lynch, G. W. Mappes, J. P. Mieux, D. P. Roman, S. H. Vogel, P. L. Wright.

ABSTRACT:

This report summarizes dioxin related research work carried out on Pentachlorophenol and other Chlorophenols during the period from early 1970 through May, 1976. The major subject areas covered are: Chlorophenol dioxin analyses, chlorination and stabilization studies on ways to suppress dioxin formation, methods of purification, bioassay studies, and dioxin precursor chemistry.

RESTRICTED REPORT: Qualified persons may obtain loan copies from Central Reports if approved by D. K. Lynch, D. P. Roman, ~~G. J. McEwan~~, or G. J. McEwan.

S. H. Vogel, D. K. Lynch
Pentachlorophenol - Dioxin & Related Process Maintenance Studies.

AUTHORS:
TITLE:

3996

REPT. N°

COPY NO.: 16



C O M P A N Y C O N F I D E N T I A L

This document is the property of Monsanto Company and the recipient responsible for its safekeeping and disposition. It contains CONFIDENTIAL INFORMATION which must not be reproduced, revealed to unauthorized persons or sent outside the Company without proper authorization.

DISTRIBUTION

COPY NUMBER

ABSTRACT ONLY

1-3 Technical Reports Library

ST. LOUIS

4 Circulate to MICC Director
of Technology, R&D Managers,
and return to Central Reports
R2C

R. W. Bucknell - B3NB
C. F. Callis - T3B
J. R. Darby - 1730
O. DeGarmo - B3NA

W. D. Robinson - R3E
C. W. Roos - B2S
L. G. Scharpf - N1A
R. J. Schatz - E3S

5-6 TSD Library WGK

M. W. Farrar - R2E
H. C. Godt - T1B

R. Schuler/
F. C. Meyer - R4B

7 Plant Process Research File

E. J. Griffith - N1A
W. C. Hammann - T3A

M. J. Scott - N1A
C. Y. Shen - N1A

8-10 D. Danna ELSA

W. K. Johnson - R2E
R. E. Keller - T1B

C. C. Sisler - R2E
A. J. Speciale - C3N

11 D. R. Cova/J. E. White T3C

W. S. Knowles - T3A
W. R. Knox - R4C

W. F. Symes - N1A
P. A. Tierney - N1A

12 T. W. Cummins WGK

F. P. LaBelle - F4WA
R. L. Liss - N1A

Q. E. Thompson - T3E
M. C. Throdahl - D1D

13 R. W. Flint/W.L.Smull WGK

E. A. Matzner - N1A
J. E. Maurer - E1SA

R. L. Wasson - T3A
J. C. Weber - B3S

14 R. L. Harness/P.E.Heisler WGK

R. H. Munch - T1B
H. K. Nason - G4ND

J. L. Wikoff - B2S
B. L. Williams - R1B

15 E. E. Hendrikse B2NA

W. B. Papageorge - B2SK
T. M. Patrick - T3B

J. J. Zeman - B2S
F. B. Zienty - T3A

16 H. J. Horner WGK

J. H. Payne - N1A
J. F. Quinn - T3B

AKRON - 1010

17 J.C.Hume/D.Metherd WGK

G. A. Raub - B3SB
W. R. Richard - T3A

A. Y. Coran
W. A. Vaughn
R. W. Wise

18 J. A. Labanosky WGK

F. S. Riordan - E2NA

19 D. K. Lynch WGK

DAYTON - 1250

20 J.E.Maurer/T.N.Wallin E2NB

E. E. Hardy

21 G.J.McEwan/L.G.Scharpf N1A

VIA D. DANNA - E15

22 J.S.Metcalf/P.G.Hamner B2NK

MELBOURNE, AUSTRALIA
MONTREAL, CANADA
LOUVAIN-LA-NEUVE

23 J.P.Mieure/M.W.Dietrich/
O. Hicks T2F

24 J.F.Quinn/R.E.Keller T3B

25 W.R.Richard/D.R.Dill R1C

CENTRAL REPORTS LIBRARY

26 D.P.Roman/W.R.Bennet N1A

M. E. Madden - R2B

27 S.H. Vogel WGK

28 P.L.Wright A2SC

COMPANY CONFIDENTIAL

When no longer needed, or upon request, return

TABLE OF CONTENTS

	<u>PAGE NO.</u>
INTRODUCTION -----	1
SUMMARY -----	1
CONCLUSIONS -----	2
RECOMMENDATIONS -----	3
PATENT STATUS -----	4
REFERENCES -----	5
NOMENCLATURE & ABBREVIATIONS -----	9
EXPERIMENTAL RESULTS & DISCUSSION -----	13
(Dioxin Analyses, Chlorination Studies, Penta Refining, BioAssay Tests)	
A. BACKGROUND - THE DIOXIN STORY -----	13
B. DIOXIN STUDIES - PENTACHLOROPHENOL/SANTOBRITE 1970 -----	13
1. Product, Process Stream & Competitive Penta Dioxin Survey -----	13
2. Discussion - Analytical Method Inadequacy - Cyclization of Dioxin Precursors -----	14
C. DIOXIN STUDIES - PENTACHLOROPHENOL/SANTOBRITE 1971 -----	15
1. Survey - Dioxins in Penta & Penta/Oil Solutions -----	15
2. Chlorination Studies - Temp. Effect on Dioxin Formation -----	16
3. Chlorine - Initiator in Dioxin Formation -----	16
4. Methods of Refining - Feasibility Study -----	16
5. Discussion - Dioxin Method of Analyses -----	16
D. DIOXIN STUDIES - PENTACHLOROPHENOL 1972 -----	17
1. Trichlorophenol Stability Studies -----	17
2. Effect of Various Chlorination Conditions on Dioxin Formation -----	17
3. Distillation Process Development & Stabilization Studies -----	18
4. BioAssay - CEF on Typical W.G.K. Penta - Lot KM-261--	18
5. W.G.K. Penta - Dioxin Analyses -----	18
6. Discussion - Highboiler & Dioxin Methods of Analyses-	19
E. DIOXIN STUDIES - PENTACHLOROPHENOL 1973 -----	19
1. Introduction -----	19
2. Chlorination Studies - Alternate Catalysts, & Pressure Chlorination -----	19
3. BioAssay - CEF & Chloracne Response - Lab Low Temp. & Distilled Penta -----	20
4. Distilled Penta	
a) Process Development -----	21
b) Distilled Penta - Compatability in Santobrite Process-	21
c) Crude Penta X Pt. vs. % Distillation Residue ---	22
d) Distillation Stabilizers/Corrosion Inhibitors---	23
e) Distilled Penta Stability in Woodtreating Solutions-	28

E.	(Cont'd.)	
5.	Recrystallization Studies. -----	28
6.	Woodtreating Penta/Oil Solutions - Dioxin Survey -----	29
7.	Penta Esters - Dioxin Analyses -----	30
8.	Dioxin Analyses	
a)	W.G.K. Penta -----	31
b)	Prill Fumes - Venturi Penta -----	31
c)	Aqueous Santobrite - Alkali Insolubles -----	32
d)	Competitive Penta & Distilled Penta - Comparison -----	32
9.	Improved GC Method - Dioxin Analyses -----	33
F.	DIOXIN STUDIES - CHLOROPHENOLS 1974/1976	
1.	Introduction -----	34
2.	Plant Demo-Dual Circulation Pump Test -----	34
3.	Dioxin Analyses -----	35
a)	W.G.K. Penta -----	35
b)	Monsanto Newport Penta -----	35
c)	Distilled Penta - Dow vs Monsanto -----	36
d)	Santophen-1 -----	37
e)	Competitive Penta - Domestic & Foreign -----	37
f)	Miscellaneous Samples -----	38
4.	Plant Demo - Low Temperature Chlorination -----	39
5.	BioAssay	
a)	CEF & Chloracne Response on Low Temp. Plant Penta & Penta Oil Solution -----	40
b)	Quantitative Evaluation of CEF Data - Plant Penta From Low Temp. Demo. -----	44
6.	Chlorination Studies	
a)	Al/S - Catalysts, Catalyst Swamping, Catalyst Impurity Effects, & Penta Sulfur Analyses -----	44
b)	H ₂ O Content Before Catalyst Addition -----	47
7.	BioAssay - CEF on Parachlorophenol, 2, 4-Dichlorophenol, Lab Penta Al/S and Al/Te Catalysts, Reichhold Penta and hexa CDD, and TCDD Solutions -----	50
8.	Low Level Dioxin Analyses - Plant & Lab Penta (No Caustic Exposure) -----	51
9.	Dioxin Precursors in Penta	
a)	Base Catalyzed Ring Closure to Dioxins -----	51
b)	Significance of Precursor Cyclization -----	54
c)	Methods of Analyses - Morpholine Treatment -----	55
d)	Cyclization in NaOH vs Morpholine -----	58
e)	Cyclization Rate of Irgasan DP-300 vs. Dioxin Precursors in Technical Penta -----	58
f)	Speculative Toxicity of Various Dioxin Precursors -----	60
g)	CEF Relation to Precursor Concentration in Penta -----	61
10.	Hexachlorobenzene In Penta -----	61
G.	CHLORINATED DIBENZODIOXINS: COMPARATIVE TOXICOLOGY -----	62
H.	PENTA TREATED WOOD - DIOXIN ANALYSES -----	62

I.	BIOASSAY - CEF & REC DATA SUMMARY -----	63
J.	"ACCURATE" DIOXIN & DIBENZOFURAN ANALYSES DATA SUMMARY -----	66
K.	AR&D SPECIAL STUDY - PLANT PENTA DIOXINS & "COOKED" ALKALI INSOLUBLES ANALYSES -----	66
L.	SUMMARY - DIOXIN METHODS OF ANALYSES DEVELOPED BY APPLIED SCIENCE AND PPT 1970 - 1976 -----	68
M.	PENTA BIODEGRADATION STUDY - PURDUE UNIVERSITY -----	68
	DESCRIPTION OF RECOMMENDED PROCESS -----	68
	ANALYTICAL PROCEDURES -----	68
	TOXICITY & HAZARDS -----	69
	ATMOSPHERIC & STREAM POLLUTION -----	69
	ACKNOWLEDGEMENTS -----	69

APPENDICIES

- A. TSD Report No. 4242-2 "Pentachlorophenol/Santobrite Dioxin Study" 8/15/70, S. H. Vogel.
- B. MICC Progress Report No. 4, Pentachlorophenol/Santobrite Dioxin Studies. Job No. 090171 11/15/71, S. H. Vogel.
- C. MICC R&D Progress Report No. 1 Pentachlorophenol/Santobrite Quality Improvement & Maintenance - Job No. 7309103, S. H. Vogel 12/15/72.
- D. MICC R&D Progress Report No. 2 "Pentachlorophenol - Manufacturing Support" Job No. 7309103 S. H. Vogel 5/31/73.
- E. ITEMS:
 - 1) WGK Penta - Dioxin Analyses (1972 - 1975)
 - 2) Competitive Penta - Metals Analyses
 - 3) Quantitative Evaluation of BioAssay Data From Low Temp. Plant Penta
 - 4) a. Carnegie Mellon University "Rabbit Ear - Chloracne Test"- Report No. CMU 74-41A Through G.
b. Biotest Lab Report No. BTL 74-28. CEF on Plant Penta Std. Conditions - Lot No. OR 212180-1.
 - 5) Special Study - AR&D Dioxin & "Cooked" Alk-Insol. Analyses on Plant Produced Penta - April 1976.
 - 6) Applied Science - Dioxin Methods of Analyses 1970 - 1976.
 - 7) WGK Plant Process Research - Dioxin/Furan Analyses in Technical Penta. Streamlined Method. June 1976.

