Restricted substances in leather

Restricted substances?
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Introduction

This publication is the third of a series that TFL is preparing in order to enhance the understanding of environmental and ecological aspects in leather manufacturing. Worldwide there is a lot of emphasis on operating in a manner that is compatible with the best ecological and environmental practices. This requires many tanneries and supply industries to have a better understanding of the whole ecological process of leather manufacturing from the start to the end.

The tanning industry uses a considerable number of natural and synthetic chemicals to convert the raw hide or skin to leather. At the same time there are increasing pressures on all industries to apply chemicals in a responsible manner using clean technology practices.

The tanneries must comply with a rapidly increasing set of regulations and commercial specifications, which restrict the use of chemical substances considered to have hazardous or toxic properties.

So it is logical that for the leather industry a good understanding of restricted substances is required today. This publication presents the topic in a clear and easy to understand manner for staff working in tanneries and the leather industry.

The first section explains the restricted substances topic.
The second section lists the individual restricted substances relevant to leather.
Restricted Substance Lists (RSL)

Who sets the requirements in RSL?

“Restricted Substance List”, or its commonly used abbreviation “RSL”, has become a common term in the tanning industry.

The first question that immediately arises is: Who sets the requirements in the RSL lists that are on the desk in the tannery office?

Basically there are 2 groups involved:

1) Legislators
   • National regulations and laws
   • International agreements and regulations

2) Manufacturers/Brands and Eco-labels
   • Eco-labels for consumer items
   • Manufacturers and brands

National regulations and laws
Each country has its own regulations and laws regarding chemicals. If we look at restricted chemical substances on a global basis, it is clear that some countries have considerably more regulations in this area than others.

World-wide the strictest regulations for chemicals are those in the European Union (EU) countries, where all the many previous chemical EU Directives have been put together into one Annex (Annex XVII) of the EU Regulation 1907/2006, commonly called REACH. This regulation is mandatory for all 26 EU countries.

The EU Regulation (and the former EU Directives) restricts either:
• the sale or manufacture within the EU of product formulations containing more than certain amounts of chemical substances.
or
• the presence of certain chemical substances in consumer goods.

What does REACH mean for the European tanner?
The European tanner purchasing chemicals from European suppliers will be required to assist in terms of defining the use of the chemicals and the exposure scenarios during their use.
The REACH registration of chemical substances and the considerable costs are the responsibility of the EU chemical manufacturer or importer. Only if the tanners are themselves importing chemicals into the EU, will they be directly involved in the registration process.

What does REACH mean for the non-European tanner?
Tanners in other parts of the world will not need to undertake any registration process but will need to be careful with the selection of their chemical products. If their leather will be exported at some stage to European customers, the leather must comply with REACH restricted substance requirements for consumer items, as given in Annex XVII of the EU Regulation. In addition, the Substances of High Concern (SVHC), as listed in Annex XIV (REACH), must not be present in the leather at more than 0.1% (= 1000 ppm).

Other countries are planning or have already started to implement similar chemical regulations to the REACH Regulation for the EU countries. The hope is that there will not be significant variations between countries in terms of the legislation. Harmonisation of the requirements would be an advantage to all.

In the USA the Federal Agencies, EPA (Environmental Protection Agency) and CPSC (Consumer Product Safety Commission) control regulations and guidelines at a national level. In addition, the individual states have their own regulations. For example, the state of
California has its “Proposition 65” regulation, which protects Californian citizens from exposure to harmful substances.

Japan has regulations for harmful substances; the most commonly seen in the leather industry is the Law 112 restricting harmful substances (e.g. formaldehyde) in household products.

China has national Standards, for example: GB 18401 and GB 20400, which limit the amount of harmful substances in consumer items.

Regulations in one area can very quickly have an impact on a global basis, this is typical of a number of EU restrictions. Many leather articles made in other parts of the world end up being sold in the EU countries. A good example is the forbidden aromatic amines from azo dyes, where the initial EU Directive quickly became the requirement world-wide.

International agreements and regulations
There are several international treaties and agreements administered by the United Nations which limit specific chemicals. Two examples of these international treaties are:

The “Montreal Protocol on Substances that Deplete the Ozone Layer”, designed to globally phase out the use of substances that can cause a reduction in the ozone layer. The Montreal Protocol has been ratified by 196 nations and requires countries to implement their own legislation. For example, the EU Regulation 1005/2009 that lists and controls the use of all the ozone depleting substances in EU countries.

