Prato textile district

The Detox Approach

and

why and how a group of textile supply chain SMEs got together to substitute SVHCs

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BuzziLab – Prato

February 23 2017
The production of Prato Textile District

Prato began to specialize in textiles in the 12th century

Prato is renowned for (carded woollens).

recent developments: yarns for knitwear, synthetic leather, synthetic fur, furnishing fabrics, nonwoven fabrics, technical fabrics, special fabrics, and knitwear.
Prato is today the largest Italian district of textile and clothing

The textile and clothing industry in Prato is today:

- **more than 30,000 direct employees,**
- **7,500 businesses in network,**
- **4,500 million Euro of turnover**

Prato produces also excellent textile machines for finishing, spinning and special textile

**Breakdown of exports of Prato in 2014 (% values)**

- Textile (yarns, fabrics, special textiles) 55%
- Chemical, plastic, mattresses and other manufactured goods 14%
- Mechanics 5%
- Clothing and knitwear 26%
The centralized waste water treatment plant

The waste water conveyed by the public sewer system of Prato to the treatment plants is purified and returned to the industrial cycle:

- 12 million m$^3$ of water is the total needs of the textile production,
- 64 km of the tubes is the length of pipes that distribute recycled water,
- 5 million m$^3$ is the amount of purified water reintroduced in textile processes:
the contribution of recycling is 40% of the total industrial water.
The Greenpeace DETOX campaign

WHY PRATO TEXTILE DISTRICT JOIN DETOX CAMPAIGN?
Prato for Detox

**Fashion brand side**
- Testing innovative sustainable textile processes
- Testing new chemicals
- Training for technicians
- Technical consulting

**Greenpeace side**
- Technical feasibility
- Development of sustainable production processes
- Training for volunteers
- Analytical investigations

**Textile district of Prato**
- Manufacturing textile industries
- Specific technical skills
- District EMAS Certification
- Water purification and recycling
- Background support for fashion
February 2016: CTN announced in early 2016 its subscription to Detox campaign. First textile district in the world that subscribe a collective detox commitments. 

http://www.greenpeace.org/detox/
July 2016

CID (Consorzio Italiano Implementazione Detox – Italian Consortium for implementing Detox approach).

✓ assure technical support for every member, even for obtain environmental and/or ethic issues

✓ promote R&D projects for implementing efficiency of production processes

✓ promote any sustainability activities of the companies.

✓ organize meeting between manufacturing companies, chemical producers, international organization involved in environmental safety, especially concerning textile and fashion market
REPLACING HAZARDOUS CHEMICALS FROM PRODUCTS/PROCESS

AND

PLANNING SUBSTITUTION

SOME CASE STUDIES
(promoted by CTN and CID)
Case study 1: chemical substitution of PFC

Companies of the textile district which follow the Detox commitment represent different parts of the textile supply chain: factories producing yarn, fabric and raw materials, dyeing plants, yarn or fabric finishing companies, producers of chemicals for the textile industry.

Within this group, only seven mills performed processing techniques in which PFCs can be involved. So, these companies worked together as integrated supply-chain to avoid and eliminate PFC from productions.
on February 2016, CTN and GIDA (company who manage the wastewater treatment plant) signed an agreement for a long-period monitoring analysis planning for recycled water for the 11 group of MRSL Detox of Prato District.

<table>
<thead>
<tr>
<th></th>
<th>18/04/16</th>
<th>28/04/16</th>
<th>09/05/16</th>
<th>09/11/16</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>M1</td>
<td>M2</td>
</tr>
<tr>
<td>PFC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>21 ng/L PFHpA</td>
<td>6 ng/L PFHpA</td>
<td>4 ng/L PFHpA</td>
<td>110 ng/L PFHpA</td>
</tr>
<tr>
<td>112 ng/L PFOA</td>
<td>27 ng/L PFOA</td>
<td>220 ng/L PFOA</td>
<td>64 ng/L PFOA</td>
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</tr>
<tr>
<td>21 ng/L PFNA</td>
<td>5 ng/L PFNA</td>
<td>54 ng/L PFNA</td>
<td>14 ng/L PFNA</td>
<td></td>
</tr>
<tr>
<td>25 ng/L PFDA</td>
<td>5 ng/L PFDA</td>
<td>63 ng/L PFDA</td>
<td>16 ng/L PFDA</td>
<td></td>
</tr>
<tr>
<td>3 ng/L PFUnA</td>
<td>1 ng/L PFUnA</td>
<td>5 ng/L PFUnA</td>
<td>1,2 ng/L PFUnA</td>
<td></td>
</tr>
</tbody>
</table>

Analysis performed by BUZZI LAB
Chemical analysis of input and output water of Prato District Companies at the sign of Detox commitment

Read the full study: http://www.consorziodetox.it/index.php/documents/?lang=en

Chemical suppliers/vendor performed PFC analysis for their water-repellent products and water-repellent fabrics

Read the full study: http://www.consorziodetox.it/index.php/documents/?lang=en

PFC: PERFORMANCES EVALUATIONS

Case study 2: chemical substitution of APEOS

In the roadmap of Detox Campaign, mills are committed to eliminate Alkylphenols away from their supply-chain.
Detox committed companies in Prato District **started an investigation plan** in order to **monitoring their supply chain** and internal manufacturing processes.