INTRODUCTION

In the late 1950's, a highly toxic compound, 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) was identified as an impurity in 2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T). This prompted concern for dioxins in other chlorinated hydrocarbons. This concern extended to Pentachlorophenol (Penta) in the late 1960's when Penta was implicated in the accidental poisoning of millions of commercially raised chicks.

Research on the dioxin subject, as it relates to Monsanto chlorophenol products, began in 1970, and is still continuing today. This report summarizes our findings to date. The work was carried out by WGK Plant Process Research and MFC R&D at G.O. Supportive work was also carried out by Applied Sciences Groups at G.O.. BioAssay testing was done outside Monsanto at the direction of our Corporate Medical Department.

For purposes of clarity and continuity, details of the work are presented in a chronological format covering the period from early 1970 to Mid-1976.

SUMMARY

The major areas studied and described in the report are as follows:

1. The amounts and kinds of dioxins found in Monsanto chlorophenol products and process streams are characterized.
2. Several approaches to Pentachlorophenol (Penta) and Santobrite Solution purification were studied. A process involving purification of Penta by distillation was developed. Optimum filtration parameters for dioxin removal from Santobrite solution were determined.
3. Molten Penta stabilization technology was developed and indirectly implemented into the plant process.
4. Chlorination studies (Lab and Plant) aimed at dioxin suppression were carried out.
5. Supportive analytical procedures were developed by PPT and by Applied Science Section at G. O.
6. Competitive Penta was routinely monitored for dioxin levels and other characteristics.
7. Fate of dioxins in Penta woodtreating processes and environment were studied.
8. Santobrite and Santobrite Solution stabilities were studied.
9. Biodegradation of refined and technical Penta was carried out by Purdue University Research.

SUMMARY (Cont'd.)

10. Dioxin literature monitoring was conducted throughout the 1970 - 1976 time period and is continuing.
11. Catomance Penta esters were analyzed for dioxins.
12. Dioxin precursor studies were carried out, and methods of analyses for precursors were developed.

CONCLUSIONS

Polychlorodibenzo-p-dioxins, polychlorinated dibenzofurans, and dioxin precursors (poly chloro-2-hydroxy diphenyl ethers) are present in technical Penta-chlorophenol. These compounds are believed to be the cause of positive "Chick Edema Factor" and Rabbit Ear chloracne response observed on Monsanto as well as competitive technical grade Penta.

Trace amounts of these impurities (but lower chlorinated) are also found in parachlorophenol, 2, 4-dichlorophenol, and Santophen-1. Presence of the highly toxic 2, 3, 7, 8 TCDD however, has not been confirmed in any of the WCK chlorophenol products MDL 0.1 ppm). Typical levels of these impurities in WCK Penta are shown in the following table:

	<u>DIBENZODIOXINS</u>	<u>DIBENZOFURANS</u>	<u>CYCLIZABLE DIOXIN PRECURSORS</u>
Tetrachloro	< 0.1 ppm	< 0.1 ppm	unknown
penta "	< 0.1	< 0.5	< 0.5 ppm
hexa "	5 - 20	30 - 90	300. +
hepta "	200 - 300	250 - 450	2500 +
octa "	400 - 1000	150 - 600	5000 +

These impurities are chlorine oxidative by-products, formed primarily during chlorophenol chlorination. Molten Penta degradation can also be a minor source of these impurities if the Penta is not stabilized with a chlorine scavenger, such as parachlorophenol. There is no evidence of gross dioxin generation in woodtreating processes. Accumulation of dioxins in the environment has not been fully studied but has not surfaced as a problem to date.

Dioxin precursors can be converted to dioxins. A number of conditions such as high temperature, photolytic, oxidative, or alkaline media favor the conversion. One or more of these conditions might be prevalent in biological systems. Hence, ingestion of dioxin precursors might produce the same pathogenic effects as ingestion of dioxins themselves. BioAssay data to confirm the purported toxicity of the precursors is lacking.

Formation of dioxins and other by-products during chlorination are moderately suppressed by using the lowest possible chlorination temperature and an aluminum/sulfur catalyst system. Penta prepared under these conditions also has reduced CEF activity. (Low temperature benefits have been demonstrated in the plant - the Al/S catalyst has only been demonstrated in the lab).

CONCLUSIONS (Cont'd.)

Penta is best purified by recrystallization or by distillation. A process to refine Penta by distillation has been developed in the laboratory. Dow Chemical Co. has introduced a refined Penta on the market and has discontinued production of technical grade Penta. Biodegradation studies by Purdue University indicate refined Penta biodegrades more rapidly than technical grade Penta.

Lack of adequate analytical procedures for dioxin, dibenzofuran, and dioxin precursors in Penta has been a perplexing handicap from the onset of the dioxin problem in 1970. Real progress has been realized in this area in recent months however. We can now quantitate dioxins and dibenzofurans in Penta by GC following a liquid chromatographic isolation procedure.

Dioxin precursors can be measured by an indirect approach which involves cyclization of the precursors to dioxins. This test unfortunately is very time consuming, and for this reason is not suitable for routine use without some refinement.

Current research on the dioxin problem is primarily in two areas: 1) refinement of analytical methods, in hopes of developing procedures which are more adaptable for routine use and, 2) isolation and collection of the various families of impurities in Penta. Chick Edema Factor activity will then be determined on each family.

The dioxin problem is currently under study by U. S., EPA and is also a concern to environmentalists in the U. S. and Western European countries.

RECOMMENDATIONS

In general terms, Monsanto should continue to study the dioxin problem as it relates to safety and environmental aspects on all WGK chlorophenol products. In specific terms, better analytical procedures are needed for accurate and routine quantitation of all families of impurities in chlorophenols. These families include diphenylethers, hexachlorobenzene, dibenzodioxins, dibenzofurans, and dioxin precursors (2-HDPE's). Secondly, accurate bioassay data is needed on each of these families.

In the long run, providing there is justification through bioassay data or regulating agency requirements, a program of impurity reduction in Penta should be initiated. Minor reductions can be made through process optimization. Major reductions would require refining.

The current plant practice of sewerage alkali insolubles associated with aqueous Santobrite solutions should be discontinued. Disposal by incineration is recommended.

Finally, in order to minimize worker exposure to dioxins and other toxic impurities in Penta, good housekeeping and adequate ventilation in working areas cannot be over emphasized. The same precautions apply to laboratory personnel when analyzing Penta.

PATENT STATUS

The following patent disclosures resulted from this work.

1. Disclosure No. D02-21-3971. Molten Pentachlorophenol stabilization by addition of salicylic acid, benzaldehyde, phenol, maleic anhydride or potassium iodide. Dioxin build-up slowed or prevented by each compound.
(S.H.Vogel) Status - Inactive
2. Disclosure No. 43-21-4196. Molten Pentachlorophenol stabilization by contact with H₂S gas. Dioxin build-up slowed or prevented.
(S.H.Vogel) Status - B Sept. 1974, Inactive Feb. 1976.
3. Disclosure No. 43-21-4197. Molten Pentachlorophenol stabilization by addition of nitroaromatics. Dioxin build-up slowed or prevented.
(S.H.Vogel) Status - Inactive Sept. 1974
4. Patent Case No. C-43-21-4024-A. Additive package for Penta oil solution color lightening, and Penta oil solution sludge inhibitor. Additives are a mixture of p-Chlorophenol, triphenylphosphite, diamylphenylphosphoric acid and di(diamylphenyl) phosphoric acid. Although not specifically stated in this case, the phosphoric acid partial esters (RT-53A) have been shown to be a very effective molten Penta stabilizer against dioxin build-up. The RT-53A is specifically used for this purpose in the proposed distillation refining process for Penta (PED Report No. P-1729). The use of RT-53A for this purpose is stated in another disclosure (No. 4133). Although the subject case was allowed, it was never issued because of fear of disclosure of too much technology to competitors.
(S.H.Vogel, D.R.Dill).
5. Disclosure No. 4133. Commercial Penta refining process by distillation.
(J. E. White, D. R. Cova). Status - Inactive July, 1973.

During the period of this work, a Dow Chemical Co. patent "Stabilized Distillation of Pentachlorophenol", Patent No. 3,816,268 (1974) was issued.²³ They claim decomposition during distillation is inhibited by presence of one or more amines, stable at the distillation temperature.

More recently, a patent (US 3909-349) by Vulcan Materials Co. was issued and also relates to Penta purification.³¹ The patent describes purification by distillation in the presence of zinc dust or ethylene thiourea which results in very light colored product.

REFERENCES

1. Schultz, K. H. - Clinical and Experimental Studies on the Etiology of Chloracne. ARCH. Klin. Exp. DERM. 206:589-596 (1957).
2. Kimmig, J. & Schultz, K.H. Occupational Acne (so-called Chloracne) due to Chlorinated Aromatic Cyclic Ethers. Dermatologia 115 (4): 540-546 (1957) Ger.
3. Kimmig, J. & Schultz, K.H. Chlorinated Aromatic Cyclic Ethers as a Cause of the so-called Chloracne. NATURWISS. 44:337-338 (1957) (Ger.).
4. Sanderman, W. et al, Studies of Wood-Protection Chemistry. IX Investigations Concerning Oily Blue Stain Protection Agents. HOLZFORSCH. HOLZVERWERT. 10 (4): 57-66 (1958).
5. Sanger, VL, Scott, L., Handy A, et al; Alimentary Toxemia in Chickens. J. AMER. VET. MED. ASSOC. 133:172-176, 1958.
6. Schmittle, S.C., Edwards, H.M., Morris, D.A. A Disorder of Chickens Probably due to a Toxic Feed - Preliminary Report. J. AMER. VET. MED. ASSOC. 132:216-219, 1958.
7. Edgar, S.A., Bond, D.S., Melius, P. et al: The Effect of a Toxic Substance in Fat on Poultry. POULTRY SCI. 37:1200-1201, 1958.
8. Flick, D.F., et al: Studies of Chick Edema Disease. POULTRY SCI. 44:1214-1222, 1965.
9. Flick, D.F., et al: Studies of Chick Edema Disease, POULTRY SCI. 46: 186-191, 1967.
10. Cantrell, J.S., et al: Search for Chick Edema Factor. CHEM. ENG. NEWS 45:10, 1967.
11. Cantrell, J.S., et al: Acta. Crystallogr., B25, 150 (1969).
12. Higginbotham, G.R., et al: Chemical and Toxicological Evaluations of Isolated and Synthetic Chloro derivatives of dibenzo-p-dioxin. NATURE 220:702-703, 1968.
13. Kimbrough, R.D.: Toxicity of Chlorinated Hydrocarbons and Related Compounds. ARCH ENVIRON. HEALTH, Vol. 25:125-131, Aug. 1972.
14. Shea, K.P. & Lindler, B., "Pandora and the Storage Tank". ENVIRONMENT, Vol. 17, No. 6, 12-15. (1975)
15. Preliminary Dioxin Implementation Plan - U. S., EPA, Office of Pesticide Programs Criteria & Evaluation Division, Wash. D.C. (1974).

