

What chemicals are restricted?

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To survive in today's global industry, tanneries must comply with a rapidly increasing set of regulations and commercial specifications. Among these regulations and specifications are the restrictions regarding the use of chemical substances considered to have hazardous or toxic properties.

In the technical world of making leather the term 'Restricted Substance List', or its commonly used abbreviation 'RSL', has become a common topic in the tanning industry.

There are differences between the types of restrictions and it is important that tanners understand these differences. Many are legally imposed by national and international regulations and others are set as specifications by eco-labels and brands.

1. Legal restrictions

For example, in the European Union (EU) countries this is very often the EU Regulation 1907/2006 (REACH) and Directives, which normally limit the amount of a restricted substance:

- in a chemical formulation
- in the consumer article

Since the tanner is supplying leather, which will then be made into consumer items, the real impact of such regulations on the leather tanner can sometimes be unclear.

2. Eco-labels and brand specification

These specifications are not regulations but are part of an agreement between the tanner and their customer. Normally these differ from regulations in that specifications limit the restricted substance:

- in the leather

Testing for restricted substances

Many tanners pass restricted substance lists with specifications and test methods onto their chemical suppliers, normally requesting that they must guarantee the chemicals comply with the same specifications. That the specifications and test methods listed are specifically for leather is often not understood. It must be understood that test methods for leather are often not suitable for testing chemicals.



Who develops test methods for leather?

Restricted substance lists often give the required ISO or EN Standard to be used for making the test. However, with the rapid increase in the number of restricted

substances, there is sometimes no 'standard' available. Therefore one often sees brief instructions like 'solvent extraction, GC-MS'. Others simply list the test method used for water analysis, which ignores the most important aspect,

namely the extraction step from leather. Leather is a complex matrix and the extraction must be validated between test laboratories. Some inter-lab trials have shown very large differences caused by different extraction procedures.

Table 1. Restricted substances that may be encountered by tanners

Restricted substance/group	Relevance for leather	Brief comments on restricted substance
Allergenic and sensitising dyes	low	Mostly these are (or were) textile dyes. These dyes are not normally used for colouring leather.
Aromatic amines from azo dyes	low-medium	The EU does not allow the use of azo dyes in consumer goods that, when reductively split, form any of the 22 forbidden aromatic amines. Azo dyes manufactured today are based on non-restricted amines.
Biocides	medium-high	Fungicides are required to protect wet skins/hides and leather from biological damage during storage and transport. Some eco-labels set emission limit values for automotive and furniture uses.
Boric acid and tetraborate (borax)	medium-high	Included in latest list of substances for consulting as possible SVHC. Has been used in deliming agents and as pH adjustment/penetration agents in leather chemical formulations.
Brominated organic flame retardants	low	A number of polybrominated organic chemicals are restricted. Used for plastics, not water soluble.
Chlorinated paraffins (short chain, C10 – C 13, SCCP)	low-medium	SCCP have been used in fatliquors but today replaced by longer chained versions.
Chlorinated phenols (PCP, TeCP and TriCP)	low	Were used earlier as fungicides, no longer used today.
Chromium (VI)	high	Trace levels of Cr(VI) can form from Cr(III) if tannery leather processing and storage are not made under reductive conditions
Dimethyl fumarate	low	Has been used as shipping container fumigant and inside shoe and upholstery packing. Not used in leather manufacture.
Formaldehyde	high	Residual formaldehyde in leather is not legally restricted in most countries, but it is restricted by eco-labels and brands. Interestingly, limits for leather are typically lower than those in the cosmetic industry!
Heavy metals	medium-high	Restrictions likely to become more stringent, especially for children's toys, this will then be taken over by eco-labels and brands for all materials. The key restricted heavy metals, such as As, Cd, Hg and Pb, are not used in leather manufacture. Care needed if Cr, Cu and Co are listed as they can be used in tannage, or dyes and pigments.
N-methyl pyrrolidone	medium-high	Some years ago restricted in California and now in the EU. Emission into auto cabin air or from furniture is restricted by manufacturers. Solvent used in finishing formulations.
Nonylphenol ethoxylate (NPEO) and nonylphenol (NP)	medium	NPEO was a commonly used non-ionic degreasing agent and detergent in the textile and leather industries. Now replaced in many countries by fatty alcohol products. Sale is restricted in the EU.
Organo tin compounds	low	Used as a fungicide in liquid textile formulations or as catalyst for PVC and PU manufacture.
Perfluorooctane sulfonate (PFOS)	low	These type of fluorochemical finishes were persistent in the environment. The PFOA/PFOS chemistry is restricted and no longer used. Today the fluorochemical products are ecologically better.
Phthalates	medium	A number of phthalates have been legally restricted in many countries, especially for children's items. Phthalates have been widely used to soften polymers. For leather, the finishing formulations have now replaced the forbidden phthalates.
Polyaromatic hydrocarbons (PAH)	low	Typically dark coloured extracts from tar, used as a softening agent for polymers. Unlikely to be used in leather.
Substances of Very High Concern (SVHC)	low-high	Candidate SVHC substances to date (Oct. 2010) are not particularly leather relevant, but the next consulting list contains boric acid and tetraborate that are relevant
Volatile Organic Compounds (VOC) - solvents	medium-high	Highly volatile solvents now not used. A few less volatile solvents, typically in finishing formulations, can be a problem to comply with total emission level requirements for automotive and upholstery specifications.

