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PROGRESS REPORT
ORGANIC CHEMICALS DIVISION
TECHNOLOGY DEPARTMENT

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TITLE
pentachlorophenol/Santobrite Dioxin Studies (continued from W.G.K. TSD Report No. 4242-2, 8-15-70, S.H. Vogel)

- OBJECTIVE
- Measure dioxin concentrations and formation rates in process, product, and end-use pentachlorophenol/santobrite streams.
 - Evaluate effectiveness of various routes of pentachlorophenol dioxin removal and suppression.

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Santobrite and pentachlorophenol (penta) each slowly increase in dioxin content when held at elevated temperatures. Solutions of penta (cyclosol-53), as well as aqueous santobrite solutions, also increase slowly 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.

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. 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.

As mentioned in our previous report, the greatest amounts of dioxins in penta are formed during the final stages of chlorination. This formation can be suppressed considerably by using milder chlorination

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conditions. Keeping the batch heat history as low as possible, especially in the later stages of chlorination is most essential. Low heat history, coupled with increased hydrogen ion concentration during chlorination, suggests further benefit in dioxin suppression. Increased hydrogen ion concentration is effected by addition of small amounts of H_2SO_4 or by chlorination under mild pressure (increases HCl concentration in the mass).

Lab tests have confirmed chlorine is the initiator in dioxin formation. 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. Subsequently, all normal penta production at this time is dioxin stabilized during the molten hold period.

Dioxins, as well as other impurities in penta, can be removed by various purification techniques. Fractional distillation, solvent extraction from sodium pentachlorophenolate solution, or recrystallization are each effective purification schemes. Fractionation however appears to be the most economical means of purification.

Future Plans and Recommendations

1. Continue to periodically monitor dioxin levels in Monsanto and competitive penta.
2. Determine if dioxin formation during chlorination can be suppressed by:
 - a. Chlorinating under pressure.
 - b. Chlorinating in presence of mineral acids.
 - c. Chlorinating in presence of solvent at reduced temperatures.
 - d. Chlorinating in presence of chlorine radical scavengers.
 - e. Chlorinating in presence of increased chloride ion concentration.
3. Continue to provide analytical support for penta purification research.

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S. H. Vogel

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