16. Huff, J.E., Wassom, J.S.: Health Hazards from Chemical Impurities - Chlorinated Dibenzodioxins and Chlorinated Dibenzofurans: Intern. J. ENVIRON. STUDIES, VOL. 6:13-17, 1974.
17. King, M.E., et al, Carcinogenesis BioAssay of Chlorinated Dibenzodioxins and Related Chemicals. ENVIRON. HEALTH PERSPECTIVES. (No. 5):163 (1973).
18. Progress Report No. 1, Organic Chem Div. Job No. 2-02-760.01-8903309, July 1970, J. P. Mieure.
19. WCK, TSD Report No. 4242-2, Pentachlorophenol/Santobrite Dioxin Study. 8-15-70, S. H. Vogel (See Appendix A).
20. Memo communication J. P. Mieure to D. R. Dill (1970). No longer in file.
21. MICC R&D Progress Report No. 1, 11-15-71, Job No. R&D 090171 -Penta Quality Improvement Studies. S. H. Vogel. (Penta Additives)
22. MICC R&D Progress Report No. 4, Pentachlorophenol/Santobrite Dioxin Studies, Job No. 090171, 11-15-71, S. H. Vogel (See Appendix B).
23. Dow Patent No. 3,816,268 - Stabilized Distillation of Pentachlorophenol. June 11, 1974.
24. MICC R&D Progress Report No. 1, Job No. 7309103 - Pentachlorophenol/Santobrite Quality Improvement & Maintenance. S. H. Vogel 12-15-72 (See Appendix C).
25. Organic R&D Progress Reports No. 1, 2, 3, & 4 - Distillation of Pentachlorophenol - Job No. 0930205 and 0930305. J. E. White, 10-25-71, 4-28-72, 7-20-72, 1-8-73.
26. PED - Distillation of Pentachlorophenol to Remove Polychloro-dibenzo-p-dioxins - Report No. P-1677, Job No. 093035 - Aug. 24, 1972. J. E. White.
27. Industrial Bio-Test Labs, Northbrook, Ill. Report No. BTL-72-49 (1972). On file at Monsanto Medical Dept. Re: Dr. P. L. Wright.
28. W.G.K. Plant - Standard Analytical Method No. 13,107. Penta Assay by GLC.
29. Addendum to Spectroscopy Method 70-20 "Hexa-and-Hepta-Chlorodioxins in Pentachlorophenol". March 2, 1971, J. P. Mieure - Applied Science. G.O.
30. Applied Science Spectroscopy Method No. 70-20. "Dioxins in Pentachlorophenol" J. P. Mieure, July 1970.
31. Vulcan Materials Co. - Patent No. US-3909-349, "Separating Penta-chlorophenol from Colored Impurities.

32. Applied Science Spectroscopy Method No. 70-15 "Analysis of Pentachlorophenol for 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin". July, 1970. J. P. Mieure.
33. MICC Progress Report No. 2 "Pentachlorophenol - Manufacturing Support" Job No. 7309103, S. H. Vogel 5-31-73 (See Appendix D).
34. MICC R&D Final Report No. 3882 Job No. 7309103 and 7311103. "Process Development for Recovery and Treatment of Aqueous Phenolic Wastes Associated with Chlorophenol Operations at W GK Plant. S. H. Vogel 6-28-74.
35. W GK AR&D Report No. 2715, June 9, 1975. Dept. 236 - Pentachlorophenol-Penta Sample Screening by Internal Marker GC. P. Riley, J. Francis.
36. Memo. "Pentachlorophenol/Chloracne/Chick Edema Disease". P. L. Wright to D. R. Dill, May 14, 1973.
37. Medical Dept. Reports CMU-73-27 and BTL-73-28A thru 28F, 1973.
38. PED Report No. P-1729 "The Distillation of Pentachlorophenol to Remove Polychlorodibenzo-p-dioxins". J. E. White, May 5, 1973.
39. MICC R&D Progress Report No. 4, Job No. 0930305 "Pentachlorophenol Purification", 1-8-73, J. E. White.
40. MICC R&D Progress Report No. 5, Job No. 1430305 "Pentachlorophenol Purification" 3-20-73, J. E. White.
41. TSD Progress Report No. 16, Job No. 91370:9000 Pilot Plant Preparation of Penta Solution, R. W. Griscom, July, 1974.
42. Applied Science, Spectroscopy Method No. 73-1, Analysis of Pentachlorophenol for 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin and other chlorodioxins. J. P. Mieure 3-14-73.
43. Monsanto Newport R&D Report No. 2, Job No. 759.72, "Dev. of Chrom. Method for Quant. Det. of Dioxins & Predioxins in Penta and Santobrite. Comparison of Methods Currently in Use by European Penta Producers." K. M. Baker, A. J. McLoughlin, R. A. Lidgett, May 20, 1975.
44. W GK AR&D Report No. 2448, "Dept. 239 - Santophen-1 - Analysis for Presence of Chlorodioxins in Product", 4-18-74 H. L. Campbell.
45. Amendment "F" to Dept. 236 Standard Manufacturing Process Description for Molten Penta, Prilled Penta, Block Penta, & Penta 60 dated Jan. 30, 1972, Amendment date Aug. 24, 1973. S. H. Vogel.
46. Amendment "H" to Dept. 236 SMPD for Penta Mfg. dated Jan 20, 1972. Amendment date April 4, 1974. S. H. Vogel.
47. W GK Plant Process Research Progress Report No. 2, "Improve Pentachlorophenol Quality", Job No. R&D 090171, 1-13-72, N.E.S. Thompson.

48. Applied Science - Special Study AC-75-SS-3, April 7, 1975, J. P. Mieure, G. W. Mappes.
49. Cutis Vol. 13, (1974) pp 585-591, "Chloracne - A Continuing Problem", J. S. Taylow, MD, Cleveland, Ohio.
50. Monsanto Newport England R&D Status Report No. 2, May 20, 1975 Job No. 759.72 R. A. Lidgett et al.
51. Further Studies on Impurities in Chlorophenols", J. CHROM. 89 (1974) 325 - 333. C. A. Nillson et al. Dept. of Organic Chem., U. of Umea, Sweden.
52. "Thermal Chemistry of Chlorinated Phenols" Advances in Chemistry Series No. 120 (1973) H. G. Langer, et al. Dow Chem. Co. Eastern Research La., Wayland, Mass.
53. "An Artifact in the Gas Chromatographic Determination of Impurities in Penta Chlorophenol", J. CHROM. 67(1972) 247-253, C. A. Nillson et al.
54. Chromatographic Evidence for the Formation of Chlorodioxins from Chloro-2-Phenoxyphenols", J. CHROM. 96(1974) 137-147, C. A. Nillson, et al.
55. Applied Sciences - Special Study S-75-SS-17, June 1975 "Chlorodibenzodioxins in Pentachlorophenol Treated with Morpholine". G. W. Mappes.
56. J. Chrom. 107(1975) 295-310 "Analysis of Polychlorinated dibenzodioxins and Furans in Chlorophenols by Mass Fragmentography." H. R. Buser.
57. Molecular Pharmacology, 9, 736-749 (1973) Alan Poland & Edward Glover "Chlorinated dibenzo-p-dioxins: Potent Inducers of δ -Amino-levulinic Acid Synthetase and Aryl Hydrocarbon Hydroxylase."
58. Applied Science - Special Study AC-75-SS-1, "Determination of Pentachlorophenol and Chlorodibenzodioxins in Wood Borings", O. Hicks, J. P. Mieure, March 27, 1975.
59. Microbial Decomposition of Pentachlorophenol. J. Water Poll. 2 pp 359-64. Kirsch, Edwin J, Etzel, J. E. (1973).
60. Oil Paint & Drug - Chem. Market Reptot Nov-17-1975, Page 26. "Dow Antimicrobials Safer - Say Purdue Researchers."

NOMENCLATURE & ABBREVIATIONS

Alkali Insolubles	- Gravimetric measurement of non-phenolic high boilers in technical pentachlorophenol.
BTL	- Bio-test Laboratories - Northbrook, Ill.
CDD's	- Chlorodibenzo-p-dioxins
CDF's	- Chlorodibenzofurans
CEF	- Chick Edema Factor
CMU	- Carnegie Mellon University - Pittsburg, Pa.
2, 4-D	- 2, 4-dichlorophenoxy acetic acid
DBF	- Chlorinated dibenzofurans
DiCDD	- Dichlorodibenzo-p-dioxin
Dioxins	- Chlorodibenzo-p-dioxins
DPE	- Chlorinated diphenylethers
ECGC	- Electron Capture Gas Chromatography
EPA	- Environmental Protection Agency
Furans	- Chlorinated Dibenzofurans
GC	- Gas Chromatography
G.O.	- Monsanto General Office - Creve Coeur, Mo.
HB	- High boiling Pentachlorophenol impurities; chlorination by-products
2-HDPE	- Dioxin precursors; predioxins; Polychloro-2-hydroxy diphenylethers; Polychloro-2-phenoxy phenol; hindered phenols.
4-HDPE	- Isopredioxins; polychloro-4-hydroxy diphenyl ether; polychloro-4-phenoxy-phenol;
hepta CDD	- hepta Chlorodibenzo-p-dioxins
hexa-CDD	- hexa Chlorodibenzo-p-dioxins
Isopredioxin	- Polychloro-4-hydroxy diphenyl ether (4-HDPE); polychloro-4-phenoxy phenol.

