



Associazione Tessile e Salute

CHEMICAL RISK IN PURE NEW WOOL TEXTILES (PNW).

1. International context.

In the global market the consumer's attention for safe and sustainable products is growing, also thanks to the pressure of environmental movements.

Therefore manufactory companies have to ensure the safety of their products declaring their compliance with Restricted Substance Lists, proposed by many private marks, by single brands or by large-distribution.

2. Hazardous substances.

The following document lists the main categories of chemicals (or the main substances) that should be check in PNW.

For a more detailed description of single components of every family and their respective limits, test methods and uses, please refer to the complete document 'Chemical risk 2'.

2.1 Arylamines (Aromatic Amines).

Azo Dyes may release one or more aromatic amines by reductive cleavage of one or more AZO groups.

Limits : 20-30 ppm

Test method: UNI EN 14362-1 (without extraction, for cellulosic and protein fibers)

2.2 Carcinogenic Dyes.

Direct or disperse dyes, normally not used for wool products, but in some cases they are used to dye sheepskins.

Limits : use prohibited

Test methods: DIN 54231 can be used only for some Disperse dyes; in the other cases a not standardized method is adopted with extraction in solvent and detection with LC-MS.

2.3 Allergenic Dyes.

Disperse dyes, normally not used for wool products, but in some cases they are used to dye sheepskins.

Limits : use prohibited

Test methods: DIN 54231 can be used only for some Disperse dyes; in the other cases a not standardized method is adopted with extraction in solvent and detection with LC-MS.

2.4 Navy Blue index No. 611-070-00-2

Used as a wool dye and also for polyamide and leather articles.

Limits : use prohibited

Test methods: Not standardized method with extraction in solvent and detection with HPLC-DAD.

2.5 Biocides and phytosanitary products

Used in wool and other keratin fibers in the raw state as: herbicides and pesticides in crops; pesticides on farms; biocidal products on items.

Limits : Wool and other keratin fibers: 0,5 mg/Kg (total) in most cases;

2 mg/Kg (total) for some Organophosphorous insecticides

Test method: IWTO Draft Test Method 59 for wool and other keratin fibers.

2.6 Pesticides and leather preservatives (PCP-Pentachlorophenol and its salts; TeCP-Tetrachlorophenol)

Used as herbicides and fungicides on row wool.

Limits : 0,05 mg/kg in textiles

Test methods: - US EPA 8081 A

- UNI 11057

2.7 ortho-Phenylphenol (OPP)

Agricultural fungicide. It is a general surface disinfectant that can be used on fibers.

Limits :from 50 mg/kg (textiles for children) to 100 mg/kg (other textiles)

Test methods: not standardized methods utilizing GC-MS LC-MS analysis for confirmation

2.8 Nonylphenol (NP) and Nonylphenol ethoxylate.

Emulsifiers, detergents, surfactants.

Limits : use prohibited

Test methods: not standardized methods with extraction in solvent and GC-MS LC-MS analysis for confirmation.

2.9 Extractable heavy metals

Contained in pigments and metal complex dyes.

Limits : see table 1

Heavy metal		Limits		
		Children ≤ 36 months	Contact with skin	No contact with skin
Antimony	Sb	≤ 30,0 mg/kg	≤ 30,0 mg/kg	≤ 30,0 mg/kg
Arsenic	As	≤ 0,2 mg/kg	≤ 1,0 mg/kg	≤ 1,0 mg/kg
Lead	Pb	≤ 0,2 mg/kg	≤ 1,0 mg/kg	≤ 1,0 mg/kg

Cadmium	Cd	≤ 0,1 mg/kg	≤ 0,1 mg/kg	≤ 0,1 mg/kg
Total Chromium	Cr	≤ 1,0 mg/kg	≤ 2,0 mg/kg	≤ 2,0 mg/kg
Chromium VI*	Cr^{VI}	≤ 0,5 mg/kg	≤ 0,5 mg/kg	≤ 0,5 mg/kg
Cobalt	Co	≤ 1,0 mg/kg	≤ 4,0 mg/kg	≤ 4,0 mg/kg
Copper	Cu	≤ 25,0 mg/kg	≤ 50,0 mg/kg	≤ 50,0 mg/kg
Nickel	Ni	≤ 1,0 mg/kg	≤ 4,0 mg/kg	≤ 4,0 mg/kg
Mercury	Hg	≤ 0,02 mg/kg	≤ 0,02 mg/kg	≤ 0,02 mg/kg
Zinc	Zn	-	≤ 50 mg/kg	≤ 50 mg/kg

Table 1

Test methods: extraction in acid sweat (UNI EN ISO 104-E04) and determination with AAS-ICP/OES/MS.

*Extraction in alkaline buffer; colorimetric detection method with diphenylcarbazide.

2.10 Formaldehyde

Used for anti crease treatments.

