What Sort of "Detox List" For the Tanning Industry?

A Contribution to Identify, Quantify and Map the Chemical Related To the Tanning Industry

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Introduction

European Regulations have objectives to improve protection of human health and the environment.

- The Water Framework Directive (WFD) aim to protect and restore surface and groundwater bodies in order to rich ecological and chemical status of all water bodies.
- REACh (EC 1907/2006), the European regulation on Chemicals (Registration, Evaluation, Authorization and restriction of CHemicals) has the objective to decrease Substances of Very High Concern that is to say carcinogenic, mutagenic or toxic to reproduction (CMRs); persistent, bio-accumulative and toxic (PBTs);

According to Greenpeace International, textile manufacturing makes use of a diverse range of process and finishing chemicals, some of which have intrinsic hazardous properties. Greenpeace's 2011 Detox report concerns hazardous, persistent and hormone-disrupting chemicals in the textile industry. Their objective is to eliminate all hazardous chemicals across the entire textile supply chain: nonylphenol ethoxylate (NPEs), carcinogenic amines, phataltes (butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP) and Diisononylphtalate (DINP)) and other chemicals.

Is the tanning industry ready to fulfill requirements on hazardous chemicals? What chemicals of the tanning industry could be affected by these shareholders? This paper is a contribution which purpose is to identify the relevant chemicals and assess the prevalent ones.

Identification of the potential chemicals for the tanning industry

From 2003 to 2007 a national inventory of hazardous substances in industrial discharge to water took place in FRANCE. Considering their toxicity for aquatic eco-systems, 106 chemicals were listed by the Water Framework Directive (2000/60/EC).
Out of 2648 industrials sites, 43 tanneries had to sample waste water and send the samples for analyses. Sampling prescriptions have been determined to be significant of a normal day activity.

Sampling was organized either on indirect discharge in urban waste water treatment plant or on direct discharge in receiving water when the tannery was equipped with a biological treatment.
The list of 106 compound consisted in metallic compounds, organic acids, aniline, benzene, toluene, ethylbenzene, and xylene, chlorobenzen, chlorophenol, chlorotoluene, volatil organic compounds, brominated compounds, Polycyclic Aromatic Compounds, Organo-Stannic Compounds, pesticides, phosphates, phtalates, and Polychlorinated biphenyls.

3 different types of substances had been defined:

- Priority Hazardous Substances List (red): These substances have to be reduced by 50% in Europe in 2015 and remove in 2020)
- Priority Non Hazardous Substances list (yellow): These substances have to be reduced by 30% in Europe in 2015
- French list (light grey): These substances that have to be reduced by 10% in 2015.

Table 1: Priority Hazardous Substances List (substances that have to be reduced by 50% in Europe in 2015 and remove in 2020)

	Occurrence in the tanning industry (% among 43 tanneries)
Tétrachloroéthylène	**28%**
Cadmium	**16%**
Trichloroéthylène	**16%**
4-(para)-nonylphénol	**12%**
Tétrachlorure de carbone	**12%**
Benzo (a) Pyrène	5%
Benzo (b) Fluoranthène	5%
Benzo (g,h,i) Pérylène	2%
Benzo (k) Fluoranthène	2%
Indeno (1,2,3-cd) Pyrène	2%
Chloroalcanes C10-C13 ; Hexachlorobenzène ; Pentachlorobenzène ; Hexachlorobutadiène ; Pentabromodiphényléther ; Tributylétain cationgamma isomère - Lindane	0%

Table 2: Priority Non-Hazardous Substances list (substances that have to be reduced by 30% in Europe in 2015)

	Occurrence in the tanning industry (% among 43 tanneries)
Phtalates (DEHP)	**84%**
Naphtalène	**67%**
Nickel	**35%**
Plomb	**33%**
Chloroforme	**30%**
Para-tert-octylphénol	**16%**
Benzène	**16%**
1,2 dichlorobenzène	**14%**
Chlorure de méthylène	7%
Fluoranthène	7%
1,2,4 trichlorobenzène	5%
1,2,3 trichlorobenzène	2%
Décabromodiphényléther	2%
Anthracène	2%
Diuron	2%
Pentachlorophénol ; 1,2 dichloroéthane ; Octabromodiphényléther ; Alachlore ; alpha Endosulfan ; Atrazine ; béta Endosulfan ; Chlorfenvinphos ; Chlorpyrifos ; Trifluraline ; Simazine ; Isoproturon	0%

