

TESCO DETOX Substitution Case-Study: Organotin compounds in a China mill

No.	Field Name	Explanations
1.	Priority Chemical Group Detected in the Wastewater / Possible from the Chemical Inventory	Organotin compounds / monomethyltin (MMT), dimethyltin (DMT), and trimethyltin (TMT).
2.	Title	Detection of 6.06 ppb of MMT, 1.89 ppb of DMT, and 14.95 ppb of mono-, di- & tri-methyl tin (TMTs) derivatives respectively, in the raw (before treated) wastewater of a textile mill in China.
3.	Abstract	This case study outlines the possible sources of organotins that were detected in the raw (before treated) wastewater of a mill based in East China, and precautions to be taken with safer alternatives to ensure no incidence in the future.
4.	Mill type	The mill undertakes continuous dyeing along with other processes such as sizing, de-sizing, scouring, bleaching, mercerizing and finishing.
5.	Process Conditions	Finishing with wet rubbing fastness improver by PD process (100-120°C).
6.	Chemicals being used in the mill (From the Chemical Inventory)	Reactive Dyes / Disperse Dyes / Vat Dyes / Scouring Agents / Wetting Agents / Migration Inhibitors / Fixing Agents / Softeners / Resins / Water Repellents / Bulk Chemicals.
7.	Possible chemical responsible for the detection	During the assessment of the mill, it was found that the mill had been using a dyestuff fixing agent called Ultrafix CHR from a non-traditional chemical supplier from China, to improve the wet rubbing fastness of the dyed fabric. Ultrafix CHR is a polyurethane (PU) based coating resin, for the synthesis of which certain organotin based compounds are used as catalysts. Therefore, the manufacturing process could result in organotin residues as non-intentional hazardous impurities in such PU based auxiliaries.
8.	Substituted substance(s)	In order to eliminate MMT, DMT, TMTs (organotin compounds) in the wastewater, the mill should select a PU based auxiliary for the wet rubbing fastness improvement which contains less than 5 ppm of mono-, di- and tri-methyl tin derivatives combined together as per the ZDHC MRSL V1.1 guideline. Preferably a chemical with no organotin residue would be used.

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9.	Other type of alternative	A feasible alternative to avoid the incidence of organotins in wastewater would be to use PU based auxiliaries synthesized using catalysts containing no organotin based compounds.
10.	Hazard assessment	Organotin compounds are organic compounds of tin that are widely used as preservatives in the textile and leather industries due to their biocide properties (antibacterial and antifungal agents). Additionally, they have also been used due to their properties as thermal stabilizers for plastics and as catalysts in polymer synthesis such as polyurethane (PU) and polyvinyl chloride (PVC). They may persist in the environment and can be toxic to aquatic life, act as immunotoxins, and impair human fertility or cause harm to unborn children, if they are above certain exposure levels. Therefore, since July 2013, they have been restricted in toys and childcare articles. The maximum migration limit is 12 ppm in category (III) materials such as polymers, paints, paper, textiles, glass and wood.

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11.	Case description	The textile mill in East China has a chemical management policy in place as well as a DAC (dyestuff/auxiliary/chemicals) Safety List for controlling the input dyes/auxiliaries/bulk chemicals, which fully complies with the legislation and goes beyond legal requirements in many respects. The DAC Safety List is used to guide the purchasing of chemicals to ensure the compliance of finished textiles with ZDHC MRSL and to minimize the environmental impact of textile manufacturing processes. However, in the last wastewater testing report (carried out in December 2018), 6.06 ppb of MMT, 1.89 ppb of DMT, and 14.95 ppb of mono-, di- & tri-methyl tin derivatives were detected in the raw (before treated) wastewater sample. By assessing the mill's chemical inventory list (CIL), production processes and recipes used prior to the date of wastewater sampling, the detection of organotins can be attributed to Ultrafix CHR from a non-traditional chemical supplier from China. It is a polyurethane (PU) based dyestuff fixing agent used to improve the wet rubbing fastness property of the dyed fabric, especially for deep shades. For the synthesis of such PU coating resins, organotin compounds are used as catalysts in production, that could result in the non-intentional presence of organotin residues in most of the PU based auxiliaries. Ultrafix CHR is the only PU based auxiliary applied in the mill and normal usage for this fixing agent is 30-50g/l. The SDS of Ultrafix CHR is available in the mill, but no commitment for DAC Safety List from this chemical supplier has been found. Recommendations to the mill: It is recommended that the mill should contact the supplier of Ultrafix CHR to explain the requirement for no organotin compounds in any chemical formulations. If it is not possible to completely eliminate organotin residues, the concentrations should be controlled below 5 ppm. The supplier should verify that Ultrafix CHR meets the 5-ppm limit with a test report from a certified third-party testing lab to ensure that the limits for organotin compounds are not exceeded.

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12.	Availability of alternative	Bismuth titanate (CAS: 12010-77-4), titanium or zirconium-based catalysts can be used for PU production instead of organotin compounds. However, the chosen alternative PU should be ZDHC MRSL compliant. The mill is advised to look for chemical suppliers who are involved in the synthesis of PU auxiliaries based on this chemistry, so that the possibility of organotins detection can be eliminated completely in future.
13.	Contact: Producer or supplier of alternative	Any ZDHC Gateway registered chemical supplier such as Everlight Chemical, Eurodye-CTC, and Zhejiang Longsheng Group Co., Ltd.
14.	Document – Type and availability	This substitution report has been prepared by BluWin Sustainable Textile Solutions (STS).
15.	Further information	https://ehp.niehs.nih.gov/doi/pdf/10.1289/ehp.730461 https://www.uskoreahotlink.com/products/manufacturing/non-toxic-pu-catalysts/ https://www.dorfketal.com/15-industry-solutions/specialty-catalysts