Limits :20 mg/kg (textiles for children), 30 mg/kg (contact with skin), 75 mg/kg (without contact with skin)

Test methods: UNI EN ISO 3071

2.11 Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA), (its salts and esters)

Surfactants for textile and leather cycles. Surfactant in the emulsion polymerization of fluoropolymers.

Limits : use prohibited

Test methods: not standardized method with extraction in solvent and LC-MS for confirmation

3. pH of the aqueous extract

Besides hazardous substances, pH of the aqueous extract is a very important parameter for wool products.

Generally accepted range: 4.0 – 7.5 (children, contact with skin)

4.0 – 9 (other textiles)

The international context and the list of requirements represent a problem for manufactory companies that must conform to customer demands.

This complex situation may be solved according to the following scheme:

- raccomandation for companies
- definition of good manufacturing practice
- open problems that need to be addressed

4. Raccomandation for companies.

- Be ensured by the supplier that products used in the dyeing process of sheepskin don't contain allergenic or cancerogenous dyes.

- Perform random analysis on the articles produced in order to investigate the presence of the hazardous substances listed above
- Address to a proper laboratory to investigate the presence of a specific chemical family (that is a lab accredited for this specific analytical test)
- Achieve good wet fastness when using metal complex dyes (that can release heavy metals);
- Don't make use of detergents containing Nonylphenol and Nonylphenoxy poly(ethyleneoxy) ethanol: it is possible to find alternative products.

5. Study and definition of the good manufacturing practices.

In general, if the "good manufacturing practices" are applied in the production, it's possible to use even highly dangerous substances without creating any problem.

If, using a dangerous substance, it's define punctually:

- The way it's transported (ex. In sealed packages);
- How it's weighted (ex. Automatic weighting);
- How it's used (ex. inside closed machines with);
- How must be treated in a depurator, if present in the waste water;
- How must be calculated the percentage of using as for a specific chemical recipe;
- Which individual protection measures must be used by workers to manage it;

are defined the conditions to utilize the substance without causing any damage to:

- The environment;
- The workers;
- The textile product customer;

A concrete example is the Sodium Dichromate:

- It's utilized as mordant in dyeing the wool;
- It's a carcinogenic substance as contains chromium VI;
- It is carcinogenic by inhalation;

If it is used following the good manufacturing practices, that is:

1. utilize the liquid form, not inhalable;
2. automatic use inside a closed system;
3. following a precise stoichiometric ratio ;

it doesn't create any problem as Cr VI is not found anywhere, nor in the air or in the waste water or in the urine of the workers or in the final fabrics.

So it's essential, when it's unavoidable to use dangerous substances due to production and quality needs, to define the right conditions of use.

6. Open problems that need to be addressed

6.1 Analytical tests.

Many analytical methods used in the textile sector are not standardized and this fact can be the cause of different results in several laboratories.

It would be advisable to start an interlaboratory work with the aim to standardize the tests starting from those on PNW.

6.2 pH range of aqueous extract. The physiological limits of this parameter have never been scientifically proven. So it's not sure that a pH 3 (possible for wool products) can cause dermatological problems. Goal: pH range compatible with skin physiology.

Steps of a possible study:

Task 1 Realization of fabrics finished with different pH
Task 2 Definition of a test procedure
Task 3 Execution of in vitro test
Task 4 Evaluation of in vitro test results
Task 5 Execution of in vivo test on volunteers on the basis of the results of task 3
Task 6 Evaluation of in vivo test results
Task 7 Drafting of a first text
Task 8 Drafting and sharing a final text

6.3 Perfluorooctane sulfonate (PFOS) – fluorocarbon resins.

The fluorinated polymers used to obtain the oleo-repellence of textiles contain the C-F bond that is among the most durable bonds, is not degraded and therefore accumulates in nature.

This problem is particularly evident in molecules with 8 carbon atoms, C8 (PFOS e PFOA).

For this reason fluorinated polymers C8 must be eliminated in Europe by January 1, 2015.

C6 have a better behaviour than C8: they are less accumulative. A mammalian takes 3,5 years to eliminate 50% of C8 while C6 are eliminated in a few tens of hours

Possible alternatives to fluorocarbon resins are finishing processes based on waxes, paraffins, polyurethanes or silicones: these finishes ensure water repellency but not oleo-repellency.

So it is fundamental to use C6 for oleo-repellency. The problem must be kept under control following the point of view of environmental associations.

The risk for the future is of not being able to accomplish more oleo-repellent wool products.

6.4 Perchloroethylene.

Apart from the perchlorethylene used in laundries, this substance is used in the textile chain for the dry cleaning of fabrics.

To date there are no alternative substances. Moreover, used according to good manufacturing practice, perfectly closed in machines, does not present any health risks. At most a few sludge exhausted to dispose of.

However it is necessary to monitor this issue because a restriction of perchlorethylene could caused many problems to wool industry.