The “Stockholm Convention on Persistent Organic Pollutants (POPs)” is signed by 151 countries. It requires the parties involved to take measures to eliminate or reduce the release of POPs into the environment. Initially 12 POP substances were identified and in May 2009 an additional 9 substances were added. These substances are chlorinated organic pesticides, brominated organic flame retardants and perfluorooctane sulfonates (PFOS).

Eco-labels for consumer items
There are an increasing number of eco-labels available. To be successful, the eco-label needs to be recognised and to be used with consumer items. In most cases, behind each eco-label is a test institute or a group of test institutes, who are responsible for monitoring the compliance and issuing of the eco-labels. In Europe, the promoting, marketing and testing for eco-labels are now a considerable commercial business for those test houses involved.

- Eco-labels and brands are usually the first to react to “chemical dangers”, which are published in media reports and by pressure groups.
- Usually the eco-labels are ahead of any legislation on the topic
- Most have established their own “restricted substance” specifications and these are often mistakenly interpreted by tanners to be official regulations for Europe.

Some typical examples of eco-labels seen in European shops on clothes and leather articles are: Oeko-Tex 100, SG Label, Blue Angel, PFI Label, etc. These labels inform the customer that the consumer article has been tested for harmful substances and is in compliance with the specifications of that particular eco-label.
Note: Many eco-labels are strongly textile oriented and, for example, restrict the total chromium (Cr) to very low values, which makes it effectively impossible that chrome-tanned leather articles can comply.

EU Footwear Eco-Label
The EU Footwear Eco-Label has been developed to use the “EU flower” eco-label for footwear that comply with restricted substances in the shoe and packaging, as well as complying with ecological requirements during the various material and shoe manufacturing operations and during its use.

The aims of this eco-label are clearly correct but without a commercial organisation promoting and marketing it, like other successful eco-labels, it will be difficult to get acceptance by the footwear industry.

Environmental impact and life cycle analysis considered by the EU Footwear Eco-Label:
- packaging
- emissions while producing material, especially leather tanneries (COD criteria for waste water, Cr recovery, short chain chlorinated paraffins, forbidden chemicals)
- energy consumption
- end of life - best use option
- PVC, nitrosamines in rubber
- durability criteria

Manufacturers and brands

Global brands
The global brands, some examples are Adidas, Nike, H&M, Clarks, IKEA, etc., publish their own lists of restricted substances and update them at regular intervals. The limit values in the lists are for leather and other materials being used by these global brands. Many tanners supplying the global brands then copy these lists and pass them on down the supply chain, for example to their chemical product suppliers, with the same limits and the same test methods. In many cases the test methods are specifically for leather and not suitable for analysing chemicals. In most cases the global brands base their specification limit values on the regulations that exist.

For example, the limit for nonylphenol ethoxylate surfactants (NPEO) in leather is often 1000 mg/kg as in the EU Regulation for chemical formulations. When a regulation does not exist, the brands establish their own limit values. For formaldehyde in leather, where there is no EU Regulation, the typical limits in leather with skin contact are 20 mg/kg for baby shoes and 75 mg/kg (Japan) / 100 mg/kg for adult clothes and shoes. If there is no skin contact, the formaldehyde limits are typically around 300 mg/kg. Interestingly the cosmetic industry allows skin contact items with considerably higher levels for releasable formaldehyde.

Automotive industry
The European automotive industry has to comply with the End of Life Vehicle Directive requirements and has set up a data base to record each component used in cars. To ensure that information on restricted substances is collected world-wide, the Global Automotive Declarable Substance List (GADSL) has been established and requires those in the supply chain to provide information for the listed 139 substances. The GADSL list is normally updated each year.

The Japanese automotive industry (JAMA) introduced in 2005 voluntary air quality standards which limit the emissions inside cars. This data was taken directly from that for emissions inside houses and corrected for the volume difference; so it also included some household substances that are not found inside a car. More important is that in addition to formaldehyde, for the first time acetaldehyde was restricted - at a very low level. Acetaldehyde is a substance that is not used in leather chemical formulations, but it is sometimes found in leather emission tests at low levels. At present the origin of this substance is not clear.

For example, the possibility that traces of acetaldehyde form during the analytical testing cannot be ruled out at this stage.

