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TITLE: U.V. Degradation of Pentachlorophenol

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ABSTRACT:

Distilled and Technical grade Penta was exposed to both natural and artificial daylight. Dioxins, Furans and hexachlorobenzene were formed as degradation products.

AUTHORS: J. A. Hinkebein

TITLE: U.V. Degradation of Pentachlorophenol

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I. INTRODUCTION

Koppers Co. reported some work on UV (Ultra-violet) degradation of Penta. They found that the higher chlorodioxins such as octachlorodibenzo-p-dioxin (OCDD) were formed in significant amounts. These dioxins also degraded but at a slower rate. This implies that the use of distilled Penta instead of technical Penta will not guarantee preventing the introduction of dioxins into the environment. It was felt that these findings should be confirmed. This report covers our work on U V degradation of Monsanto technical Penta and Dow's EC-7 distilled Penta.

II. SUMMARY and CONCLUSIONS

1. Penta degrades in U V light with a increase in dioxins and furans. The amount of dioxins in distilled Penta were as high as those in technical Penta for some samples.
2. U V degradation also forms significant levels of hexachlorobenzene (HCB).
3. In long term tests, the distilled Penta appeared to degrade faster than technical Penta. This resulted in the dioxins/furans and HCB levees rising to a maximum which then decreased. The dioxins/furans remained approximately constant in the technical Penta.
4. Penta degraded much faster in the presence of oil. The oil did not appear to increase the dioxin degradation rate.
5. Our results were generally in agreement with those reported by Koppers.

III. RECOMMENDATIONS

No additional work is planned on this project because we are going out of the Penta business in the U.S.

IV. REFERENCES

1. Notebook pages 306996, 307000, 1220604, 5, 6, 9, 22.
2. Koppers Progress Report No. II, Fate of Chlorodibenzodioxins in Outdoor Exposure of Penta-Treated Wood, M. A. Phillips and S.J. Ondrey, Oct., 1976.

V. ACKNOWLEDGEMENTS

The analyses were performed by P. R. Michael of J.P. Mieure's group in MIC Applied Sciences. The U.V. exposure work was performed by: J. K. Sears and G. G. Mahnken of N.W. Touchette's group in MIC Plastics R&D.

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SUBJECT TO PROTECTIVE ORDER.VI. DETAILS

1. Experimental

Solutions containing 15 mg of Penta per ml were made up in benzene. Solutions were prepared with Monsanto technical Penta, Dow EC-7 distilled Penta and, for one series of tests, Baker purified Penta. These solutions were applied to 1-3/4 x 5 inch strips of Whatmans No. 42 filter paper in 1/2 ml aliquots. This gives a loading of 7.5 mg per strip. This loading was used by Koppers to simulate Penta treated wood. One group of samples were also impregnated with 142.5 mg of oil (Lion #1 solvent) to determine the effect of the oil base of penta solutions. After the strips were dried, they were mounted between two pyrex plates. The edges of the pyrex plates were then wrapped with teflon tape to hold the plates together and to retard evaporation of the penta. The samples which were exposed to artificial light were mounted in holders and placed in the Fade-ometer. The instrument was an Atlas Electric Devices Model FBA-R Fade-ometer. The light source is a carbon arc with filters to simulate daylight. The control samples were stored in the dark during the period that the other samples were exposed. The samples exposed to natural sunlight were placed on the building roof. After exposure the samples were extracted with benzene and analyzed by GLC with an electron capture detector.

2. Results

In the first series of tests the effects of natural sunlight versus the fade-ometer and oil versus no oil were compared. The data are shown in Table 1. The analysis of the unexposed samples are in agreement with what would be expected for the various penta samples. The dioxins/furans are quite low in both EC-7 and Baker Penta. The HCB is high in the EC-7 sample which is typical for this material. The dioxin/furan and HCB level of the Monsanto technical penta is also typical. The low penta recoveries were apparently due to loss by evaporation since a fresh strip gave 100% recovery.

The samples exposed to sunlight showed a large increase in both dioxins/furans and HCB. The Monsanto technical Penta was somewhat different from the other samples in that the OCDF decreased and the HCB showed a much larger increase. The penta recovery was also much lower. For all three samples, the dioxins and HCB formation appeared to be much more favored than the furan formation.

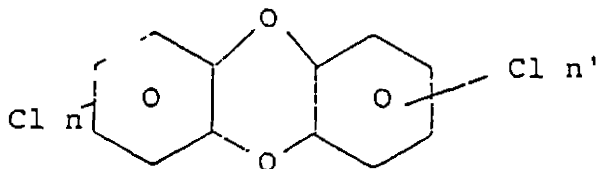
The samples which were exposed in the fade-ometer were run in duplicate. In general there was good agreement between the duplicate samples. The fade-ometer results were also in good general agreement with the sunlight samples.