M&MT	- Mechanical & Materials Technology @ W GK
MDL	- Minimum Detection Limit
MICC	- Monsanto Industrial Chemicals Co.
non-phenolics	- High boiling chlorinated compounds found in technical Pentachlorophenol that contain no hydroxy group; alkali insolubles; chlorobenzenes, chlorodiphenylethers, chlorodibenzo-furans, chlorodibenzo-p-dioxins.
OCDD	- Octachlorodibenzo-p-dioxin
para	- p-Chlorophenol
PED	- Process for Engineering Design
Penta	- Pentachlorophenol
Penta CDD	- Pentachloro-dibenzo-p-dioxin
PPT	- W GK Plant Process Technology
Precursor	- Predioxin; polychloro-2-hydroxy diphenylether (2-HDPE); polychloro-2-phenoxyphenol
Predioxin	- dioxin precursor; polychloro-2-hydroxy-diphenyl-ether; polychloro-2-phenoxy phenol; hindered phenols (2-HDPE)
R&D	- Research & Development
rate of rise	- Final segment of phenol chlorination to Penta-chlorophenol when batch temperature parallels crystallizing point from 125°C. up to end of batch at ~185°C.
REC	- Rabbit Ear Chloracne; chloracne test by Carnegie Mellon University, Pittsburg, Pa.
RT53A	- 50:50 mixture of di-Amylphenyl phosphoric acid and di-diamylphenyl phosphoric acid; high molecular weight partial acid ester of phosphoric acid MOI additive in Penta & Molten Penta stabilizer.
Santobrite	- Sodium salt of technical Pentachlorophenol.
Scrap Penta	- Chunks of Penta from Prill Tower.
SMFD	- Standard Manufacturing Process Description

- | | |
|---------------|--|
| Spread | - Degree C difference between chlorination temperature and crystallizing point during rate of rise in chlorination of phenol to Penta. |
| SPS-30 | - 30% (wt) sodium Pentachlorophenate (Tech.) in water. |
| SPS-21 | - ~ 20% (wt) sodium Pentachlorophenate in water - represents typical feed to Penta oil solution in Dept. 716. |
| 2, 4, 5-T | - 2, 4, 5-Trichlorophenoxy acetic acid |
| TCDD | - Tetrachlorodibenzo-p-dioxin |
| TCP | - 2, 4, 6-Trichlorophenol |
| tri-CDD | - Trichlorodibenzo-p-dioxin |
| Venturi Penta | - Sublimed Penta in exit air during prilling which is collected in a Venturi Caustic Scrubber. |

EXPERIMENTAL RESULTS AND DISCUSSIONA. THE DIOXIN STORY

Dioxins first became a concern in late 1957. K. H. Schultz¹, in his study of chloracne cases at a 2, 4, 5-trichlorophenoxy acetic acid (2, 4, 5-T) factory, traced the cause to an impurity in the 2, 4, 5-T. The impurity was identified as 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (TCDD). About the same period, Schultz also studied and found TCDD to be responsible for 31 cases of chloracne in a German 2, 4, 5-Trichlorophenol factory.² The cases had originated in 1953, when workers were exposed to decomposition products generated in a run-away reaction of caustic and 1, 2, 4, 5-tetrachlorobenzene. Ensuing studies^{3,4} revealed that TCDD was not only chloroacnegenic, but also extremely toxic. This prompted intense concern for TCDD, and dioxins in general, in other chlorinated hydrocarbons. The concern extended to Pentachlorophenol (Penta) in the late 1960's when Penta was implicated as a source of "Chick Edema Disease". Millions of commercially raised chicks had died mysteriously in 1957.⁵ The disease was labeled "chick edema disease" and had the common feature of increased amounts of pericardial fluid (hydro-pericardium). At first glance, an epidemic seemed apparent. It was soon discovered that residues of certain distilled animal fats in the chick's diet would induce the chick edema syndrome.^{6,7} Intense studies on the "toxic fat" promptly ensued.^{8,9} It was not until 1967-69 that chlorodibenzo-p-dioxins (CDD's) were identified in the toxic fat.^{10,11} Concurrently, synthesized CDD's were also shown to produce the chick edema disease.¹² Hence, the source of CDD's in the toxic fat was speculated to have come from commercial Penta contamination in the leather and tanning industry where the fats originated as by-products.

There have been other instances of dioxin poisoning in the environment. Among these were X-disease in cattle,¹³ and most recently, horse poisonings at three riding stables in central and eastern Missouri.¹⁴

Recent literature cites numerous toxicological studies on the subject of dioxins and more studies are currently in progress.¹⁵ To date, CDD's have been shown, or suspected to be, responsible for occurrence of chloracne in humans, liver disease in several species, X-disease in cattle, chick edema disease, teratogenic effects on mammals, and mutagenic effects in bacteria.¹⁶ Carcinogenicity has also been suggested.¹⁷

Monsanto is continuing to study the dioxin problem - particularly as it relates to the safety and environmental aspects of Penta. Our findings to date are presented in the following sections of this report.

B. DIOXIN STUDIES - PENTA/SANTOBRITE - 19701. Product/Process Stream & Competitive Penta Dioxin Survey

Work first began on the dioxin problem in the early part of 1970. After analytical method development by Applied Science,¹⁸ a study was carried out with the following objectives:

- B. 1. (Cont'd.)
- a. Measure the dioxin concentrations in all Penta/Santobrite process and product streams.
 - b. Measure the dioxin concentrations in competitive Penta and Santobrite.
 - c. Define possible ways to reduce or eliminate the dioxins.

The details of this study are presented in WGK TSD Report No. 4242-2 "Pentachlorophenol/Santobrite Dioxin Study", 8-15-70, S.H. Vogel (Reference No. 19). The report is found in Appendix A. In summary, the major findings from the study were as follows:

- a. Heptachlorodibenzo-p-dioxin (hepta CDD) and Octachlorodibenzo-p-dioxin (OCDD) were found in finished Penta and in Santobrite. OCDD was found in concentrations up to 5000 ppm. Hepta levels were in the 500 ppm range.
- b. Somewhat lesser amounts of OCDD and hepta CDD were found in Santobrite and Santobrite aqueous solutions. Some of these dioxins are removed during processing as alkali insolubles at the cone settler. These insolubles are still routinely sewerred (1976). [Santobrite production was discontinued in 1971. Santobrite solution is still being manufactured however and is a feed stream to Penta oil solution (Dept. 716).]
- c. Dioxins are primarily formed during the later stages of chlorination. They also form, but at slower rates, during the molten hold period prior to prilling. There was also evidence of further dioxin formation in Penta/oil solutions when the solutions were cooked for an extended period of time at wood treating temperatures.
- d. Lower chlorinated dioxins (<hepta CDD) were not detected in any product or process streams. Levels of about 1 ppm tetra CDD (TCDD) were found in the chlorination mass at the tri-tetrachlorophenol chlorination stage.²⁰
- e. Competitive Penta and Santobrite were found to be comparable in dioxin content to Monsanto's products.
- f. Laboratory chlorination study suggests dioxin formation can be moderated by milder chlorination conditions.

2. Discussion - Analytical Method Inadequacy - Cyclization of Dioxin Precursors

Dioxin method of analysis utilized in these studies involved an initial caustic clean-up of Penta/benzene solution and quantitation by flame ionization GC (MDL 50 ppm) against an OCDD standard solution.¹⁸

B. 2. (Cont'd.)

We have just recently learned however that the initial caustic (NaOH) clean-up procedure causes cyclization of some dioxin precursors (polychloro-2-hydroxy diphenyl ethers) to dioxins. Thus the reported values are inflated. In addition, since the precursors are hindered phenols, they do not have good solubility in the caustic. Hence, they are not totally extracted by the caustic. This leads to further inflation of the dioxin values due to thermal cyclization of the precursors to dioxins in the GC. ⁵⁴

The caustic catalyzed cyclization phenomena also tells us we are probably generating dioxins in the plant in all aqueous Santobrite solutions. A small excess of caustic is normally present in these solutions. Most of the generated dioxins are likely being removed as alkali insolubles at the cone settler and are currently sewered. These insolubles should be handled with extreme caution due to suspected high concentrations of hexachlorodibenzo-p-dioxin (as well as hepta CDD & OCDD). The solution itself should also be handled with extreme care due to remaining dissolved dioxins. Toxicological data on this solution is lacking.

C. DIOXIN STUDIES - PENTA/SANTOBRITE - 19711. Survey - Dioxins in Penta & Penta/Oil Solutions

Research efforts during 1971 were primarily directed at development and implementation of our MOI/MOT additive package for the Penta process.²¹ Some dioxin work in the areas of problem definition, chlorination studies, stabilization, and purification approaches was carried out however. These studies are reported in detail in MIC R&D Report No. 4, "Pentachlorophenol/Santobrite Dioxin Studies" Job No. R&D 090171 (11-15-71), S. H. Vogel (Reference No. 22). The report is found in Appendix B. Some of the major findings are summarized here and in the following immediate sections.

Further assessment of dioxins in Penta/Santobrite and Penta/Oil solution revealed:

- a. Santobrite and pentachlorophenol (Penta) each slowly increase in dioxin content when held at elevated temperatures. In each case, the formation rate increases with temperature. Typical temperatures however, in end-use processes are quite moderate (80 - 220°F.). Formation rates at these temperatures are very meager. For this reason, dioxin build-up in treating plant oils or their sludges is negligible.
- b. Finished Penta and Santobrite contain at least three different dioxins - hexa, hepta, and octa chlorodibenzodioxin. Octachlorodibenzodioxin (OCDD) is the major dioxin present. Other lower chlorinated dioxins have not been detected in finished Penta or Santobrite. Trace amounts (~1 ppm) of 2, 3, 7, 8-tetrachlorodibenzodioxin (TCDD) however, have been detected at the "dichlor" stage of Penta chlorination.

C. 1. b. (Cont'd.)

Ultimately further chlorination transforms TCDD to the higher chlorinated dioxins (hexa-octa). TCDD if present in Penta, is < 0.5 ppm which is the detection limit of our test. "Block" Penta contained comparable levels of dioxins to that found in Prills.

2. Chlorination Studies - Temp. Effect on Dioxin Formation

Limited studies once again show dioxin formation during chlorination can be suppressed through lower temperature chlorination.²² This is particularly true during the final stages of chlorination when dioxin formation rates were shown to be most rapid (Hepta CDD and OCDD). There was also suggestion that maintaining a higher hydrogen ion concentration in the mass during this period would further suppress dioxin formation rates.

3. Chlorine - Initiator In Dioxin Formation

Chlorine was shown to be the initiator for dioxin formation in molten Penta.²² When free chlorine in molten Penta is eliminated, dioxin formation is stopped. Introduction of small amounts of chlorine scavengers to molten Penta just after chlorination, effectively prevents further dioxin formation. Phenol and para-chlorophenol are examples of such scavengers. Para-chlorophenol is currently being used in the plant in conjunction with MOI/MOT additives. Consequently, all normal Penta production at this time is dioxin stabilized during the molten hold period.

4. Methods of Refining - Feasibility Study

Various purification techniques were shown to be feasible ways of refining Penta.²² Distillation, solvent extraction from sodium pentachlorophenate solution, and recrystallization were each effective in removing dioxins and other impurities from crude Penta. Distillation appeared the most economical means. Development of a distillation process for refining by J. E. White of Organic Research began in 1971²⁵ and continued into 1972 & 73.