The JAMA test procedure involves sampling air from inside a car and this is now in the process of being formalised as an ISO Standard (ISO 12219-1). For those involved in supplying leather and other car interior materials, this is not a practical procedure for evaluating individual items. Several test methods for sampling air using samples in closed bags or chambers have been developed as more practical ways of
analysing the emissions. At this stage there are still variations in the temperature, humidity and air flow between the methods.

**What chemicals are restricted?**

There are important differences between what is being restricted and it is important to understand this.

**EU Regulations (REACH) and Directives**
- either – limit the amount of restricted substance in a chemical formulation.
- or – limit the amount of restricted substance in the consumer article.

**Eco-labels and brands**
- their specifications restrict the substance in the material (e.g. leather).

**Specifications and test methods**
Many tanners pass restricted substance lists with specifications and test methods onto their chemical suppliers, asking them to guarantee that the chemicals comply with the same specifications as they must meet for the leather. That the specifications and test methods are specifically for leather is often not understood. The test methods listed are in most cases only relevant for testing leather and not suitable for testing chemical products. For example, requests to test dyes for formaldehyde (EN ISO 17226-2) and Cr(VI) (EN ISO 17075) using colorimetric test methods is simply not possible. Trying to determine the formaldehyde content in chemicals according to EN ISO17226-1 gives wrong results, since this test method requires an acidification to low pHs, causing the break-down and possible release of bound formaldehyde from the chemical. It is correct to acidify a water extract of the leather to determine the formaldehyde content, but it is not correct to acidify a chemical solution.

One commonly listed test method for heavy metals, EN 71-3, is a method for toys. What many do not realise is that the extraction process is made with a hydrochloric acid solution between pH 1.0 – 1.5, in order to simulate the conditions inside the human stomach. These very acid conditions are likely to extract some Cr from chrome tanned leather and there could be difficulty for leather to comply with the extractable Cr limit.

For extractable heavy metals the new method, EN ISO 17072-1, which uses a synthetic perspiration solution at pH 5.5, is a realistic and correct test for leather. Many brands and eco-labels have recognised that for clothes the synthetic perspiration extraction method at pH 5.5 (typically written EN ISO 105-E04) corresponds to the real-life situation and they use this extraction specification.

**Who develops test methods for leather?**
Most of the restricted substance lists also show 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 quite often no international leather method available and many simply list brief instructions like “solvent extraction, GC-MS”.

RSL lists often give 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. 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 such a method. The international ISO Standards are verified by validated inter-lab trials to check that the test procedure is robust and gives consistent results between laboratories.
How are detection limits established?
The detection limits for test procedures should be based on inter-lab trials using the best available test procedures. Sometimes the limit is based on several factors, such as the extraction from a difficult matrix like leather, which causes background noise in chromatograms. Once the analytical result variability between labs exceeds 50%, then typically this is the detection limit for this method. Important is that the detection limits are not established using pure substances, since this ignores the critical impact of the leather extraction. Very important is that detection limits for test procedures are recognised and respected; recently there have been 2 cases of detection limits being reduced below what the test procedures can reliably measure. For example, the 30 mg/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 as well a reduction reaction to cleave 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 30 mg/kg limit. To find some restrictions now requesting a 20 mg/kg limit with the comment – we want to be sure we are under the 30 mg/kg limit of the EU – ignores the scientific logic for detection limits. Similarly, the EN ISO 17075 Standard for Cr(VI) in leather clearly explains that 3 mg/kg is the lowest reliable detection for the procedure. However, some restrictions now list a requirement to measure to 2 mg/kg and list the same test method – it is not possible!

It must not be forgotten that it is not the detection limit of the reference sample in pure solvent that counts, but rather the detection in the leather extraction matrix, which can be a complex mix of side reactions and extracted materials that are removed from the leather.

What are natural environmental limits?
All around us there are traces of various chemical substances. Requests for exceedingly low levels of restricted substances can very often be close to or even below the levels found in nature. The leather industry uses water from rivers and wells, the chemical industry uses technical grade raw materials, so it is clear there will be natural levels for some restricted substances. Also often overlooked is that our natural raw material, namely the hides and skins, will also contain natural trace levels of restricted substances; for example, heavy metals. Some recent requests for lead (Pb) levels in leather of less than 0.1 ppm are probably lower than that typically found in the natural environment.
What chemicals are of concern?