Several test houses have their own internal test procedures, but until the procedures can be verified by inter-lab comparison trials it is often difficult to validate a method. International standards are verified by validated inter-lab trials to check the test procedure is robust and gives consistent results.

How are detection limits established?

The detection limits for test procedures should be based on inter-lab trials using the best available test procedures.

The detection limits for test procedures need to be respected; recently we have two cases of limits being reduced below what the test procedures can reliably measure. The 30mg/kg limit for aromatic amines in EN ISO 17234-1 was verified in several inter-lab trials. The analytical technique requires an extraction from leather and also a chemical reaction to split up the azo dyes and form the amines. The resulting complex matrix means that the background noise and interference from other extracted substances in the chromatogram was the key factor in establishing this limit. To find some restrictions now requesting a 20 mg/kg limit with the comment – ‘we want to be sure we are under the 30mg/kg limit asked for by the EU’ – ignores the scientific logic for detection limits. Similarly, the EN ISO 17075 Standard for Cr(VI) in leather clearly explains that 3mg/kg is the lowest reliable detection for the procedure, however, some restrictions now list a requirement to measure to 2mg/kg and list the same test method – it is not possible!

What are natural environmental limits?

All around us in our surroundings there are traces of various substances. Requests for exceedingly low levels of, for example heavy metals, can very often be close to or even below the levels found in nature. The leather industry uses hides and skins which have been exposed to nature, as well as water from rivers, the chemical industry uses technical grade raw materials, so it is clear there will be natural levels for some restricted substances. For example, requests for lead (Pb) levels in leather to be less than



0.1mg/kg are likely to be lower than the natural levels typically found in some environments.

What chemicals are of concern?

RSL lists range from small lists to very large lists with many hundreds of different chemical substances. However, only a few of the listed substances are of real concern for the manufacture of leather.

Table 1: some of the most frequently mentioned restricted substances has been prepared to give a simplified overview. The restricted substances are grouped into similar chemical types. The list is not exhaustive, but covers those substances

typically encountered in every day requests from the tanning industry. The relevance of each substance group to the leather manufacturing industry is estimated based on our experiences over recent years. Brief comments are given to help give an understanding of the background to each type of restricted substance; the remarks are especially focused on the restrictions imposed within the EU.

To have a more detailed description of the individual restricted substances, please have a look at the new TFL ECO Guideline on Restricted Substances, which is now available. ■

