TFL ECO TEC ET

# Restricted substances in leather

» TFL Eco Guidelines – Your guide through the maze of RSL lists

TFL – Great chemicals. Excellent advice.

# Contents

## Restricted Substances list



## Information on Restricted Substances

# Introduction

This publication is the latest update of our volume on Restricted Substances and is part of a series that TFL is preparing in order to enhance the understanding of environmental and ecological aspects in leather manufacturing. Worldwide there is increasing 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 start to finish.

Chemicals, whether from synthetic or natural origin, play a significant role in the the tanning industry since they end up either in the final leather and potentially also in wastewater, sludge, by products and gaseous emissions. There is increasing pressure to use chemicals which do not harm the consumer and the environment and to apply them in a responsible manner using clean technology practices. 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.

Restricted Substance List
has become a common term
in the tanning industry.

National regulations and laws

# A multitude of regulations

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

It is important to distinguish between a
- **Product Restricted Substance List** (often called PRSL) which restricts the use of chemicals in the final product (i.e. leather) and
- **Material Restricted Substance Lists** (i.e. MRSL issued by ZDHC) which addresses restricted chemicals in the chemical product used for making leather.

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, Ecolabels, NGO's and consortiums (such as ZDHC)**
- Ecolabels for consumer items
- Restricted Substance Lists (RSL) for consumer products like leather
- Restricted Substance Lists for chemical products (i.e. MRSL issued by ZDHC)

## 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.

**REACH**

Worldwide 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-REACH 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 a chemical from a European supplier will be required to disclose to the chemical supplier the use of such chemical to ensure that a valid, risk based exposure scenario for the identified use can be established. The REACH registration of a chemical substance and the considerable costs associated with it are the responsibility of the EU chemical manufacturer or importer of the chemical. Only if the tanners are themselves importing chemicals into the EU, they will 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).

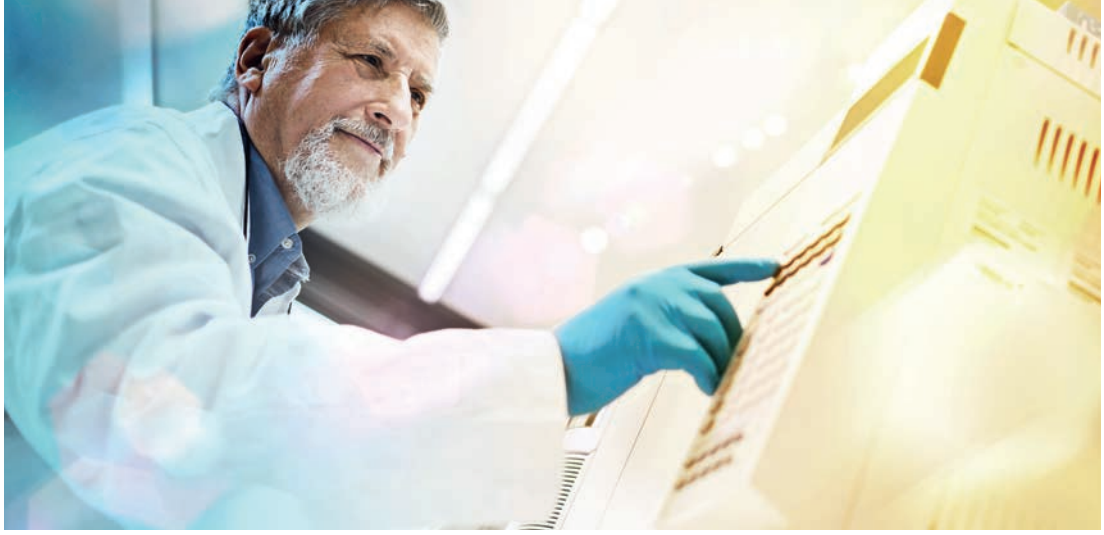
Other countries are planning or have already started to implement similar chemical regulations to the REACH Regulation for the EU countries. The hope is that there will not be significant variations between countries in terms of the legislation. Harmonisation of the requirements would be an advantage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

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 certain harmful substances whose presence has to be listed on consumer items with appropriate warning phrases.

**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 or in countries which exercise similar chemical regulatory practices. A good example is the forbidden aromatic amines from azo dyes or PCP (Penta Chloro Phenol), where the initial EU Directive quickly became the requirement worldwide.



## 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 implemented 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 perfluoroctane sulfonates (PFOS).