Table 3: French list (substances that have to be reduced by 10% in 2015)

	Occurrence in the tanning industry (% among 43 tanneries)
Zinc	**98%**
Chrome	**93%**
4-chloro-3-méthylphénol	**79%**
Cuivre	**77%**
Toluène	**67%**
Xylènes (Somme o,m,p)	**58%**
Ethylbenzène	**37%**
Biphényle	**35%**
Tributylphosphate	**26%**
Isopropylbenzène	**23%**
Arsenic	**23%**
Mercure	**16%**
1-chloro-4-nitrobenzène	**14%**
2,4,6 trichlorophénol	**14%**
4-tert-butylphénol	**14%**
Dibutylétain cation	**14%**
1,4 dichlorobenzène	9%
4 chlorophénol	9%
1-chloro-3-nitrobenzène	7%
1,3 dichlorobenzène	7%
1,1,1 trichloroéthane	7%
Acénaphtène	7%
2 chloroaniline	5%
1-chloro-2-nitrobenzène	5%
Chlorobenzène	5%
1,1,2 trichloroéthane	5%
2,4 dichlorophénol	5%
Chlorure de vinyle	5%
1,2 dichloroéthylène	5%
Monobutylétain cation	5%
4 chloroaniline	2%
Acide chloroacétique	2%
1,1,2,2 tétrachloroéthane	2%
PCB 138	2%
3,4 dichloroaniline ; 1,2,4,5 tétrachlorobenzène ; 3 chloroaniline ; 4-chloro-2 nitroaniline ; Epichlorhydrine ; 1,3,5 trichlorobenzène ; 2 chlorophénol ; 2,4,5 trichlorophénol ; 3 chlorophénol ; 2-chlorotoluène ; 3-chlorotoluène ; 4-chlorotoluène ; 1,1 dichloroéthane ; 1,1 dichloroéthylène ; 3-chloroprène ; Chloroprène ; Hexachloroéthane ; Hexachloropentadiène ; 2-nitrotoluène ; Nitrobenzène ; triphénylétain cation ; alpha Hexachlorocyclohexane, PCB 101 ; PCB 118 ; PCB153 ; PCB 180 ; PCB 28 ; PCB 52	0%

Figure 1 shows all results for substances with an occurrence above 10% (that is to say that the substance had been detected in more than 5 tanneries out of 43).