RSL lists range from small lists with the key substances relevant for leather, to very large lists with many 100s of different chemical substances. However, only a few of the listed substances are of real concern for leather. In the following section the most relevant substances for leather have been put into groups and are reviewed in detail. Listed here are the groups of chemical substances.

Legally restricted chemical substances
The following chemical substances are restricted through legal restrictions.

- Allergenic and sensitising dyes
- Aromatic amines from azo dyes
- Boron containing substances
- Brominated organic flame retardants
- Chlorinated paraffins (short chain, C10 – C 13, SCCP)
- Chlorinated phenols (PCP, TeCP and TriCP)
- Chromium (VI)
- Dimethyl fumarate
- Heavy metals
- N-methyl pyrrolidone
- Nonylphenol ethoxylate and nonylphenol
- Organotin compounds
- Perfluorooctane sulfonate (PFOS)
- Phthalates
- Polyaromatic hydrocarbons (PAH)
- Substances of Very High Concern (SVHC)

Chemical substances restricted by eco-labels and brands
The following chemical substances can be restricted by eco-labels and brands.

- Formaldehyde
- Acetaldehyde (air emission)
- Biocides (air emission)
- Volatile organic substances (VOC) (air emission)

Summary

It is a problem for tanners to find their way through the jungle of regulations and customer requirements for restricted substances. Many substances in the long lists have no relevance for the leather industry; take the example of a tanner requesting a written statement that there is no asbestos fibres in the leather chemicals he is using.

Harmonisation of the large numbers of restricted substance lists would be a very positive thing for all concerned, but unfortunately it is probably unrealistic in today’s environment. The tanner and the chemical supplier will have to learn to work with an increasing number and types of restrictions to the best of their abilities.

Keeping up-to-date with restricted substance regulations and lists is not easy as there are continually new restrictions being introduced. The Substances of Very High Concern (SVHC) part of the REACH Regulation is starting to look at substances on a risk-analysis basis. It already has some 38 candidate substances and will no doubt add more in the next months and years. A publication like this one can only give a picture of the situation as of 2010.
Information on Restricted Substances (alphabetic order)

Here is listed some basic information about each of the restricted substances that could be relevant for leather. These substances or group of substances are the ones typically encountered and are not an exhaustive list of all restricted substances. The information below is only an overview and the individual regulations need to be consulted for full details.

To help find the restricted substances quickly they are listed in alphabetical order.

 Listed at the end of this section are several substances and substance groups that are not relevant for leather, but are still very often requested.

### Allergenic and sensitising dyes
- These dyes are typically disperse dyes, which are used for colouring textiles. The problem occurs with skin contact to the coloured material.
- Disperse dyes are not water-soluble so are not normally used for dyeing leather.

### Aromatic amines from azo dyes
Azo dyes are some 90% of all leather and textile dyes. Azo dyes break down under reductive conditions to form aromatic amines.
- 22 aromatic amines are forbidden in the EU Regulation 1907/2006 Annex XVII and listed in Appendix 8. These 22 amines are known to be carcinogens or potential carcinogens.

The EU Regulation specifies in Appendix 10 the test method for each type of substrate and in Annex XVII defines the detection limit of 30 mg/kg for each amine in leather. The official test method for leather is CEN ISO/TS 17234; this method is now updated and replaced by EN ISO 17234-1.

Until now eco-labels and brands have used the EU limit of 30 mg/kg, however;
- In 2009 China introduced a 20 mg/l limit and some global brands have started to also specify this limit which is lower than the EU Regulation.

- The leather extraction and chemical reaction step gives a complex matrix and analysing at less than 30 mg/kg can result in considerable variations and possible wrong assignments of amines. This was the reason for setting the limit value at 30 mg/kg in the EU Regulation.

#### Careful:
A small number of eco-labels restrict 2 additional aromatic amines that are not forbidden. Some test houses measure the presence of the forbidden amine, 4-aminoazobenzene, by analysing for the 2 amines, 4-aminooaniline (p-phenylene diamine) and aniline, both which are not forbidden. Depending on the reduction conditions it is possible that for the widely used black dye, C.I. Acid Black 210, some 4-nitroaniline is reduced to 4-aminooaniline, which can lead to test houses giving a false positive result for 4-aminoazobenzene. The new method, EN ISO 17234-2 should be used for testing leather for 4-aminoazobenzene.