## Ecolabels for consumer items

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

- Ecolabels and brands are usually the first to react to "chemical dangers", which are published in media reports and by pressure groups
- Usually the Ecolabels 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 Ecolabels seen in European shops on clothes and leather articles are: Oeko-Tex 100, SG Label, Blue Angel issued by the German Government for Environment, 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 Ecolabel.

**Note:** Many Ecolabels 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.

**Behind each Ecolabel stands mostly a test institute or a group of test institutes.**

**The MRSL List by ZDHC:**
The MRSL issued by ZDHC can be seen as an important approach consolidating valuable RSL data into one managebale list of restricted chemicals.

**EU Footwear Ecolabel**
The EU Footwear Ecolabel has been developed to use the "EU flower" Ecolabel 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 Ecolabel are well intended but without a commercial organisation promoting and marketing it, like other successful Ecolabels, it will be difficult to get acceptance by the footwear industry.

EU Footwear label addresses the Environmental impact and life cycle analysis considering:
- Packaging
- Emissions while producing material, especially leather tanneries (COD criteria for waste water, Cr recovery, short chain chlorinated paraffins, forbidden chemicals)
- Energy consumption and product environmental footprint
- End of life – best use option
- PVC, nitrosamines in rubber
- Durability criteria

## Manufacturers, brands, NGO's

**ZDHC Programme –**
**Zero Discharge of Hazardous Chemicals**
The ZDHC foundation is a collaboration of Green Peace with global signatory brands, value chain affiliates and associates whose goal is the elimination of hazardous chemicals from the textile and footwear supply chain. The ZDHC programme is based on Input Stream Management which means regulating the use of hazardous chemicals right from the beginning of the value chain. ZDHC has established a **Material Restricted Subtsance List (MRSL)** not only for textile industry but also recently for leather chemicals. The MRSL list gives allowable limits of hazardous substances and the related testing methods for such chemicals. The MRSL is based on data from important national and international regulations and studies but also on the input from brands and manufacturers. The MRSL can be seen as an important approach consolidating valuable RSL data into one managebale list of restricted chemicals.
The MRSL list is a living document and currently does not include biocides and substances like formaldehyde which are addressed by individual RSL and regulations.

**Global brands**
The global brands, some examples are Adidas, Nike, H&M, Clarks, IKEA, etc., publish their own lists of restricted substances (RSL) 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 use or 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 various regulations that already 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 but there are brands which set limits as low as 100mg/kg (100ppm).

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. Often allowable limits in RSL lists are not clearly science or risk based but are a precautionary measure or result from 'green' competition.

**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 worldwide, 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.

In the recent past an increased emphasis is put on interior car air quality where car seat leather plays an important role with regards to emissions of volatile substances, which are hazardous and of potentially unpleasant odor.

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. (see page 16).

The **GB/T 27630-2011 (Guidelines for Air Quality Assessment of Passenger Vehicles)** issued by the Chinese Ministry of Enviornmental Protection goes in a similar direction as JAMA but including further hazardous substances (see page 16)

## Chemical substances of concern in leather manufacture

RSL lists range from small lists with the key substances relevant for leather, to very large lists with many hundreds of different chemical substances of which only a few are of real concern for leather. In the following section the most relevant substances for leather are put together (They are reviewed in more detail in section Restricted Substances) (see page 16)

**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 and related PFOA)
- Phthalates
- Polyaromatic hydrocarbons (PAH)
- Substances of Very High Concern (SVHC)

**Chemical substances restricted by Ecolabels, brands and manufacturers**

The following chemical substances can be restricted by Ecolabels and brands:

- Formaldehyde
- Acetaldehyde (air emission)
- Biocides
- Hazardous volatile organic substances (VOC)

**Global Automotive Declarable Substance List:** Despite the fact that RSL product lists contains hundreds of substances only few are of real concern.


**Difficult problems for tanners:**
The most promising approach however in this direction is the Material Restricted Substance List for chemical products used for leather manufacture.

## How to comply with the various RSL lists?

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 considering the various interest of all stakeholders it is not easy to achieve in today's environment. The most promising approach however in this direction is the Material Restricted Substance List for chemical products used for leather manufacture. It list all chemical substances which should not be present in a chemical product beyond a given limit. The MRSL is issued by ZDHC a multistake holder association where NGO, brands and chemical manufacturers (via the LWG-Leather Working Group) and other experts working together. The MRSL list is being updated continuously and represents state-of-the-art knowledge on restricted substances. It is an approach which is based on Input Stream Management which means avoiding restricted substances right from the beginning of leather manufacture.