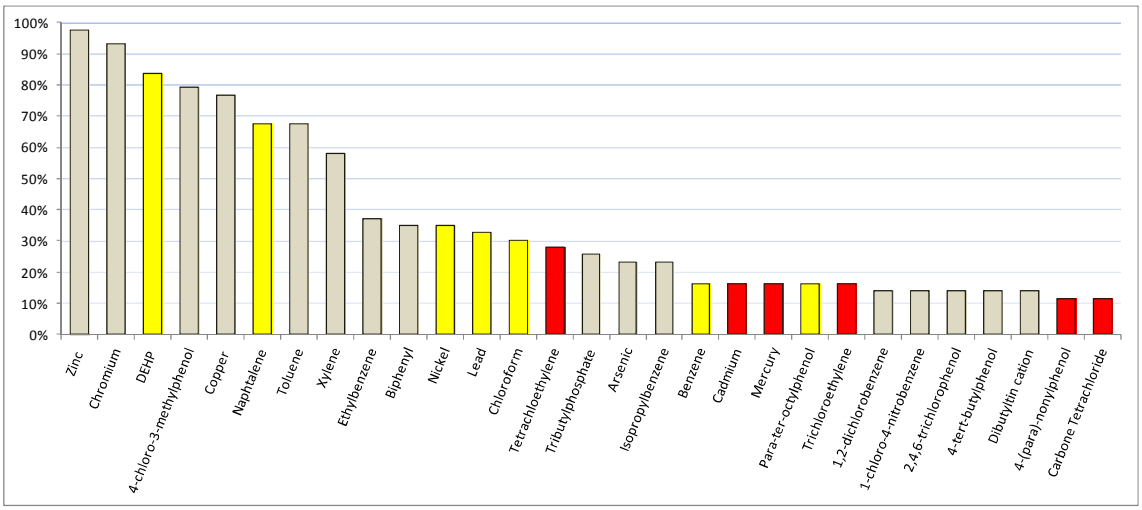

Figure 1: Substances detected in more than 10% of the 43 tanneries

Chemicals detected in more than 10% of the 43 tanneries	
Arsenic	
Benzene	Lead
Biphenyle	Naphtalene
Cadmium	*Nickel*
Carbone tetrachloride	*Mercury*
Chromium	Nonylphenols
Copper	*Octylphenols*
Chloroform	*4-terbutylphenol*
4-chloro-3-methylphenol	Tetrachloroethylene
1-chloro-4-nitrobenzene	Toluene
1,2-dichlorobenzene	*Tributylphosphate*
Dibutyletain cation	Trichloroethylene
DEHP	2,4,6-trichlorophenol
Ethylbenzene	Xylene
Isopropylbenzene	Zinc

Quantification

From that list of 29 substances, it was decided to quantify the chemical with more accuracy. Sampling of the normal day activity for each tannery was planned on 6 days (once every month during 6 months by using flow proportional 24-hour representative composite sample).

The operation was organized in 17 tanneries. Again, sampling was organized on waste water discharge either indirect discharge in urban waste water treatment plant or direct discharge in receiving water when the tannery is equipped with its own biological treatment.

It was decided to consider to fixe some rules. All tanneries that release more than what can be accepted by the environment will have to reduce their flow. The rules are the following:

- All concentrations have to be bellow 10 times the Environmental Quality Standards (EQS)
- All flow have to be less than 10% of the Maximal Admissible Theoretical Flow to protect the environment

By following these rules, out of the 17 tanneries and the 29 substances, some tanneries (not all of them) had to monitor and could have to reduce the quantity for 5 chemicals.

Substances quantified above the "environmental limits"	Objectives of reduction
Tétrachloroéthylene	50% reduction in 2015 and totally removed in 2020
Zinc	10% reduction in 2015
Chrome	10% reduction in 2015
4-chloro-3-méthylphenol (Chlorocresol)	10% reduction in 2015
Copper	10% reduction in 2015

Mapping

Next step consist in determining what these chemical are used for in the tanning industry.

Tetrachloroethylene (or perchloroethylene or PERC)
The origin of tetrachlorethylene in tanneries is well knows. When degreasing skins, some tanneries would use tetrachloroethylene in closed wessels. Following that degreasing step, the skins are pickled and tanned. Some of the tetrachlorethylene might remain in the skin and be released in the pickling or tanning floats.
The substance is classified in the European Union:

- R40 Limited evidence of a carcinogenic effect
- R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

The International Agency for Research on Cancer has classified tetrachloroethene as a Group 2A carcinogen, which means that it is probably carcinogenic to humans.
That substance is a challenge for the tanning industry and solutions have to be identified for some sheepskin tanneries. This might be a challenge for the IULTCS members to find alternative solution to degrease sheepskin and pig-sheep in all cases (tensioactives, enzymes, white spirits, …

Chromium

Chromium is the easiest part of the mapping. chromium III is the most widely used tanning agent. All sites complied with the national specifications. Some tanneries did not comply with the Maximal Admissible Theoritical Flow. Technics to reduce the chromium flow rate were then proposed:

- Chromium floats exhaustion
- Optimization of the collect of the chrome containing floats
- Modification in the tanning and/or retanning steps
- Optimization of the waste water treatment plant

4-chloro-3-methylphenol (Chlorocresol)

4-chloro-3-methylphenol was quantified ion 5 tanneries. In order to map the substance in the tanning process, sampling was organized totally differently. Instead of a 24-hour representative composite sample in the waste water steam, the sampling was organized on each tannery steps such as soaking, liming, pickling, tanning, dying, retanning, finishing, etc.