### Biocides
The EU Directive 98/8/EC, Biocidal Products Directive (BPD), controls and regulates the use of biocides, they are not part of REACH. Registration of a biocide is very expensive and only a few active biocide substances are expected to be available for the leather industry in the near future.

Biocides are applied to raw hides & skins (bactericides) and in pickling/tanning (fungicides) to stop the leather being damaged during transport and storage. Some of the chlorinated phenol type of biocides are now restricted. Only a few fungicides dominate the leather industry usage. The big 4 fungicides are commonly known by their abbreviations, for example, PCMC (para-chlor-meta-
cresol), OIT (2-n-octylisothiazolin-3-one), OPP (ortho-phenylphenol), TCMTB (2-(thiocyanomethylthio) benzothiazole).

The eco label, “Der blaue Engel” (the blue angel), gives recommendations for allowable limits in leather of the active fungicide components: PCMC < 300 mg/kg, OIT < 100 mg/kg, OPP < 500 mg/kg and TCMTB < 500 mg/kg.

Biocides are also used to stabilise chemical products that contain natural or biodegradable substances. These can be susceptible to bacteria or fungi attack. However, the quantity of biocide that would then be applied to the leather with the chemical is some 100 to 1000 times less than is applied to protect leather in the beamhouse process.

**Specific TFL comment:**
TFL has ARACIT® bactericides and as partner of Thor, a manufacturer of biocides, TFL promotes the Acticide fungicides based on OIT.

**Boron containing substances**
Boric acid and disodium tetraborate, commonly called borax, have recently been notified as candidates in the SVHC decision making process. They are classified as toxic for reproduction. These boron compounds are widely used in many industries and if they do become SVHC substances, then their limited use in some leather industry processes will need to be replaced.

Boric acid is used in some deliming formulations and borax has been used in small amounts in leather chemical formulations to adjust the pH and penetration.

**Specific TFL comment:**
Leather made with the international range of TFL leather chemicals would comply with the SVHC requirements.

**Brominated flame retardants**
A group of polybrominated flame retardants are restricted. They are used in plastics.
(They are not water soluble so not suitable for wet-end leather applications).

**Specific TFL comment:**
The SELLA® tec products from TFL do not contain polybrominated organic flame retardants.

**Chlorinated paraffins (SCCP, short chain)**
Short chained chlorinated paraffins (SCCP) are those with a chain length of C10 – C13.

EU Regulation 1907/2006 (formerly as EU Directive 2002/45/EC) restricts the marketing and sale of SCCP in preparations to a maximum of 1% (= 10 000 mg/kg).

Analytical methods to determine SCCP in leather are still being developed. Currently there is no validated test method available.
Note: the medium chain MCCP (C14 – C17) and long chain LCCP (C18 – C30) chlorinated paraffins are not restricted by EU Regulation. The presence of MCCP must be listed in the Safety Data Sheet.

Specific TFL comment:
The international range of CORIPOL® fatliquors from TFL comply with the EU Regulation restricting SCCP.

Chlorinated phenols (PCP, TeCP and TriCP)
Chlorinated phenols were previously used extensively to inhibit mould growth. The 3 chlorophenols listed are now forbidden in consumer products:
- PCP (pentachlorophenol)
- TeCP (tetrachlorophenol)
- TriCP (trichlorophenol)

The detection level of 5 mg/kg has become the accepted limit using the EN ISO 17070 test method for leather.

Specific TFL comment:
TFL does not use PCP, TeCP and TriCP in the TFL range of leather chemicals.

Chromium (VI)
The hexavalent chromium oxidation state (Cr(VI)) is carcinogenic and restricted by the EU. The detection limit is 3 mg/kg in the leather test method, EN ISO 17075. This is the level generally accepted for Cr(VI) in leather. Some eco-labels and brands try to be one step better and specify 1 or 2 mg/kg, but they list the same test method. This is not correct as the ISO Standard method includes information clearly pointing out how the 3 mg/kg detection limit was established. Lower detection limits cannot be justified with this technique.

The Cr-containing chemicals used in the manufacture of leather are based on Cr(III). However, during manufacture it is possible that traces of Cr(III) can be oxidised to form Cr(VI) if the application process is not kept under reductive conditions. This is one restricted substance where, through the choice of the application process, the tanner is responsible for avoiding its presence.