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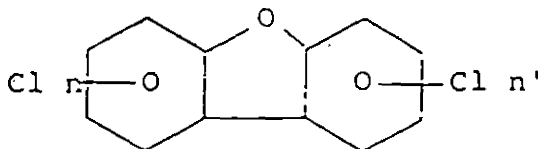
The samples treated with oil before exposure showed almost complete penta loss but little change in the dioxin/furan/HCB levels. The only significant difference between these samples and the unexposed samples was the moderate increase in OCDD for the EC-7. In another series, the penta impregnated strips were exposed for three days, treated with oil, and then exposed another three days. The results from these samples are similar to the previous oil treated samples. This data implies that the dioxins/furans/HCB levels are not effected by the oil. Koppers was of the opinion that the oil accelerated the degradation of these materials.

Table 2 gives the results of a longer term test. The fade-ometer was used as the U.V. source in these tests. The dioxins analyses were completed on only the unexposed, 12 day, and 24 day samples because the project was deemphasized when we decided to get out of the penta business. A total of 46 days had elapsed between the time that the samples were prepared and the time that they were extracted for analysis. This was primarily due to the fade-ometer being shut down over week ends. The penta recoveries show a uniform decrease with exposure. In comparing Monsanto technical penta with EC-7, it appears that Monsanto technical penta is more volatile than EC-7 but EC-7 degrades faster. The dioxin/furan levels in the unexposed samples appeared normal. The HCB levels were low indicating a loss by evaporation. The exposed Monsanto technical samples did not show much of a change in the dioxin/furan level. This may be due to these materials degrading at about the same rate as they were formed. The 12 day EC-7 sample shows high levels of dioxins/furans/HCB and shows that under certain conditions distilled penta can produce as much or more dioxins/furans/HCB as technical penta. The 24 day EC-7 is showing a decrease in the dioxin/furan/HCB levels indicating that they are degrading faster than they are being formed since there is very little penta left to degrade.

The general structures of the dioxins and furans are given below:



(n+n')-Chlorodibenzo-p-dioxin



(n+n')-chlorodibenzofuran

N and n' can have any value from 0 to 4.

TABLE 1
U V DEGRADATION OF PENTA - 3 DAY

		Exposure		
	Unexposed	Sunlight 3 days	3 days	3 days
Low EC-7				
Penta recovery (%)	70	71	45	41
OCDD (ppm)	0.9	785	522	585
OCDF (ppm)	0.4	11	35	28
hepta CDD+CDF (ppm)	<0.1*	406	199	270
hexa CDD+CDF (ppm)	<0.1	126	32	37
HCB (ppm)	101	886	1374	1136
Monsanto Technical				
Penta recovery (%)	62	16	25	22
OCDD (ppm)	1105	1479	2335	1673
OCDF (ppm)	112	82	329	125
hepta CDD+CDF (ppm)	475	2192	1158	606
hexa CDD+CDF (ppm)	18	986	227	36
HCB (ppm)	26	6628	5473	3268
Baker Purified				
Penta recovery (%)	71	66	41	37
OCDD (ppm)	12	1108	561	390
OCDF (ppm)	<0.1	1.6	44	12
hepta CDD+CDF (ppm)	1.7	481	200	112
hexa CDD+CDF (ppm)	<0.1	134	25	917
HCB (ppm)	6.8	1207	1244	1015

CDD or CDF = chlorodibenzodioxin or furan

HCB = hexachlorobenzene

* detection limit - corresponds to 1×10^{-9} gram.

EXPOSURE

Fade-ometer

3 days with oil 3 days w/o oil + 3 days w/oil

0.74	0.71
57	568
<0.1	41
2.7	270
<0.1	42
95	1277

0.58	0.59
1114	2412
98	383
514	1207
45	237
38	6109

0.79	0.79
8.7	1192
<0.1	95
4.4	413
<0.1	53
8.0	2082

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TABLE 2
U V DEGRADATION OF PENTA - 24 DAY EXPOSURE

Days Exposed *			Penta recovery (%)	HCB (ppm)	OCDD (ppm)	OCDF (ppm)	hepta CDD+CDF	hexa CDD+CDF
Monsanto tech		0	24	7.1	1200	200	507	26.7
"	"	3	20.80					
"	"	6	17.07					
"	"	9	8.17					
"	"	12	4.8	733	867	111	387	58.7
"	"	15	5.61					
"	"	18	3.35					
"	"	21	2.91					
"	"	24	1.87	2187	1053	127	467	71.7
Dow	EC-7	0	41.30	34.7	0.4	2.1	2.3	0.4
"	"	3	39.07					
"	"	6	25.73					
"	"	9	10.21					
"	"	12	2.53	2653	2293	520	1333	160
"	"	15	1.22					
"	"	18	0.43					
"	"	21	0.38					
"	"	24	0.19	360	946.7	74.7	426.7	73.3

* U V exposure time. 46 days elapsed between preparing the samples and extracting with benzene for analysis.

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