5. Discussion - Dioxins Method of Analyses

As in our first study (1970), method of analysis for dioxins utilized an initial caustic clean-up step.³⁰ Because of this, hepta & OCDD dioxin values are inflated (See Section B, 2. for explanation). TCDD analyses were carried out by J. Miere of Applied Science at G.O. by GC/mass spectroscopy (a modification of the then newly developed ECGC method for dioxin analyses - Method No. 70-20).^{30, 32}

D. DIOXIN STUDIES - PENTACHLOROPHENOL - 19721. Trichlorophenol Stability Studies

Research on the dioxin problem in 1972 covered a number of areas. Included were studies on molten Penta stabilization, trichlorophenol stability/reactivity, chlorination studies, and competitive Penta monitoring. These studies are presented in detail in MICC R&D Progress Report No. 1, Job No. 7309103- Pentachlorophenol/Santobrite Quality Improvement and Maintenance - S. E. Vogel, 12-15-72 (Reference No. 24). The report is found in Appendix C. Major findings in other areas are described in following immediate sections of this report.

We had observed in chlorination profiles of Phenol $\longrightarrow$ Pentachlorophenol that a surge of high boiler (HB) formation normally occurred when trichlorophenol was near maximum concentration. A HB hump would occur in the chlorination profile. We also observed terminal HB content in Penta was lower when the hump was lower. Chlorination and stability studies were carried out on 2, 4, 6-trichlorophenol to determine what conditions favored or suppressed HB formation in this stage of the chlorination. Temperature was shown to be the most critical factor effecting HB formation. Acidity of the mass was also found to be important. H_2SO_4 and HCl were each effective stabilizers against HB formation in molten trichlorophenol (in absence of Cl_2). Bases accelerated HB formation. No alternate catalyst system showed measureable benefits.

2. Effect of Various Chlorination Conditions on Dioxin Formation

Extensive chlorination studies ²⁴ aimed at establishing more optimum chlorination conditions to minimize HB levels in Penta were carried out in 1972. The major findings were as follows:

- a. Heat history, or minimal temperatures throughout the entire chlorination is most essential. It is most critical during the later stage of chlorination.
- b. Catalyst concentration, catalyst addition point, Cl_2 rate, mass mobility, Cl_2 bubble size, and system pressure (10 lbs.) had little or no effect on terminal HB content in Penta.
- c. No alternate catalyst systems (besides aluminum) showed a benefit.
- d. Chlorination in the presence of solvents at lower temperatures resulted in significant HB reduction.

These studies are presented in detail in Reference No. 24.

D. 3. Distillation Process Development & Stabilization Studies

Studies on the development of distillation process for Penta refining began in Feb. 1971 by J. E. White of Organic Research. ²⁵ This work continued in earnest up to August 1972 at which time a Process for Engineering Design document was issued. ²⁶

One of the major problems encountered in the development of the distillation process was low yields due to thermal degradation of the Penta. The use of p-chlorophenol was tried as a stabilizer, but would not stand up under the harsh distillation conditions. (p-Chlorophenol had earlier been shown to be an effective stabilizer for molten Penta in the plant ²²). A search was made for a more effective stabilizer. Several compounds were screened. ²⁴ In summary the studies revealed the following:

- a. Best performers were those compounds which readily react with chlorine or chlorine radical, and were thermally stable themselves at the test temperatures; ~~as at 1000-1200°C.~~
- b. Resorcinol, B-naphthol, paraffin wax, and RT53A²¹ were the most effective compounds found.

RT53A was recommended for use as stabilizer in Penta distillation. It was chosen over the other compounds primarily due to its known compatibility in end use Penta - (was currently an ingredient in our additive package ²¹).

Dioxin analyses in support of the distillation process development in 1972 were also carried out. The leachability of dioxins from soil by water was also tested and found to be nil. These and other process development work are presented in detail in Reference No. 24.

4. BioAssay - CEF on Typical W GK Penta - Lot KM-261

During 1972, Penta Lot KM-261 (typical product) was submitted to Industrial BIO-TEST Labs, Northbrook, Ill. for Chick Edema Factor (CEF) studies. The results of the studies are found in Report BTL-72-49 which is on file in the Medical Department at G.O. (Reference No. 27). The sample elicited a positive CEF response at 150 ppm dietary concentration, but not at 50 ppm. This was our first instance of confirmation that commercial Penta could produce the Chick Edema disease.

5. W.G.K. Penta - Dioxin Analyses

Monitoring of dioxin levels in W GK manufactured Penta began on a frequency basis in 1972. Values obtained on 1972 material, and on Penta produced in subsequent years are presented in Appendix E.1. Applied Science, Method No. 70-20 was used for all analyses. ^{29, 30} See following discussion section for comments on results.

D. 6. Discussion - High Boiler & Dioxin Methods of Analyses

Highboiler (HB) method of analysis²⁸ used in the trichlorophenol (TCP) and Penta chlorination studies was by a normalized GLC procedure. The same HB response factor used for Penta analysis was used for HB determination at all stages of chlorination. This may have caused slight inflation of HB values at the lower stages of chlorination. Regardless of this, the values are valid for comparative purposes.

As in our earlier dioxin studies (1970 - 71), the method of analysis for dioxins, utilized an initial caustic extraction of a Penta/benzene solution.^{29,30} All hepta-CDD and OCDD values are therefore erroneously high. (See Section B.2 for explanation). Again however, the values are valid for comparative purposes. In addition, all hexa CDD values reported include co-eluting chlorodiphenylethers.²⁹ Aside from comparative purposes, the values should be disregarded.

E. DIOXIN STUDIES - PENTACHLOROPHENOL - 19731. Introduction

Feasibility studies concerning by-product reduction during chlorination, purification procedures, and molten Penta stabilization were carried out in early 1973. These studies are presented in detail in MICC Progress Report No. 2, Job No. 7309103, S. H. Vogel, 5-31-73 (Reference No. 33 - See Appendix D). Research efforts during the later portion of 1973 were primarily directed toward process development for chlorophenol waste treatment, and recovery of Penta from prill fume scrubber liquor.³⁴ Some minor dioxin studies, covering a number of areas were carried out in latter 1973. This work, along with the major findings in Reference 33, are summarized in the following immediate section of this report.

2. Chlorination Studies - Alternate Catalysts & Pressure Chlorination

Again chlorination temperature was found to be the most important variable affecting by-product formation during chlorination.³³ Chlorine assay was also shown to be important. Low assay chlorine (98% and lower) gives higher HB as well as lower chemical assay. Chlorinating under pressure (up to 38 lbs.) had no measurable effect on suppression of dioxin or HB formation. No alternate catalyst systems were found that had any measurable benefit over aluminum. A large unexplained variation in HB content was observed in replicate batches made at standard as well as amended conditions.

A normalized GLC procedure²⁸ was used for Penta HB determination on all samples. We have recently learned this method will occasionally give low HB values on Penta that has been chlorinated

E. 2. (Cont'd.)

to higher than normal X Pt. ($>178.5^{\circ}\text{C.}$). Polymeric HB's do not elute from the GLC. This phenomena was discovered when we went to an internal maker GLC method to measure yields/composition in Penta distillation studies.²⁵ Since that time, we have also observed HB values reported by the analytical section on routine Penta product are occasionally low.³⁵ (The normalized GC procedure is still in use.) Because of the method inaccuracy, all HB values reported in reference No. 33 should be viewed with some skepticism.)

Dioxin values reported in Reference No. 33 are also questionable (except for comparison purposes) due to the method of analysis used. (See Section B, 2 for explanation.)

3. BioAssay CEF & Chloracne Response - Lab Low Temp. & Distilled Penta

About mid-1973, Monsanto Medical Dept. carried out a Toxicon data base search to secure information on chlorodioxins as related to CEF and chloracne diseases.³⁶ The search indicated the most potent inducers were:

trichlorodibenzo-p-dioxin	
tetrachlorodibenzo-p-dioxin	
hexachlorodibenzo-p-dioxin	isomers not
tetrachlorodibenzofuran	specified
pentachlorodibenzofuran	

The search also revealed data showing OCDD and Hexa CDD were not readily absorbed by the chick in CEF studies, and were therefore not nearly as toxic as the lower chlorinated homologues. It was suggested that TCDD was probably the major causative factor in CEF disease due to its most severe toxicity.

Following this search, a series of six pentachlorophenol samples were submitted to BTL and CMU for CEF and chloracne testing with the hope of developing a more precise relationship of dioxin concentration to biotesting responses. Three of the Penta samples selected were lab preparations from chlorination studies³³ made earlier in 1973. These samples had shown reduced amounts of dioxins and HB's. For the most part, they exemplified low temperature chlorination. Samples of Monsanto Lab refined (distillation), and Dow's EC-7 refined material were included in the tests. Our standard KM-261 lot was also resubmitted.

<u>SAMPLE</u>	<u>LOT NO.</u>	<u>IDENTIFICATION</u>
A	OR 210598	Lab prepared - in Perchloroethylene solvent
B	OR 211535	" " - Low Temperature
C	OR 211525	" " " " - high level Cl ₂
D	OR 211544	Monsanto Commercial KM-261
E	OR 211544	Dow EC-7 (distilled)
F	OR 214234	Monsanto - Lab distilled

E. 3. (Cont'd.)

The results of the Chloracne tests ³⁷ indicate that samples A, B, and C were essentially equivalent and produced the "least detectable change". Sample D, the commercial material, produced a marked effect and the distilled samples were essentially without effect in these tests.

With respect to CEF toxicity, ³⁷ neither the solvent chlorination or distilled samples showed a response at the highest level (1500 ppm) tested. Samples B & C were negative at the 500 ppm level, while KM-261 was positive at this level (lowest dietary level tested). KM-261 was positive at 150 ppm in an earlier test (Reference No. 27).

The encouraging results from these tests prompted a trial of low temperature chlorination in the plant which was carried out in early 1974. Results of this trial are presented in a later section of this report. (See Section F, 4.)

4. Distilled Pentaa. Process Development

Some major modifications to the 1972 PED for Penta distillation, P-1677 (Reference No. 26) were made in early 1973. The major changes were: 1) elimination of the need for dichlorobenzene condensing solvent, 2) an increase in tetrachlorophenol content of the crude and refined Penta, and 3) a reduction in the typical dioxin content of the product. This work was carried out by J. E. White of MIC R&D. The amended PED document for Penta distillation - Report No. P-1729 was issued in May, 1973. (Ref. No. 38)

b. Distilled Penta - Compatability in Santobrite Process

There was some concern that dioxins would build up again when distilled Penta was used in the preparation of Santobrite or Santobrite aqueous solutions (by Monsanto or a Penta user). To answer these questions, the following experiments were run (OR 211701).

Distilled Penta, Lots OR 214233 and OR 214234, were composited. A 30% aqueous Santobrite solution was prepared. A portion of the solution was oven dried at 110°C. for 2 hours to simulate Santobrite manufacture. Another portion was neutralized with aqueous HCl. The released Penta was collected by filtration and air dried. Analysis of this material was used to determine if dioxins were generated during the 30% solution preparation (a simulation of SPS-30 manufacture).