Not included in the MRSL list are biocides and products like formaldehyde, acetaldehydeand chromium(VI) which need to be addressed individually and be tested for. Apart from these the ZDHC-MRSL list is likely to cover the rest of the RSL requirements from brands and manufacturers. TFL uses the ZDHC–MRSL requirements as a base for their RSL management policy which also takes into account other legal requirements.

## TFL Product Compliance Policy

### 1. Regulatory compliance

The chemicals of TFL listed in Annex A of this declaration:

- Comply with the European Union (EU) regulations 1907/2006 (REACH) and 1272/2008 (CLP Regulation). As required by these EU Regulations, TFL identifies hazards in Section 2 of the respective Safety Data Sheet (SDS) and lists substances classified as hazardous to health or the environment clearly in Section 3 of the respective SDS. The SDS is the legally prescribed document regarding safety of individual chemical products supplied.

- Comply with the REACH requirements for Substances of Very High Concern (SVHC) in REACH Annex XIV (authorisation) and in the Candidate List for SVHC (according to art. 59.1 of REACH).

TFL products listed in Annex A are in compliance with the SVHC and SVHC candidate list, including its concentration limit requirements. The SVHC candidate substance list is updated every 6 months and available at: http://echa.europa.eu/candidate-list-table

- Comply with the restricted substance requirements of REACH Annex XVII REACH Annex XVII contains the EU restrictions for the manufacture, marketing and use of chemical substances, and is available at: http://echa.europa.eu/addressing-chemicals-of-concern/restrictions/substances-restricted-under-reach

- Comply with EU Biocide Regulation 528/2012TFL leather chemicals comply with EU regulation 528/2012 concerning the sale and use of biocidal products. The text of the regulation is available at: https://echa.europa.eu/regulations/biocidal-products-regulation/legislation

**2. Compliance with the requirements of the Manufacturing Restricted Substances List (MRSL) of ZDHC (Version 1.1, December 2015)**

TFL has issued a separate Product Compliance Statement which is updated regularly and which applies to all TFL products. In a special Annex it also lists the (trace) level amounts of formaldehyde, phenol and metals contained in some TFL products. It also listss biocide actives TFL is using and which all comply with EU Biocide Product Directive (BPD). Such a Product Complaince Statement is a living document since the substance lists are continually being updated. Many of them derive from REACH where Substances of Very High Concern are identified on a risk and science based analysis and put onto the SVHC list (see page 6).

Based on practical tests and experience TFL believes that by using their products in a correct way it is possible to make leather which is safe to the consumer and the environment and which satisfies all major RSL requiremenst in the industry.

**Verification of a chemical supplier's conformance**

It is the right of a leather manufacturer to know how trustworthy a RSL statement issued by a chemical supplier really is. If he can rely on a chemcials suppliers statement he will be able to eliminate a lot of (unnecessary) testing of his final product and focus on substances which can be formed or reduced during manufacture (e.g. Cr(VI), formaldehyde, acetaldehyde).

In the textile chemical industry audit and certification systems for chemical suppliers already exist (i.e. BlueSign, GOTS, OekoTex Eco Passpart). For the leather chemical industry discussions are on the way to develop something similar. For the time being, however, chemical suppliers are doing self assessments based on internal audits etc.

TFL has established an internal system which consists of own chemical testing and chemical testing of raw material (chemical substance) suppliers. TFL will align with an external audit and certification system as soon as an appropriate one is in place.

It is very clear that chemical substances need proper and meaningful testing while avoiding unnecessary testing. It is important to note that the increasing requirements to ensure chemical safety generate significant costs throughout the supply chain and these will inevitably be reflected in the price of the final product.

Withouth specifiying and using the correct test method for a RSL substance test results are not reliable.

How are detection limits established?

# Test methods and specifications

In the following more detailed technical information will be given on those restricted substances relevant to leather and the related test methods and specifications.

**Chosing the right test method**

Many tanners pass restricted substance lists (which they e.g. receive from customers/brands), together 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 in brand or manufactuerer RSL lists are in most cases only relevant for testing leather and not suitable for testing chemical products. Withouth specifiying and using the correct test method for a RSL substance test results are not reliable.

**Formaldehyde testing**

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.

**Testing for heavy metals**

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 much more realistic and correct test for leather. Many brands and Ecolabels 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.