The campaingn showed that chlorocresol is quantified on different steps of the process. In some tanneries, it is identified only for the finishing steps. In other case, it was also quantified in other floats such as deliming and bating, pickling and tannind steps, dyeing and fatliquoring,

Chlorocresol is used for its bactericide and fungicide properties. Since 1989, 4-chloro-3-methylphenol is an alternative for pentachlorophénol. It is used as

- Bactericide or fungicide for the preservation of hides and skins during the process. In such uses, concentration of chlorocresol in the chemicals can reach 20%.
- Bactericide or fungicide to preserve chemicals of the finishing department. In such uses, concentration of chlorocresol in the chemicals should remain bellow 1%. Most of the time it is not identified in the chemical safety data sheets.

Chlorocresol is classified

- R43 May cause sensitization by skin contact
- R 50 Very toxic for aquatic organisms

It is a substance of the liste "Liste II" de la directive 76/464/CEE. As a European objective, quantities have to be reduced by 10% before 2015.

It is still possible and authorized to use chlorocresol. Other bactericides and fungicides are also available to protect hides and skins or chemicals.

An interesting aspect of 4-chloro-3-methylphenol is that it is biodegradable in aerobic conditions. Biological effluent treatment plant, most widely used technique used when indirect discharge might reduce the quantity of chlorocresol released in the environment. More results are expected concerning that aspect.

Copper and Zinc

An unexpected aspect of that project was that copper and zinc are ubiquitous in most tannery waste water:

- 98% of occurrence for zinc
- 77% of occurrence for copper

Quantities for the 17 tanneries are presented in next table.

Tannery	Copper (g/day)	Zinc (g/day)
Tannery 1	5	32
Tannery 2	3	7
Tannery 3	21	109
Tannery 4	7	23
Tannery 5	7	59
Tannery 6	2	9
Tannery 7	5	33
Tannery 8	8	9
Tannery 9	1	1
Tannery 10	4	9
Tannery 11	11	6
Tannery12	3	7
Tannery 13	1	8
Tannery 14	0	1
Tannery 15	5	89
Tannery 16	1	1
Tannery 17	1	9
	85	**412**

Most Chemical Safety Data sheets do not give any information related to copper and zinc. As it is not a hazardous chemical, it does not need to appear on the CSDS.

The step by step study of all chemical operations shows that these 2 metallic substances are relatively ubiquitous in all tannery operations: soaking, degreasing, liming, deliming, pickling, dyeing, finishing. Some operations content less of these 2 metals: tanning, retanning and fat liquoring.

Conclusion

Out of 106 chemicals, 29 have been identified in pre-treated tannery waste water. When considering their potential impact on water bodies, 5 chemicals were remaining.

Only one of them is considered as a potential hazard: tetrachloroethylene. It is used in very specific conditions in which most of the perchlorethylene is recycled. It concerns only the degreasing steps of some sheepskins. Alternative solutions such as tension actives or white-spirit are possible in most degreasing cases.

Trivalent chromium, because of the potential quantities has to be bewared off. Floats exhaustion, optimization of the collection of chromium containing floats, modification in the tanning and retanning recipe, chemical treatment are solutions to avoid the release of chromium III in the water bodies.

Chlorocresol, zinc and copper are not considered as hazardous. Chlorocresol release should be bewared of thanks to good housekeeping procedures. A few more investigations aim to check its biodegradability in biological plants.

These results are rather promising for the tanning industry. However, the tanneries that have been assessed are located in France. All the assessed sites are equipped with chemical effluent treatment plants and it is a geographical area under REACh control. Next step would be challenge tanneries in other area with other management habits and practices. Thanks to that experiment, CTC has developed a ready-to-use analytical package dedicated to the control of Hazardous Substances in water bodies in order to comply with either European Regulations or more unexpected "*Detox Requests*".