**Analytical results of singles companies are available on own website**

**Full data on CTN web side:**
https://www.confindustriatoscananord.it/media/DETOX/CTN_APEOS_CaseStudy_2016_DEF_ENG.pdf
APEOS

Total positive samples (> 1 mg/Kg)

<table>
<thead>
<tr>
<th>Year</th>
<th>Total</th>
<th>Positive</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>2015</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>2016</td>
<td>13</td>
<td>1</td>
</tr>
</tbody>
</table>
Finished product

- Positive samples (> 1 mg/Kg): 52.4% (2014), 42.1% (2015), 27.1% (2016)

APEOS
Case study 3: chemical contamination of dyestuffs for fashion industry

TOPIC: case study for evaluation of chemical contaminations of more-frequently used dyestuffs in Prato Textile District and consequent substitution of high-contaminated ones

Chemical analysis was restricted only to four groups of substances (respect to the 11 priority groups of Detox Commitment)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MRSL DETOX Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxylated Alkylphenols – APEOS</td>
<td>1 mg/kg</td>
</tr>
<tr>
<td>Aromatic amines from azocolorants</td>
<td>1 mg/kg</td>
</tr>
<tr>
<td>Chlorophenols</td>
<td>0.05 mg/kg</td>
</tr>
<tr>
<td>Phthalates</td>
<td>10 mg/kg</td>
</tr>
</tbody>
</table>

Companies involved in this case study were the dyeing mills who signed Detox Commitment
AROMATIC AMINES DERIVED FROM AZOCOLORANTS
Test method compliant to **UNI EN ISO 14362-1:2012 Annex F.**
Brief description of test method: a weighted sample of dye is treated in citric buffer with sodium dithionite (reductive cleavage). The released amine/s is/are extracted in organic solvent and quantitatively analised by **GC-MSMS and LC-MSMS.**

Limit of Detection: 0.01 mg/kg
Limit of Quantification (MRSL): 1 mg/kg

APEOS / CHLOROPHENOLS / PHTHALATES
Test Method: **in-house method** (developed by Buzzi Lab) was used by high-resolution mass spectrometry/time-of-flight liquid chromatography (**LC-QTOF equipment**).
Brief description of test method: a weighted sample of dye is dissolved in organic solvent and directly analized by LC-QTOF.

Limit of Detection: APEOS and Chlorophenols: 0.01 mg/kg – Phthalates: 0.1 mg/kg
Limit of Quantification (MRSL): APEOS: 1 mg/kg – Chlorophenols: 0.05 mg/kg – Phthalates: 10mg/kg
### SUMMARY: 228 dyestuffs analysed

<table>
<thead>
<tr>
<th>Group</th>
<th>LIMITS</th>
<th>TOTAL NON-COMPLIANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MRSL Detox</td>
<td>ZDHC v 1.1-2015</td>
</tr>
<tr>
<td>Aromatic Amines</td>
<td>1 ppm</td>
<td>150 ppm</td>
</tr>
<tr>
<td>APEOS</td>
<td>1 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>Chlorophenols</td>
<td>0.05 ppm</td>
<td>50 ppm (20 ppm PCP-TeCP)</td>
</tr>
<tr>
<td>Phthalates</td>
<td>10 ppm</td>
<td>250 ppm (sum)</td>
</tr>
</tbody>
</table>
# Example of report

<table>
<thead>
<tr>
<th>COLOR INDEX</th>
<th>Chlorophenols</th>
<th>Phthalates</th>
<th>Aromatic Amines</th>
<th>APEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIRECT BLACK 112</td>
<td></td>
<td></td>
<td></td>
<td>NPEO 1.8</td>
</tr>
<tr>
<td>DIRECT BLACK 22</td>
<td>PCP 0.16</td>
<td></td>
<td>4-chloro aniline 12.8</td>
<td>NPEO 45.4</td>
</tr>
<tr>
<td>DIRECT BLACK 19</td>
<td></td>
<td></td>
<td>4-chloro aniline 29.2</td>
<td>NPEO 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4,4’-thiodianiline 17.5</td>
<td></td>
</tr>
<tr>
<td>DIRECT BLACK 80</td>
<td></td>
<td></td>
<td>4-aminodiphenyl 3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-naphthylamine 1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-chloro aniline 35.8</td>
<td></td>
</tr>
<tr>
<td>DIRECT BLUE 199</td>
<td></td>
<td></td>
<td></td>
<td>NPEO 93.7</td>
</tr>
<tr>
<td>DIRECT BLUE 299</td>
<td></td>
<td></td>
<td>2-naphthylamine 11.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-chloro aniline 1.6</td>
<td></td>
</tr>
<tr>
<td>DIRECT BLUE 218</td>
<td></td>
<td></td>
<td>3,3’-dimethoxybenzidine 5.9</td>
<td>NPEO 1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>o-anisidine 1.3</td>
<td></td>
</tr>
</tbody>
</table>

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Thank you for attention

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