**Testing VOC emissions**

The JAMA test (issued by the Japnese Automotive Industry) 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 (i.e. TSM 0508G-2009, VDA 278) as more practical ways of analysing the emissions. At this stage there are still variations in the temperature, humidity and air flow between the different methods.

**Test methods for leather:**
Leather is a complex matrix and the extraction must be validated between test laboratories.

**Who develops test methods for leather?**
Most of the restricted substance lists 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 – this 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.

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

## Restricted substances relevant to leather manufacture

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.

**Acetaldehyde**

Acetaldehyde recently attracted a lot of attention by car makers particularly in the Asian automotive market. In GB/T 27630-2011 (the Chinese Regulation) limits for acetaldehyde emissions from car leather are set to be 0.2 mg/m$^3$ which is extremely low and far beyond any health risks. Acetaldehyde is not being used in the manufacture of any leather chemical product and even if present in trace amouts in chemical products those do not contribute to the acetaldehyde readings. It has to be assumed that acetaldehyde is continuously formed by oxidation or fermatation of certain substances (fats, sugars, etc.) but also during the testing.

**Specific TFL comment**

The only way to achieve above low levels is the use of a scavenger product. TFL has developed the product A 3210 which can be used in wet-end and finishing applications to suppress acetaldehyde formation.

**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 normally not used for dyeing leather.

**Specific TFL comment**

TFL does not use any of the above types of allergic or sensitizing dyes in their leather dye range of: SELLA® Cool, SELLA® Derm, SELLA® Fast, SELLA® Star, SELLAFLOR®, SELLASET®.

**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 Ecolabels 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 Ecolabels 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-aminoaniline (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-aminoaniline, 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.

**Specific TFL comment**
All TFL dyes (SELLA® Cool, SELLA® Derm, SELLA® Fast, SELLA® Star, SELLAFLOR®, SELLASET® ) do not contain azo dyes made with the forbidden amines. Most commercially available azo dyes do not break down to give these forbidden amines.

**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 Ecolabel, "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.

Biocides found often in waste water emissions from tanneries are not only from products used during leather manufacture but can also derive form the animal raw hides where pesticides etc. are being used for protecting animals from diseases.

**Specific TFL comment**
TFL uses biocides which comply with the EU Biocidal Product Directive and the 'Blue Angel' (Blauer Engel) issued by German Enviornmental Ministry.

**Restricted substances:**
These substances are the ones typically encountered and are not an exhaustive list of all restricted substances.

The international ISO Standards are verified by validated inter-lab trials.

**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:**
SELLA® Tec products from TFL used for fire protection 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.

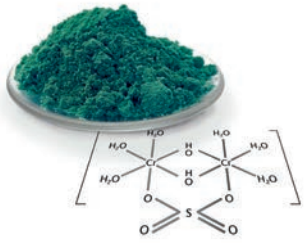
**Note:** The medium chain MCCP (C14–C17) and long chain LCCP (C18–C30) chlorinated paraffins are not restricted by EU Regulation nor by the ZDHC Leather MRSL list. The presence of MCCP must be listed in the EU-Safety Data Sheet.

**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.



**Uses of Chromium:**
The Cr-containing chemicals used in the manufacture of leather are all based on Cr(III).

**Chromium (VI)**
The hexavalent chromium oxidation state (Cr(VI)) is allergenic and carcinogenic if inhaled and thus 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 Ecolabels 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 all based on Cr(III). However, during manufacture it is possible that traces of Cr(VI) can be formed if certain measures in the the application process are not properly followed. Most important are good removal of natural grease, avoidance of fatliquors with high content of unsaturated fats and any oxidising agents. Use of vegetable tannins and anti-oxidants help to suppress the formation of Cr(VI) whereas low humidity and high temperature can trigger their formation particularly in the presence of unsatured fats. Cr(VI) 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 dyes based on stable organic Cr(III)-complexes 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 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. Post formation of Cr(VI) however can not be ruled out especially if an excess amount of unsaturated fats are present.