Two more portions of the 30% solution were cooked at 80°C. with and without contact to steel coupon. Samples were taken from each at 1, 5, 12, and 30 days for dioxin analyses. This test was designed to detect any detrimental effects during SPS-30 storage.

E. 4. b. (Cont'd.)

<u>SAMPLE</u>	<u>Hepta CDD</u>		<u>OCDD</u>	
Composited distilled Penta	N.D.		0.5 ppm	
Oven dried Santobrite (2' @ 110°C)	N.D.		0.5 ppm	
Penta Released & Air Dried	N.D.		0.5 ppm	
	<u>WITH STEEL CONTACT</u>		<u>WITHOUT STEEL CONTACT</u>	
	<u>Hepta CDD</u>	<u>OCDD</u>	<u>Hepta CDD</u>	<u>OCDD</u>
SPS-30, 1 day @ 80°C.	≤0.1 ppm	0.5 ppm	≤0.1 ppm	0.5 ppm
SPS-30, 5 days @ 80°C.	≤0.1	0.5	≤0.1	0.5
SPS-30, 12 days @ 80°C.	0.3	1.3	0.5	1.2
SPS-30, 30 days @ 80°C.	*	2.4	*	1.5

* Unable to determine due to GC co-eluting interferences. Dioxins by Method 70-20.

The first set of results above indicate no change in dioxin content due to Santobrite or SPS-30 preparation conditions. The second set of results (SPS-30 cooking) suggest a slight or meager build-up of dioxins with time. Contact with steel may accelerate the build-up slightly. There was also a noticeable build-up of low boiling unidentified non-phenolics in each of the SPS-30 samples. There was also a slow build-up of one high-boiling non-phenolic which eluted 3 - 4 minutes beyond OCDD on the GC. No attempt was made to identify these unknowns.

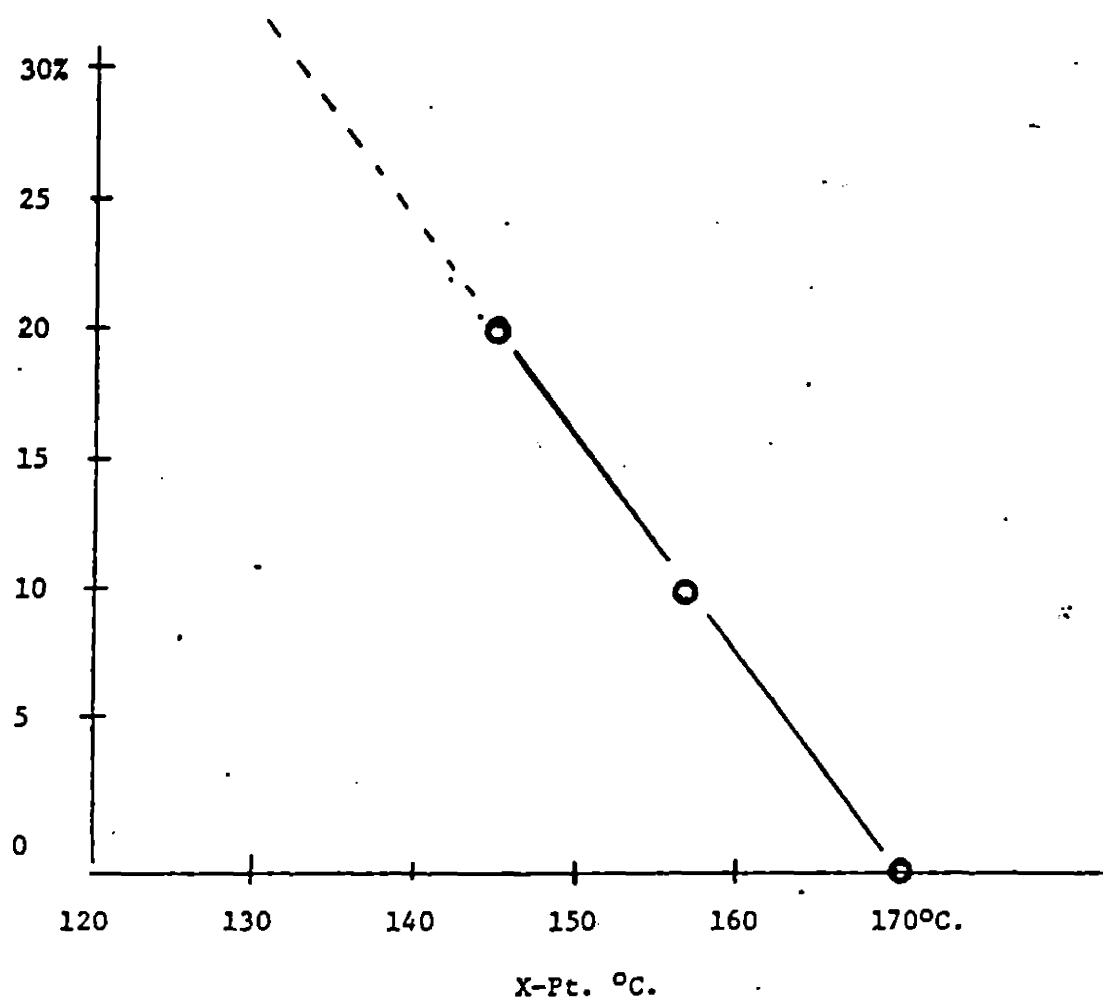
c. Crude Penta X-Pt. VS. % Distillation Residue (OR 211708)

Crude Penta feed to distillation,³⁸ is expected to have a crystallizing point of about 170°C. Blending distillation residue with the crude feed should lower the X-Pt. This would permit reduced molten storage temperature prior to refining, and thus less thermal degradation. In addition and more importantly, this residue might be blended with Penta chlorination mass, and thus allow a significant reduction in chlorination temperature due to lower X-Pt. Hence less dioxins and HB's would be formed, and thus improve the overall yields of the chlorination/refining process.

Distillation reboiler residue, Lot OR 214240, and crude Penta, Lot OR 214240, were blended at various proportions and X-Pt determined. (See Graph, Page 22 a.)

X-Pt is indeed suppressed by addition of the residue. Since the residue is already highly chlorinated, it is not likely to chlorinate further. Finishing the Penta chlorination at temperatures no higher than 145°C., are expected to result in much less by-product formation, as was the case when PCE solvent was used.³³ The feasibility of using the residue as a "chlorination solvent"

22 a.



OR 211708
S.H.Vogel
9/4/73

E. 4. c. (Cont'd.)

has not been demonstrated yet, mainly because of insufficient quantities of residue available to try it. If Monsanto does decide to pursue refining by distillation, we should consider utilizing the residue in this manner as a means of improving yields/economics.

d. Distillation Stabilizers/Corrosion Inhibitors

Although RT 53-A had been demonstrated to be a useable and effective decomposition inhibitor in Penta distillation, it did possess some disadvantages. It's cost was high, availability somewhat uncertain, and lastly, showed some thermal instability itself in the distillation process.³⁸ (Low boiling degradation products were found in the vent scrubber system.) We had shown in earlier stabilization studies that Penta decomposition could be retarded or stopped when raw chlorine in molten Penta was eliminated.²² High corrosion rates were also of concern in the reboiler and preheater in the proposed distillation system.²⁵ It was therefore desirable to find an RT 53-A alternate which would: 1) provide some corrosion inhibition and, 2) provide stabilization by consumption of raw chlorine.

A number of commercially available corrosion inhibitors as well as various organic residue streams available throughout Monsanto were screened for corrosion inhibition on A-235 steel in molten Penta. All tests were carried out at 220°C. for periods of 10 days or more. The inhibitor (0.3% by wt.) was first added to Penta in a 100 ml stoppered vial. The vials were then immersed in a heated oil bath. After the Penta came to temperature, A-235 steel coupons were added to each. Three groups of inhibitors were screened in this manner. Our original plan was to select the samples which showed good corrosion inhibition. The selected samples would then be analyzed for dioxins to determine stabilization effectiveness. Our plan was sidelined (other priorities) and the dioxin analyses were never run. Some indication of stabilization effectiveness is apparent however, from the color of the Penta sublimate which collected on the underside of the vial stopper in each test. White sublimate is indicative of stabilization; without stabilization, the sublimate is yellow.

E. 4. d. (Cont'd.)

MOLTEN PENTA (220°C.) 258 HRS.CORROSION INHIBITOR SCREENING TESTS (A 285 STEEL)SERIES NO. 1 (OR 211704)

INHIBITOR (0.3% Wt.)	MPY	COMMENTS
Control - No Additive	2	Moderate ccc under deposit, light pits and craters.
Edwin Cooper's RT 53-A	2	Light ccc under deposit, light pits and craters.
Stripped RT 53-A (211587)	3	Moderate ccc under deposit, moderate pits and craters.
Triphenyl Phosphate Residue	1	Same as above.
Tricresyl Phosphate Residue	4	Light ccc under deposit, moderate pitting and cratering.
Cresylic Acid Residue	3	Moderate ccc under deposit, heavy pits and craters.
S-140 Residue (W.G.K.)	3	Light ccc under deposit, light pitting and cratering.
N ₂ CP Residue (Queeny)	4	Light to moderate ccc under deposit, light to moderate pits and craters.
Triphenyl Phosphite	2	Light ccc under deposit, light cratering and pitting.

The coupons were examined by WGM M&MT. We were surprised at the low corrosion rates in all samples, especially the control sample. We had expected the rates to be comparable to those experienced in the distillation studies (50 mpy & higher). ²⁵ Fresh molten Penta from the plant was used in these tests. In the earlier tests, ²⁵ Prill Penta had been remelted. We therefore surmised the difference in corrosion rates might be due to different moisture levels in the Penta. Remelted prills would be watter.

In the next two sets of inhibitor screening tests, we used remelted Penta (Lot KM-509).

MOLTEN PENTA - CORROSION INHIBITIONSCREENING TESTS ON A-285 STEEL, 220°C., 2 WKS.SERIES NO. 2 (OR 211711)

INHIBITOR	(0.30%) —	SUPPLIER	MPY	SUBLIMATE COLOR @ 3 DAYS	DISCUSSION OF INSPECTION
Control - Remelted KM-509			2	Yellow	Medium all over cratering, light pitting.
RT 53-A	-----	Edwin Cooper	2	White	Moderate to heavy all over cratering, light pitting.
Polyrod-0515	-----	Hercules	3	White	Medium all over cratering, light pitting.
Polyrod-1100	-----	Hercules	2	White	Light to moderate all over cratering, light pitting.
Polyrod-1110	-----	Hercules	2	White	Moderate all over craterin light pitting.
Unamine O	-----	Lonza	3	White	Moderate to heavy craterin light pitting.
Unamine OZ	-----	Lonza	3	White	Heavy all over cratering, light pitting.
1275-1 Nirus AOL.	-----	Morton	3	White	Light to medium all over cratering, light pitting.
NPA	-----	CAB Geigy	2	White	Heavy all over cratering, light pitting.
Sarkosyl	-----	CAB Geigy	3	White	Medium to light all over cratering, light pitting.
Amine O	-----	CAB Geigy	3	White	Medium all over cratering with some areas of heavy cratering. General light pitting, Several areas of medium depth pits.
RE-410	-----	GAF	2	White	Light to moderate all over cratering, light pitting.

