Santobane (DDT)

Monsanto Production History:

Considerable interest shown by the U.S. Army in DDT and the fact that Monsanto produced all of the major raw materials required for its manufacture prompted the company to enter the market. Interim production of Santobane (Monsanto's trade-name for technical grade DDT) was initiated in the W Building at the Queeny Plant in the spring of 1944. Within a few months, full-scale production commenced in Dept. 45 (EE Building) of the same plant.

Because of increased demand, additional production began in February, 1947 in Dept. 259 at the Krummrich Plant employing the same process as practiced at the Queeny Plant. Within the next few years, the Krummrich facilities became the dominant producing unit, and the Queeny operation was phased out.

Production and sale of Santobane by Monsanto ceased in 1957, because of stiff competition from a West Coast producer who had a more favorable raw material position. The impact of DDT's poor biodegradability and potential human health effects had not yet been felt.

Synopsis of the Process:

The *para - para* isomer [1,1-di(*p*-chlorophenyl)-2,2,2-trichloroethane] is the active ingredient in technical grade DDT. Santobane contained about 78% of this isomer. The rest of the product was mainly the *ortho - para* and *ortho - ortho* isomers. The low crystallizing point and waxiness of the product was caused by the presence of these two by-products.

Chloral hydrate was made by chlorinating ethanol in the presence of ferric chloride catalyst. The chloral hydrate was dehydrated to chloral by distillation in the presence of sulfuric acid.

The refined chloral and chlorobenzene were then reacted as 99+% sulfuric acid was added. This reaction is acid catalyzed and will not proceed if water is present. Thus, strong sulfuric acid was used which also served as a dehydrating agent. In the early years of production, a mixture of concentrated sulfuric acid and 25% or 35% oleum was employed. That portion of the chlorobenzene which did not react, and a small amount of the *ortho - para* and *ortho - ortho* by-products, were sulfonated by raising the temperature. The acid layer was drained off carrying with it these sulfonated by-products.

The product was then quenched with water and melted. Acidic material in the product was neutralized with sodium bicarbonate solution, and the product washed with water. The washed product was granulated by spraying it into water which was seeded with fine DDT crystals. The granular product was then filtered, dried, and packaged.

Chemical Reactions:

A. Step 1 - Chlorination (formation of chloral hydrate)

$CH_3CH_2OH + 4Cl_2 \xrightarrow{FeCl_3} Cl_3CCHO + 5HCl$

ethanol — chlorine — chloral — hydrogen chloride

$Cl_3CCHO + H_2O \longrightarrow Cl_3CCH(OH)_2$

water — chloral hydrate

Side Reaction

$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$

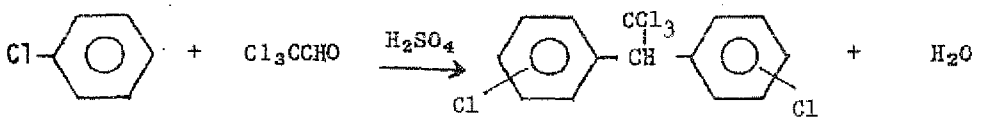
ethyl chloride

B. Step 2 - Distillation (formation of chloral)

$CCl_3CH(OH)_2 \xrightarrow{H_2SO_4} CCl_3CHO + H_2O$

chloral hydrate — chloral

C. Step 3 - Condensation (formation of Santobane)



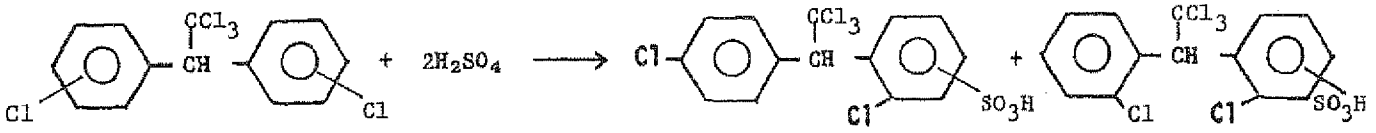
chlorobenzene

Santobane
78% *para - para* isomer
22% *ortho - para* and
ortho - ortho isomers

Side Reactions

sulfuric acid

sulfonated chlorobenzene (chlorobenzenesulfonic acids)



ortho - para and
ortho - ortho
DDT isomers

sulfonated
ortho - para
DDT isomer

sulfonated
ortho - ortho
DDT isomer

+ 2 H_2O

D. Step 4 - Neutralization and Washing (removal of residual sulfuric acid and sulfonated by-products)

$$H_2SO_4 + 2\,NaHCO_3 \longrightarrow Na_2SO_4 + 2CO_2 + 2H_2O$$

Note: During 1954 and 1956, amendments were approved eliminating the $FeCl_3$ catalyst in the chlorination (Step 1), again using a mixture of sulfuric acid and oleum in the condensation (Step 3), and employing an excess of chlorobenzene in the condensation (Step 3) to improve yield. None of these changes affected the basic features of the process.

References:

1. Fraser, W. D. "Tentative Process on DDT"; Job No. 117-1728, Org. Chem. Div.; March 28, 1944.

2. Meriage, P. and S. A. Urban. "Tentative Process, Dept. 45 (Queeny Plant), Manufacture of Santobane (Tech. Grade DDT)"; February 15, 1946.

3. Hedworth, R. L. and L. A. McDonald. "Description of Manufacturing Process for Santobane, Dept. 259 (Krummrich Plant)". Includes three Approved Amendments; July 15, 1953.

4. Telephone conversation with W. S. Knowles.

5. Fraser, W. D. "Final Report on DDT and Related Products, Part I, Development and Demonstration of a Process for DDT", Job No. 117-1728, Org. Chem. Div., 11/11/44.

6. Hedworth, R. L., "Process Description for the Manufacture of Santobane (DDT) in Dept. 259 (Krummrich Plant)", 12/17/54.

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