**Dimethyl fumarate**
Dimethyl fumararte is a solid, which sublimes 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 any of 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 articles, especially those in skin contact
- Ecolabels and brands set formaldehyde limits, e.g. as 20mg/kg (20 ppm) for children and 75mg/kg (75 ppm) for adult shoes
- The automotive industry has limits for formaldehyde in the leather (often 10 ppm) and for 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). Trace levels are listed in separate TFL Statement of restricted substances. 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 chrome-tanned leather to comply. Ecolabel limits for heavy metals are often much lower and normally they also specify total metal. For example, some textile Ecolabels set very low limits for total Cr. Obviously achieving these lower levels is not possible with Cr-tanned leather.
Other Ecolabels, such as the SG Label, accept chrome-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
- Ecolabels often specify extraction with a pH 5.5 synthetic perspiration solution (prepared according to ISO 105-E04)

Often there are requests from certain brands for metal-free leather. Such request should be specified for ‘free of toxic heavy metals’ since presence of non-toxic metals can be critical to achieve certain performances (e.g. high light fastness of metal dyes. Metal-free leather according to EU guidline is specified as as containing less than 0.1 % of Cr(III), Al, Ti, Zr, Fe.

**Specific TFL comments:**
Other than Cr(III), TFL is not adding the above heavy metals (As, Cd, Cr, Hg, Pb, Sb, Ba, Se) to any TFL product. Metal content of TFL dyes and pigments are listed in separate TFL Statement of Restricted Substances.

Some dyes are organic metal complexes of either Cr(III), Co, Cu or Fe. This information is listed in section 12 of the TFL Safety Data Sheet. The TFL dyes and pigments also comply with the stringent 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:**
No product in TFL range uses NMP and NEP (N-ethylpyrrolidone).

**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, Ecolabels 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 (mono-butyl tin) are restricted chemicals. These are used as antimicrobals, 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 any leather chemical product.

**Perfluorochemicals (PFC)**
The fluorochemicals based on C8 chemistry, eg. 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 an ISO method still in development.The corresponding acid form, PFOA, is usually also restricted by brands and Ecolabels. The same applies for chemicals based on C6 Fluor Chemistry. Fluorochemical products based on C4 chemistry have by far the lowest degree of bioaccumulation and toxicity among all fluorochemical products. Nevertheless some of the brands have decided to completely restrict the use of PFC.

**Specific TFL comment:**
TFL does not have PFOS or PFOA in the fluorochemical products it supplies. TFL fluorochemical products are all based on C4 chemistry.

**Phenol**
Some RSL lists regulate the content of free phenol. Phenol is used in the manufacture of polymers (synthetic tanning agents) and as in the case of formaldehyde trace amounts can be found in some of these products.

**Specific TFL comment:**
Some TFL products from SELLATAN®, SELLASOL® range contain traces of free phenol resulting from the polymerisation process. Trace level amounts are listed in the separate TFL Statement of Restricted Substances.

**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.
Ecolabels 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. Naphtalene, the most simple PAH substance, is not intentionally used in leather manufacture but present in trace level in some dispersing products.

**Specific TFL comment:**
TFL does not use PAH substances intentionally in leather chemical products. Naphtalene can, however, be found in trace levels in some dispersing agents. Levels are listed in separate TFL statement for Restricted Substances and do not exceed any allowable limits of major RSL and MRSL.

**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 168 chemical substances in the SVHC candidate list, but at present none have yet been assigned SVHC status in Annex XIV which would then mean that substances could not be generally used and need authorisation for a particular use. 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 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. Presence of a SVCH substance in chemcials products at levels higher than 0.1 % needs to be declared and user

needs to be informed by the chemicals supplier on its safe use. The current 168 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 Ecolabels 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 %. In the manufacture of active TFL sales products no SVHC substance is being used.

**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( i.e VDA 278 test method ) The results can be influenced by the time since the leather was made and the storage method. The Very Volatile Organic 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.
VOC emissions of special interest coming from leather are formaldehyde, acetaldehyde, benzene, toluene, xylene, ethylbenzene, styrene, acrolein, NMP and NEP and these are all including various RSL and regulations.

**Specific TFL comment:**
By using TFL products it is possible to comply with the total VOC emission requirements for above mentioned substances set by brands, Ecolabels and OEM's.

**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 and 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 worldwide 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 hydrochlorofluoro-carbons (HCFC)
- Heavy metals: arsenic (As), beryllium (Be), bismuth (Bi), cadmium (Cd), mercury (Hg), selenium (Se)
- Nickel metal
- Pesticides
- Polychlorinated biphenyls (PCB) and terphenyls (PCT)
- Polyvinyl chloride (PVC)

# Glossary

**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.

Are there any final concerns?

# Is leather a save product?

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 various innovative product technologies. One example of them is the TFL White Line Technology which complies 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 allergenic reaction.

Our products all comply with highest standards regarding hazardous substances and environment sound production.

01-2017