The Cr(VI) oxidation state does not form organic complexes, so the stable organic Cr(III)-complex dyes do not form Cr(VI) in the leather.
Careful: Analyses for total Cr measure all the oxidation states of chromium. This technique cannot be used to determine the Cr(VI) content.

Specific TFL comment:
The Cr-containing TANNESCO® syntans from TFL contain only Cr(III) salts, no Cr(VI) is present.

The use of the novel product SELLASOL® C6 in the last step of wet-end operations helps to eliminate the presence of any Cr(VI) in the leather. SELLASOL® C6 can also retard or prevent the formation of Cr(VI) during transport or storage.

Dimethyl fumarate
Dimethyl fumarate is a solid, which sublime to a gas. It has good anti-fungal properties, so it has been used in sachets inside the packaging for sofas, shoes and boots, especially those items being exported from Asia to Europe.

Dimethyl fumarate is an allergic sensitizer at low concentrations and can cause severe skin rashes and irritations.

Since 2009 the EU has forbidden the marketing of any products containing dimethyl fumarate. It is not used as a biocide for leather, the problem was caused by the inclusion of dimethyl fumarate inside the packaging and it depositing on the surface of the consumer goods.

Careful: Dimethyl fumarate is commonly referred to as DMF in publications and the media. It should not be mixed up with the solvent dimethyl formamide that chemists have traditionally called DMF.

Specific TFL comment:
TFL does not use dimethyl fumarate in the TFL leather chemical products.

Formaldehyde
Formaldehyde is used extensively for making industrial chemicals. For example, in the leather industry many syntans are formaldehyde polymers. Once the formaldehyde has reacted it is no longer present as formaldehyde. Some small residues of unreacted formaldehyde can occur in a few products, typically melamine resins and some cationic dye fixing agents.

Different analytical procedures are used to measure the free unbound formaldehyde and the hydrolysable formaldehyde (only released by interaction with water).

For leather used in automotive seats the free formaldehyde test (emission into air) is important. For leather in shoes with skin contact the water extraction method determines the free and hydrolysable formaldehyde.

There is currently no EU regulation restricting the use of formaldehyde in leather.
- Japan and China have restrictions for clothes, especially those in skin contact
- Eco-labels and brands set formaldehyde limits
- The automotive industry has limits for formaldehyde emissions into the cabin air

Careful: select the correct analytical methods for leather.
- water extraction (EN ISO 17226-1) – measures free and hydrolysable formaldehyde
- emission into air (EN ISO 17226-3) – measures free formaldehyde

Specific TFL comment:
The SELLATAN® and SELLASOL® syntan products are either low formaldehyde or formaldehyde-free (for both the free and hydrolysable formaldehyde). With suitable application processes, leather can be prepared to comply with the very low residual formaldehyde requirements given above.

For example, by using a syntan like SELLATAN® WL-W and the auxiliary syntans SELLASOL® HFN, SELLASOL® FTF or SELLASOL® MI, it is possible to make leathers that are free of residual formaldehyde.

The MAGNOPAL® polymer retanning agents are free of formaldehyde.
Heavy metals
EU limits for heavy metals in consumer items have been introduced via the EN Standard for extractable heavy metals in toys. In the USA the CPSC sets levels for heavy metals in consumer items. The EN 71-3 method has defined the following maximum limits for extractable heavy metals: As: 25 ppm, Cd: 75 ppm, Total Cr: 60 ppm, Hg: 60 ppm, Pb: 90 ppm, Sb: 60 ppm, Ba: 1000 ppm, Se: 500 ppm. The low pH extraction process could make it difficult for Cr-tanned leather to comply.

Eco-label limits for heavy metals are often much lower and normally they also specify total metal. For example, some textile eco-labels set very low limits for total Cr. Obviously achieving these lower levels is not possible with Cr-tanned leather. Other eco-labels, such as the SG Label, accept Cr-tanned leather and restrict only the extractable Cr and Cr(VI).

Careful: check if the specification is for extractable or total metal content and check which extracting agent is specified!
- the extraction is at pH 1 – 1.5 for the EN 71-3 method for toys
- eco-labels often specify extraction with a pH 5.5 synthetic perspiration solution (prepared according to ISO 105-E04)

Specific TFL comments:
Other than Cr, TFL is not adding the above heavy metals (As, Cd, Cr, Hg, Pb, Sb, Ba, Se) to the international range of TFL products.

