

Monsanto

FROM (NAME & LOCATION) W. B. Bennet/D. P. Roman - N1A

DATE	February 18, 1976	cc	P. G. Hamner - B3SC
			E. E. Hendrikse - B2NA
SUBJECT	PENTACHLOROPHENOL		J. S. Metcalf - B2NC
	ENVIRONMENTAL STATUS		J. P. Mieure - T2F
REFERENCE			P. A. Tierney - N1A
			S. H. Vogel - 1740
TO	L. G. Scharpf, Jr. - N1A		P. L. Wright - A2SC

1. Background

Pentachlorophenol enjoys widespread use as a wood preservative. Commercial grades have been found to contain up to 2500 ppm chlorinated dibenzo-p-dioxins. The predominant dioxin is octachlorodibenzo-p-dioxin, one of the least toxic members. Evaluating pentachlorophenol toxicity in animals revealed that some untoward effects (chloracne, chick edema disease, and histopathologic alterations) were caused by chlorinated dibenzo-p-dioxin content. Purified pentachlorophenol did not produce these effects.

The basic molecular structure of dibenzodioxin is given in Figure 1, along with a concise summary of the toxicology of the family of chlorinated dibenzodioxins. The most toxic member of the family, 2,3,7,8-tetrachlorodibenzodioxin (TCDD), was discovered as an impurity in the herbicide 2,4,5-T and its presence in the environment has focussed attention on the entire spectrum of dioxins.

The probable mode of formation of OCDD (octachloro-dioxin) under penta manufacturing conditions is shown in Figure 2. Less highly chlorinated dioxins could be formed from lower chlorinated phenols. Other impurities known or assumed to be present in commercial penta are shown in Figure 3.

2. Environmental Considerations

TCDD (and probably other dioxins) was found to be immobile in soils, not readily taken up by plants, subject to photodecomposition, persistent and only slowly degraded in soils. Despite these properties efforts to find TCDD in soils heavily treated with herbicides found far less TCDD than expected. Most analyses to establish its presence in wildlife have been negative. A widely publicized finding of less than one ppb in Vietnamese fish is suspect.

Pentachlorophenol was first implicated in 1957 when millions of broilers died with symptoms of excessive pericardial fluid ("chick edema disease").

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Certain feed fats were implicated and traced to by-product tallow (fleshing greases) recovered from hides treated with tri- and penta-chlorophenol preservatives.

Concern has been expressed that OCDD (major dioxin in penta) might be readily reduced to the more toxic hexachlorodibenzodioxin in the environment but this has not been demonstrated. Meager reports on migration of dioxins into soil from penta-treated wood posts give negative findings.

3. Human Safety

HCDD (hexachloro-dioxin), which is present in commercial penta, has been shown in animal tests to cause chloracne. Reports of incidence of chloracne in humans engaged in manufacture and use of penta in wood treatment are conflicting. The EPA is conducting a survey of wood-treating operations. Monsanto is in the process of examining its own medical records and industrial hygiene practices in the manufacturing department.

4. Analysis of Monsanto Penta

Analytical techniques for the minor constituents of penta have changed continually since 1970. The present best technique consists of isolating non-phenolic components by alumina column chromatography and analysis by electron-capture GC with confirmation by mass spectroscopy. Limited data on our production penta indicates no TCDD and no penta-dioxins detectable in our product. Hexa-, hepta- and octa-dioxins are about 15, 200 and 500 ppm. Interferences in mass spectrometry procedure have to date not permitted an estimation of the level of chlorinated dibenzofurans. No information on "pre-dioxins" (or their possible toxic properties) is available except they are known to be present.

5. Dioxin Removal

Dioxins can be removed from penta (to appreciably less than 30 ppm total) by recrystallization or by distillation. Cost of a distillation installation would be high (est. \$8M) and added production cost would be 20-25c per pound.

6. Biological Tests

Penta has an LD₅₀ of 270 mg/kg in rats. At levels below the lethal dose penta gives positive response in chick edema testing and positive acne response in the rabbit ear test. A number of experimentally produced penta samples (lab and plant) have shown lower response, but only distilled penta showed no response. There is, however, a distinct discrepancy in the chick edema tests in that the response found for commercial penta was greater than could be accounted for by the dioxins present.

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7. Political Climate

Environmental groups are pressing loudly for banning 2,4,5-T and other dioxin-containing herbicides (e.g. a full-page article replete with cartoon in the Washington Post, 1-25-76, partly funded by the Fund for Investigative Journalism). Hence, the EPA is under political pressure despite the negative findings outlined above. Penta is tarred by the same brush since it contains dioxins, though the highly toxic TCDD is generally recognized to be absent. EPA is concerned about penta-dioxin, but we have not found it in penta by our best techniques. EPA has requested its Science Advisory Board to review the health hazards charged to penta, the economic impact of cancelling penta on a use basis, and health implications of use of alternative wood preservatives.

Dow Chemical has commercialized a distilled pentachlorophenol with 30 ppm (max.) total dioxins and has urged EPA to restrict production to this type of material. Other producers feel that the type of dioxins in penta pose no problem if use is restricted to wood treating for outdoor use.

8. Research Plans

Research will concentrate on the areas of industrial hygiene and the analysis and biological testing of minor constituents as follows:

- a. The nature and extent of health problems, if any, in the chloro-phenol, penta and Santophen® 1 units will be found and preventive measures recommended if needed;
- b. Penta will be separated into phenolic and non-phenolic components for individual bio-testing in an attempt to clarify anomalies in our present analytical/toxicological correlations;
- c. The technique of liquid chromatographic separations will be used to better identify minor components (particularly "pre-dioxins" and chlorinated dibenzofurans) and, to the extent possible, provide samples for toxicological testing;
- d. Dioxins analyses will be obtained for all products from the chloro-phenols complex where data now is admittedly sketchy;
- e. Some effort will be expended on investigation of migration of dioxins from treated wood into the surrounding soil;
- f. Monsanto will participate in government committees on dioxins research and possible round-robin analytical testing.

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February 18, 1976

Page 4

The economics of Santophen 1 manufacture depend to a marked extent on manufacture of penta from by-products of the Santophen process. Research is under way on a process to lessen this by-product formation appreciably.

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