MOLTEN PENTA - CORROSION INHIBITORSCREENING TESTS ON - A 285 STEEL 200°C. - 2 WKS.SERIES NO. 3 (OR 211721)

INHIBITOR (0.30%)	SUPPLIER	MPY	SUBLIMATE COLOR @ 3 DAYS	COMMENTS *
Control - Remelted KM-509		2	Yellow	Medium to moderate all over cratering and light pitting.
SB-10-----Air Products Chem.		2	White	Same as above.
Virco Pet 20-----Mobil		5	White	" " "
Tyfo Amine-D -----Hawthorn		5	White	" " "
Nopco Chex. RA-----Diamond Shamrock		5	White	" " "
Corexit 7802 -----Exxon		3	White	" " "
Armohib 28 -----Arnak		4	White	" " "
Wrico-514 -----Wright Chem.		3	White	" " "
WayFos-MM40-----Wayland		3	White	" " "
WayFos-M60-----Wayland		3	White	" " "
WayFos-A-----Wayland		2	White	" " "
RM-510-----GAF		2	White	" " "
PE-510-----GAF		2	White	" " "

* CURSORY EXAMINATION BY M&MT.

E. 4. d. (Cont'd.)

Again, all corrosion rates observed (Series 2 & 3), were lower than anticipated. There was actually no meaningful differences in corrosion rates observed in any of the tests. All inhibited samples and control samples in the three sets of tests had near-equivalent corrosion characteristics on A-285 mild steel. There was also no difference in corrosion rates between fresh molten Penta and remelted Penta. None of the corrosion rates observed were even severe enough to be considered unacceptable - thus mild steel could not be ruled out as a material of construction for the distillation process.

Nearly every inhibitor tested gave evidence of "dioxin" stabilization as indicated by the white sublimate generated in each test. The sublimate was yellow in all control samples. Actual stabilization effectiveness on all inhibitors is unknown however, since dioxin analyses were not run.

A number of the inhibitors could probably be used in place of RT 53-A in the distillation process. The thermal stability and tarring/charring characteristics of the inhibitors should be tested first however.

In the course of our chlorination studies,³³ the following compounds were also tested for effectiveness as molten Penta stabilizers. All tests were carried out at 200°C. for 7 hrs.

(METHOD 70-20)				
<u>No.</u>	<u>Test</u>	<u>Hepta CDD</u>	<u>OCDD</u>	<u>Chem. Assay</u>
1	Control - not cooked	0.029%	0.28%	97.1%
2	Control - Cooked	0.052%	0.64%	94.9%
3	NO ₂ - (Sparge)	0.068%	0.69%	-----
4	H ₂ S - (Sparge)	0.035%	0.32%	96.8%
5	o-Chloronitrobenzene(1.0%)	0.064%	0.70%	-----
6	p-Chloronitrobenzene(1.0%)	0.048%	0.54%	-----
7	Nitrobenzene (1.0%)	0.052%	0.60%	-----

H₂S appeared to be very effective. This compound should be considered for use as a stabilizer in Penta distillation since it would also have the advantage of stabilizing the distillate as well as feed, reboiler, and column material. There was no detectable H₂S odor in the solidified sample. Of the other compounds tested, only p-Chloronitrobenzene showed some stabilization effectiveness.

E. 4. e. Distilled Penta - Stability in Woodtreating Solutions

One question raised about pure Penta was whether or not dioxins would build up again in Woodtreating solutions. If dioxins were formed under the treating conditions, it would hardly make sense to remove dioxins in the first place. To answer this question, 5% Penta solutions in two different woodtreating oils were prepared - then cooked to simulate treating conditions. Additive and non-additive current commercial Penta solutions were also prepared in one of the oils and similarly cooked. All samples were cooked while in contact with a rusty steel coupon. Cook temperature was 190°F (somewhat higher than maximum anticipated in woodtreating processes). (OR 211583).

<u>IDENTIFICATION</u>	<u>OCDD (Method 70-20)</u>		
	<u>0 Hrs.</u>	<u>120 Hrs.</u>	<u>336 Hrs.</u>
Pure Penta in Shell-Med.Arom.	<25 ppm	<25 ppm	<25 ppm
Pure Penta in Mobil-Certrex	<25 ppm	<25 ppm	<25 ppm
Additive Penta in Shell Med. Arom.	0.46%	0.42%	0.45%
Non-additive " " " " "	0.56%	0.56%	0.53%
Additive Penta-as is-not cooked	0.53%		
Pure Penta-as is-not cooked	1.2 ppm		

Applied Science spectroscopy Method No. 70-20 (Ref. No. 29), with the modification of no benzene during caustic extraction, was used to analyze the Penta/oil solutions. Due to interfering oil components, the MDL for OCDD was 25 ppm. Lower chlorinated dioxins were not resolved well enough to allow quantitation. OCDD did not build up in any of the solutions during the two week cook period. The tests indicate Pure Penta is not likely to increase in dioxin content in woodtreating processes.

5. Recrystallization Studies

Late in 1972, there were indications that distillation of crude Penta might not remove TCDD completely. Secondly, there was also fear TCDD might build up again during storage of molten distillate. Thirdly, however, we had just learned that by improved recrystallization techniques, we could prepare pure Penta with less than 100 ppm total dioxins with just one recrystallization. Past work had indicated two or more recrystallizations would be required to get below the 100 ppm level.²² The need for only one recrystallization made the economics of refining by this approach much more attractive. Additional recrystallization studies were then carried out and are presented in Reference No. 33 (See Appendix D).

The key to efficient dioxin removal in recrystallization of Penta is adequate removal of the mother liquor from the crystals. This is accomplished by repeated washing with fresh solvent.

E. 5. (Cont'd.)

This revelation led to expanded and extensive recrystallization studies by MICC R&D. These studies are presented in detail in the following two MICC, R&D Progress Reports by J. E. White: Report No. 4, Job No. 0930305, 1-8-73 and Report No. 5, Job No. 1430305, 3-20-73 (References 39 & 40).

In summary, a number of recrystallization solvents were evaluated. Penta yield losses, due to unprecipitated Penta from the solvent were high in all cases. Thus, "economically", refining by recrystallization didn't match refining by distillation, and work on the recrystallization approach was terminated in the Spring of 1973.

6. Wood Treating Penta/Oil Solutions - Dioxin Survey

Our first survey of dioxins in Penta/oil solutions is presented in Reference No. 22. At that time (1971) we concluded that build up of dioxins in wood treating solutions was meager to negligible. In addition, a survey of the wood treating industry failed to reveal any past or current problems of toxicity to workers or users attributable to dioxins. (There were some hearsay instances of chloracne however when materials were handled in a non-hygienic manner.) Aside from our finding in 1971, another survey of dioxins in treating solutions was made in 1973. Treating solution samples were obtained from two treatment plants designated as follows:

<u>Sample No.</u>	<u>Identification</u>	<u>Source</u>
1	Fresh solution in Mobil Certrex 50-C	Wyckoff*
2	Solution from Boulton measuring tank - over 200 hours treating/heating - Shell oil	Wyckoff
3	Sludge from cylinder (Retort)	Wyckoff
4	New Mix	Baxter**
5	#7 Storage	Baxter
6	#7 Storage - sampled during low level	Baxter

* Wyckoff Co., Seattle, Washington

** J. H. Baxter Co., Eugene, Oregon

Penta contents of the solutions were first determined by simple hydroxyl titration (OR 211567). Applied Science, spectroscopy Method No. 70-20 with the following modifications was used to determine hepta CDD and OCDD levels; 1) Oil sample weight varied such that each contained 1.0 gram of Penta and, 2) Benzene omitted during caustic extraction steps. Control Penta solutions in Certrex 50-C and in Provalent 4A oil were also

E. 6. (Cont'd.)

prepared and analyzed to test method validity.

<u>SAMPLE IDENTIFICATION</u>	(ASSAY) Wt. %	ppm Dioxins (Penta Basis)	
	<u>PENTA</u>	<u>hepta CDD</u>	<u>OCDD</u>
Wyckoff #1	5.49	400.	6500.
Wyckoff #2	6.34	300.	2600.
Wyckoff #3 (Sludge Free)	6.33	300.	3300.
Wyckoff #3 (Homogenous)	5.65	300.	4300.
Baxter #4	11.00	320.	2900.
Baxter #5	6.06	330.	2800.
Baxter #6	6.07	400.	3000.
#7, Penta in P4A Oil	5.06	(Used for assay control)	
#8, Penta in Certrex 50-C	10.16	500.	1800.
#9, Penta, used in 7 & 8.	---	400.	1800.

Except for sample 1, all dioxin values are comparable to typical levels found in prill Penta. Replicate analyses of sample no. 1 varied as much as 3400 ppm (OCDD). Two modified methods were tried in efforts to improve precision and reproducibility. One involved benzene dilution and filtration of the oil sample prior to caustic clean-up. The other involved azeotropic removal of the oil from saponified sample. Neither approach was any better than the initial method. In spite of method problems, the tests indicate there is probably no gross build-up of dioxins in treating processes.

The reason for the inconsistent results in the tests is now thought to have been due to exposure of the samples to caustic. Caustic causes cyclization of dioxin precursors to dioxins (See Section B,2, for explanation).

7. Penta Esters - Dioxin Analyses

Early in 1973, Catomance of England (Monsanto customer) requested dioxin analyses on a series of Penta esters prepared by them from recrystallized Penta. The samples were analysed by the following procedure. (OR 210571-4).

- (1) 1.0 grams ester is dissolved in 10 ml nanograde benzene and 5 ml of morpholine (Fisher Cat. No. M-263) in a 4 oz. capped bottle.
- (2) Mix for 30 minutes with magnetic stir bar.
- (3) Transfer to 250 ml separatory funnel.
- (4) Complete the analyses as described in Applied Science, Spectroscopy Method No. 70 - 20 (Reference No. 29 & 30). The morpholine is removed in the normal washing procedure.

E. 7. (Cont'd.)

The tests are summarized in the following table. A number of control samples using our standard technical Penta (Lot KM-261) are included to illustrate the effect of morpholine on dioxin values. A 1.0 gram sample was used in all tests.