Some dyes are organic metal complexes of either Cr, Co, Cu or Fe. This information is listed in section 12 of the TFL Safety Data Sheet. The TFL dyes and pigments comply with ETAD guidelines for heavy metals.

N-methyl pyrrolidone
N-methyl pyrrolidone (NMP) has been extensively used as a high boiling point solvent and flow-improver in finishing formulations. In the Californian Proposition 65 legislation, NMP was classified as toxic for reproduction. In the EU, the classification has now been changed to toxic for reproduction and from the end of 2010 any product formulation containing quantities of NMP above 0.1% must list this in the Safety Data Sheet. Most brands and automotive manufacturers now do not allow the use of NMP in finishing products.

Specific TFL comment:
TFL has a NMP-free range of RODA® finishing products.

Nonylphenol ethoxylate and nonylphenol
The EU Regulation requires that nonylphenol (NP) and nonylphenol ethoxylate (NPE or NPEO) are not to be used in preparations at levels greater than 0.1% during leather (or textile) processing if the waste water is discharged. The generalised form of these type of substances is written as APEO (alkylphenol ethoxylate).

Until recently the nonylphenol ethoxylates were used extensively as non-ionic surfactants and emulsifiers in the textile and leather industry. In Europe they have now been replaced by alternative surfactants.

In order to show NPEO containing preparations have not been used, Eco-labels can require less than 100 mg/kg in leather.

Specific TFL comment:
The TFL international range of BORRON® surfactants are not based on nonylphenol ethoxylate.

Organotin compounds
TBT (tributyl tin), DBT (dibutyl tin) and MBT (monobutyl tin) are restricted chemicals. These are used as antimicrobials, e.g. in paints for boats.

Tin compounds can be used as catalysts in the production of PU polymers. Trace levels of organotin compounds may be present in PU finishes but after application they will be fixed.

Specific TFL comment:
TFL does not add restricted organotin compounds to the leather chemical products.

Perfluorooctane sulfonate (PFOS)
The fluorchemical of the type PFOS (perfluorooctane sulfonate) has been found to be persistent in nature...
so it has been forbidden. The EU Regulation limits PFOS to 0.005% by mass in consumer goods. Analytical methods are complicated and still in development. The corresponding acid form, PFOA, is usually also restricted by brands and eco-labels.

**Specific TFL comment:**
TFL does not have PFOS or PFOA in the fluorchemical products it supplies.

**Phthalates**
6 phthalates (DINP, DEHP, DNOP, DIDP, BBP and DBP) are restricted in the EU.

These are used as softening agents in plastics to give it the required flexibility.

The EU Regulation limits individual phthalates to 0.1% (= 1000 mg/kg) in chemical preparations.

Eco-labels and leather shoe manufacturers typically set limits of < 500 mg/kg total phthalates in leather.

**Specific TFL comment:**
TFL does not use the restricted phthalates in the leather chemical products.

**Polycyclic aromatic hydrocarbons (PAH)**
Polycyclic aromatic hydrocarbons (PAH) are present in tar oils. These typically dark coloured extracts are used as cheap softening agents in rubber and some plastics. It is most unlikely that they would be used by the leather industry.

**Specific TFL comment:**
TFL does not have PAH in the leather chemical products.

**Substances of Very High Concern (SVHC)**
Substances of Very High Concern (SVHC) are an important new part of the REACH Regulation (EU 1907/2006) in the EU. After a consultancy process and risk evaluation, those substances that are considered to be SVHC will be listed in Annex XIV of the EU Regulation. Currently there are 38 chemical substances in the SVHC candidate list, but at present none
have yet been assigned SVHC status in Annex XIV. Each EU member country can introduce substances (with supporting documentation) for the candidate list. After this, the candidate substances undergo a risk assessment process before the decision is made about becoming a SVHC substance in Annex XIV. The risk assessment evaluation is an important step in judging the potential harm of chemical substances.

The EU Regulation requires that special efforts should be made in manufacturing processes to replace the use of any Annex XIV listed SVHC substances.

Consumer articles, e.g. leather, containing more than 0.1% of a SVHC substance will not be allowed to be imported into the EU region.

The current 38 candidate SVHC substances, except for the recently announced boric acid and disodium tetraborate, are not likely to be used by today’s leather industry.

Specific TFL comment:
As soon as a chemical substance is put on the candidate list many brands and eco-labels react immediately restricting the use of the candidate substance. From a legal point of view, candidate chemicals can still be used and in many cases the residual amount in leather may not exceed 0.1%.

Volatile Organic Compounds (VOC)
Volatile organic compounds (VOC) refer to organic solvents, especially those with a boiling point between 50°C – 260°C. If present, these organic substances can be emitted into the air during leather production, especially in the finishing process. The EU regulates the amount of VOC output that can be emitted into the air with respect to leather manufacture.

The automotive and upholstery industries place restrictions on the VOC emission from leather. Both industries have different test methods and requirements. The VOC is measured by heating the leather in a closed chamber and the individual emitted VOC substances are determined by a mass spectrometer. The results can be influenced by the time since the leather was made and the storage method. The very volatile compounds (VVOC) are those with a boiling point below 50°C. The semi-volatile organic compounds (SVOC) have boiling points between 260°C – 400°C.

Specific TFL comment:
By using suitable TFL products it is possible to comply with the total VOC emission requirements set by brands and eco-labels.

Restricted substances not relevant to the leather industry

Some tanneries give to their chemical suppliers long lists of restricted substances that they have received from their customers. Many of the listed substances have effectively no relevance for the leather industry of today. For many of them the only reason for listing seems to be for completeness and perhaps to make additional tests.

Typical non-relevant substances for leather are:

- asbestos
- blue colorant
  The EU Regulation 1907/2006 (formerly in EU Directive 2003/03/EC) bans the use of a “blue colorant”, Index No. 611-070-00-2. According to current knowledge this forbidden blue colorant has never been sold to the world-wide leather industry. No samples of the dye have been able to be located so it is not possible to analyse for this colorant.
- chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC)
- heavy metals: arsenic (As), beryllium (Be), bismuth (Bi), cadmium (Cd), mercury (Hg), selenium (Se)
- nickel metal
- pesticides
- polycyclic aromatic hydrocarbons
- polychlorinated biphenyls (PCB) and terphenyls (PCT)
- polyvinyl chloride (PVC)
Is leather safe?

Considering the many possible substances of concern, one may ask how safe leather really is and how safely it can be made?
The simple answer is: Leather made with state of the art technology and chemicals is a very safe product. It is possible to manufacture leathers that comply with the most stringent requirements as to restricted substances and no health risks can be associated with such leather, which is formed from a natural product.
This requires that manufacturers take care to select the appropriate processing chemicals and apply them correctly. TFL has been pioneering the area of ecological leather manufacturing through the development of the TFL White Line Technology.
Leathers made with White Line Technology comply with the very stringent SG Label standards. White Line leathers have been tested by dermatologists on highly sensitive test persons and found not to cause any allergic reaction.
ARACIT®
Preserving agents for the short-term preservation of fresh-hides and for soaking.

BORRON®
A range of surfactants and degreasing agents, as well as sequestering agents. High efficiency, tailor made products for all process steps.

CORIPOL®
A range of fatliquoring agents based on natural and synthetic fatty substances.

RODA®
The TFL range of products suitable for use in the finishing of leather in all types of manufacturing processes.

SELLA® COOL
A range of selected dyes that comply with the TFL COOL System requirements. They do not absorb radiation in the near-infrared, which restricts the rise of temperature on the leather surface when it is exposed to sunlight.

SELLA® DERM
A range of concentrated solutions of homogeneous, salt-free, mainly metal complex dyes in water-miscible and environmentally acceptable organic solvents.

SELLA® FAST
A large range of acid and direct dyes for the coloration of leather where good levelness, covering power, brilliance, shade consistency and good fastness properties are required.

SELLA® STAR
A compact range of special acid dye mixtures to produce various brown, beige and olive shades, featuring good general fastness properties.

SELLA® tec
A group of leather chemical products suitable for manufacturing flame retardant leather.

SELLASET®
A range of 1:2 metal complex acid dyes especially suitable for trichromatic dyeing systems.

SELLASOL®
A range of auxiliary syntans for the retanning of leather.
For further information have a look at www.tfl.com or contact ecology@tfl.com