<u>SAMPLE IDENTIFICATION</u>	<u>hepta CDD</u>	<u>OCDD</u>
1) KM-261-Normal work-up (Method 70-20)	0.030%	0.383%
2) KM-261-Normal work-up (Method 70-20)	0.031%	0.380%
3) KM-261-25 ml Morp.-not cooked-Immediate normal work-up.	0.026%	0.305%
4) KM-261-25 ml Morp.-1 hr. Boil-Normal work-up.	0.057%	0.885%
5) KM-261-5 ml Morp.-24 hr. @ 25°C. Normal work-up.	0.021%	0.275%
6) KM-261-5 ml Morp., 10 ml benzene, 30 min. Stir @25°C., Normal work-up.	0.029%	0.2450%
8) Catomance Recrystallized Penta	4.3 ppm	18.2 ppm
9) Tech. Pentachlorophenyl Laurate (Catomance)	679. ppm	6869. ppm
10) Tech. Pentachlorophenyl Laurate (Ventron)	159. ppm	7160. ppm
11) Pentachlorophenyl Laurate (Catomance)	0.7 ppm	16.6 ppm
12) Pentachlorophenyl Acetate (Cantomance)	0.2 ppm	2.3 ppm

This was our first indication that time/temp. exposure of technical Penta to morpholine would cause dioxins to increase. For this reason, analysis of the esters was carried out under conditions which would minimize this exposure. We did not recognize at the time that aqueous caustic would also cause dioxins to increase. We surmised that dioxin precursors were implicated, but did not investigate further. No comment is made about dioxin values obtained on the ester sample since nothing was known about preparation conditions etc. We now know however that dioxin values on all samples which originally contained dioxin precursors are probably inflated (See Section B, 2 for explanation).

8. Dioxin Analysesa. W.G.K. Penta

Dioxin analyses were run on every 10th lot of W.G.K. Penta produced during 1973. These, along with values on every 10th lot from other years are presented in Appendix E. 1. Method No. 70-20 was used. ^{29, 30} (See comment regarding validity of values Section B, 2.)

b. Prill Fumes (Venturi Penta)

Exit air from Penta prilling contains Penta fumes. This "sublimed" Penta is collected by passing the exit air

E. 8. b. (Cont'd.)

through a Venturi scrubber containing caustic solution - thus the name Venturi Penta. Penta collected in the solution was analyzed for dioxins. (Penta released from solution by acidification with H_2SO_4 , then filtered, washed, & air dried.) Chlorophenol analyses were also run on the released/dried Penta. Some lower chlorophenols were probably lost due to solubility in water. (OR 211760) (Dioxins by Method 70-20)

Phenol	0.40%
p-Chlorophenol	0.30%
tri-Chlorophenol	0.10%
tetra-chlorophenol	15.96%
Penta Chlorophenol	83.25%
High Boilers	40.10%
Hepta CDD	24 ppm
OCDD	55 ppm

Phenol comes about through degradation of our tri-phenyl phosphite additive. p-Chlorophenol is also an additive. As expected, dioxin values are very low since the Penta is essentially sublimed material.

Bioassay tests for CEF on a 48% Penta/oil solution prepared from the Venturi liquor in Pilot batching (Reference No. 41) came out negative at highest dietary level tested (1500 ppm). Chloracne response on this solution was not determined. These tests are discussed in more detail later in this report (See Section F. 5.).

c. Aqueous Santobrite - Alkali Insolubles

Alkali insolubles were collected by filtration from aqueous Santobrite solution sampled at the dissolver in Dept. 236. The dried insolubles were analyzed for dioxins by Method No. 70-20 procedure.

Hepta CDD	3.9%
OCDD	10.2%

These results paralleled earlier values on this material.²² The Santobrite solution represented a mixture of Penta from prill fumes and scrap Penta.

d. Competitive & Refined Penta (211706 & 211520)

Penta produced by domestic competitors was collected and analyzed for dioxins. Applied Science Method No. 70-20 was used for analyses.^{29, 30} Our standard lot KM-261 is included in the analyses summary table below for comparison purposes.

E. 8. d. (Cont'd.)

	<u>SAMPLE IDENTIFICATION</u>		<u>Hepta CDD</u>	<u>OCDD</u>
1)	Monsanto	KM-261	0.030%	0.38%
2)	Reichhold	Lot 312173	0.063%	0.24%
3)	Reichhold	Lot 6-6-73	0.065%	0.22%
4)	Reichhold	Lot 342273	Typical	0.30%
5)	Reichhold	Lot 352473	0.052%	0.21%
6)	Vulcan	QC 086	0.090%	0.44%
7)	Dow	0825223711D	0.065%	0.37%
8)	Dow	0819223120A	0.079%	0.31%
9)	Dow	EC-7 (Lab Sample)	0.9 ppm	34 ppm
10)	Monsanto Distilled, OR 194436		1.7 ppm	4.6 ppm

There is no gross difference in dioxin content between any of the technical grade samples. The Reichhold Penta dioxin GC chromatograms are a little different from the other samples. Peaks normally eluting just prior to hepta CDD and just prior to OCDD are absent or extremely small. (See Section B, 2 concerning accuracy of dioxin values.)

During 1973, we received our first sample of Dow's experimentally refined Penta. The sample was analyzed for dioxin content by our routine method and is compared to Monsanto's experimentally refined Penta in the preceding table of analyses. The sample had the physical form of prills and was somewhat "off" white in color. Examination of crushed prills under the microscope indicated an amorphous crystal. This type of crystal is formed when molten Penta is rapidly cooled. This indicated the material had been prilled from the molten state, rather than through compaction of crystals - say from recrystallization. This served as a clue to their mode of refining and distillation seemed most likely.

Monsanto refined material is somewhat lower in dioxins and is also white instead of "off" white.

9. Improved GC Method - Dioxin Analyses

During 1973, Applied Science developed an improved method of analyses for TCDD in Penta (Reference No. 42). The improvement was in the manner of sample clean-up. Instead of caustic extraction for phenolics removal, a benzene solution of the sample is chromatographed over alumina. Although the method was developed primarily for TCDD analyses, it was suggested it might also be

E. 9. (Cont'd.)

used for quantitation of higher chlorodioxins in Penta. Initial evaluation of the method for OCDD analyses indicated low recoveries. In a later evaluation (256755) the recovery problem is improved by better Al_2O_3 chromatographing conditions. We have just recently (1975) gone to routine use of this method for hepta CDD and OCDD analyses in Penta since it avoids the precursor cyclization problem (See Section B. 2 for explanation).

F. DIOXIN STUDIES - CHLOROPHENOLS - 1974/19751. Introduction

Work described in the following immediate section of this report was carried out intermittently during 1974 & 1975. Subject matter, for the most part, is presented in chronological order. Areas covered include Plant tests, Lab chlorination studies, Biotest data, Dioxin analyses on various Chlorophenols, Dioxin precursor study, hexachlorobenzene analyses, and dioxin mechanism of formation. The work was carried out at W.G.K. Plant Process Research. Some supportive analytical work was also done by Applied Science Group of G.O.

2. Plant Demo - Dual "Circulation - Pump" Test

In early 1974, the plant conducted a test in which two circulation pumps were used to circulate chlorination mass through the external heat exchanger during chlorination. Circulation is usually done with only one pump. Our hope was to increase cooling efficiency through increased circulation rate. Thus, X-Pt/batch temperature spread might be reduced which would result in a lower dioxin/HB product because of reduced "heat history". Mass transfer would also be increased which might further suppress dioxin/HB formation. Data from the tests are presented in the following table. Normal circulation rate (1 pump) is approximately 430 gpm through the exchanger. Dual pumps gave about 530 gpm as determined by pump amperage change. (OR 212175)

No.	Cl ₂ Assay	Type Phenol	Cir. 130°C. Pumps	Final Spread	r.r. Hours	** r.r. Heat		Chem. Assay	X Tetra	X Penta	X HB	X MOI	X MOT
						History							
2	96Z	VP	1	2.8°C.	6.6°C.	1.75	12.4	97.5	5.9	86.4	7.7	4.0	65.0
3	94	VP	1	2.6	6.6	1.92	15.7	98.2	6.0	87.0	7.0	4.0	55.0
8	96	F	1	3.0*	6.4	2.33	12.0	97.5	5.2	87.5	7.3	4.0	68.0
0	94	VP	1	3.0*	6.4	2.00	15.9	97.7	5.4	87.0	7.6	2.0	53.0
1	94	F	1	3.0*	6.9	1.67	13.2	97.5	5.3	87.4	7.3	2.0	62.0
4	92	VP	2	3.8	6.4	2.33	16.4	96.8	4.9	85.8	9.3	6.0	39.0
5	94	F	2	2.8	6.4	2.00	17.4	97.9	4.7	87.6	7.7	4.0	37.0
6	94	F	2	2.8	5.6	2.25	19.4	96.8	4.6	86.0	9.4	4.0	55.0
7	94	F	2	2.6	6.2	1.75	14.4	97.8	5.8	86.9	7.3	2.0	63.0

* Estimated VP = Virgin Phenol F = Fractions Phenol r.r. = Rate of Rise
 ** (mm)² area between X-Pt. & batch temp. - from 130°C. batch temp. to end of batch (from strip chart).

F. 2. (Cont'd.)

High boiler (HB) contents vary widely from batch to batch. There was no apparent HB reduction when using two pumps. There was also no discernable effect on other quality features. On the basis of these findings, and the cost and time involved, dioxin analyses on the samples were not run. (Chlorine feed rates may have also varied from batch to batch, which would, in turn, affect rate of heat generation and thus the "spread".) GLC was by internal marker method (OR 211759). This is the same method as Reference No. 28, but with diphenylether internal marker added.

3. Dioxin Analysisa. W.G.K. Penta

Dioxin analysis was run on every 10th lot of W.G.K. Penta produced in 1974, and on a portion of the lots produced in 1975. These, along with dioxin analyses from previous years, are presented in Appendix E. 1. Again, Method No. 70-20^{29,30} was used for analyses. For this reason, values are inflated (See Section B. 2. for explanation).

b. Monsanto Newport Penta (OR 256718)

A survey of dioxins in Monsanto Newport Penta was made in February 1975. Sample identification and analyses are presented in the following table.

<u>BATCH</u>	<u>< hepta CDD</u>	<u>hepta CDD</u>	<u>Pre-OCDD*</u>	<u>OCDD</u>
332-End of Chlorination	818 ppm	1251 ppm	397 ppm	4612 ppm
" 1/2 Flaked	775	1225	459	4980
" Final Flakes	749	1403	389	5542
441-End of Chlorination	897	1448	253	4974
" 1/2 Flaked	852	1325	219	5128
" Final Flakes	920	1322	267	5253
447-End of Chlorination	738	1248	351	5329
" 1/2 Flaked	988	1672	389	5737
" Final Flakes	632	1690	393	7151

* This compound is probably Octochlorodibenzofuran.⁴³

Method of analysis was 70-20.^{29, 30} The OCDD response factor was used for lower chlorodioxin quantitation. (Relative response factors are near unity - OR 211536). The <hepta CDD values represent all eluting non-phenolics prior to hepta CDD elution.

OCDD values on the average are about 2000 ppm higher than typical W.G.K. Penta. OCDD also increases slightly during