Step 2 Sustainability

Online Course

UNIT 2
Sustainable Materials and Components for Footwear

How to Implement Sustainable Manufacturing in Footwear
- New Occupational Profile and Training Opportunities -

How to Implement Sustainable Manufacturing in Footwear - New Occupational Profile and Training Opportunities

Credits

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UNIT 2 - Sustainable Materials and Components for Footwear

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Summary

"Unit 2 - Sustainable Materials and Components for Footwear" is dedicated to the footwear materials that are actually available and may be used in footwear production, as well as their environmental impact. This manual intends to be a tool to support footwear technicians in the selection of most suitable materials to develop more ecological and sustainable footwear products.

This manual is organized in 8 technical chapters:

- Chapter 1 – Introduction, briefly describes the footwear industry in terms of worldwide production and introduces the main materials and components that may be used in footwear.
- Chapter 2 – Concepts and definitions related with materials and sustainability.
- Chapters 3 to 6 describe the materials used in the footwear production, their characteristics and properties, production processes, potential environmental impact, recommendations for lower environmental impact, new more sustainable materials and quality control and requirements.
- Chapter 7 – Eco labelling and eco certification of materials and footwear products, addresses the EU footwear ecolabel and other certification schemes.
- Chapter 8 – Quality Control and requirements, describes briefly the most relevant tests dedicated to footwear and footwear properties.

In Chapter 9 are presented the manual bibliographic references and in Annex I the tables with the performance requirements for footwear materials and components.

1. Introduction

In 2014 the worldwide production of footwear reached 24.3 billion pairs, up by 8% from the previous year. The distribution of footwear production by continents (quantity) in 2014 was 3% in Europe and Africa (each), 2% in North America, 5% in South America and 88% in Asia. In the same year the footwear consumption by Continents was 17% in Europe, 8% in Africa, 15% in North America, 7% in South America, 52% in Asia and 1% in Oceania. Europe is the largest importer of footwear, with a share of 40%, followed by Asia and North America with 26% and 23%, respectively. Africa, South America and Oceania represent 12% of imports.

Currently, the population is more sensible to the topics related with sustainability and ecology, looking and demanding for more information about the materials, products and production processes impact on the environment. More than ever, consumers are conscious of the impacts that certain activities have on the planet and its resources, pressuring companies to assume their responsibilities.

The growing population and increased consumption of footwear per capita may result in higher loads on the environment, namely on air, water and soils, associated to the production of the materials, components and footwear products. Additionally, the disposal of footwear at the use end-life needs to be taken in more account.

Footwear products usually result from the combination of a great variety of materials and components that are selected by considering the design, application and performance required. In a simple way, a shoe can be divided in two parts:

- Upper part, consisting in the elements of shoe above the bottom.
- Lower part, which include the entire bottom of a shoe, such as, insock, insole and sole.

F1. **Scheme of shoe parts**

The most common materials actually used is footwear include namely:

- Leather, textiles and synthetic materials, in the upper part.
- Leather, vulcanized rubber, thermoplastic rubber (TPR), polyurethanes (PU), thermoplastic polyurethanes (TPU), Ethylene vinyl acetate (EVA), polyvinylchloride (PVC), among others, in the lower part.
- Metal or composite shanks, metallic nails, textile or leather laces, metallic eyelets, polymeric slide fasteners, polymeric or wood based heels, composite and polymeric toe cap.

The adequate selection of materials and components assumes a great importance on the overall sustainability of the footwear products through its life cycle. With the goal of developing more ecological and sustainable products, in what concerns the materials and components selection and incorporation, it is essential to consider the following factors that will be detailed in the next chapters.

Materials and components features to develop more sustainable footwear:

- Type of material & components (e.g. recycled, recyclable and/or biodegradable).
- Origin and transportation associated.
- Materials (e.g. leather, polymers) produced by eco-friendly processes and that use the minimum amount of chemicals and energy on their production process.
- Water based solvents and glues.
- Lighter, durable and good quality.
- Elimination of unnecessary materials & components.
- Minimization of hazard and restricted substances.
- Material produced with renewable sources.
- Produced by simplified manufacturing production processes.
- Produced with reduced air pollution, water consumption and generation of solid wastes and noise.
- Reused, recycle or valorised at the end of their production and of products life cycle.

2. Concepts/definitions

In last years have emerged in the market various concepts associated to materials and products namely "more environmentally friendly" or "sustainable". However, these concepts are not completely clear to the consumers and in many cases to the producers or commercial agents. It is frequent to find on the market products that have associated characteristics/properties, as a selling argument, that are not the more adequate to that case. It is also common to find products that are nominated as biodegradable, natural or recyclable, among others, without showing any evidence or tests proof. To distinguish the "more environmentally friendly" or "sustainable" concepts some simple and simplified definitions are following introduced:

NATURAL MATERIALS are all products or physical matter from plants, animals or soil. The minerals and metals which can be extracted from them (without any modification) are also placed in this category.

RENEWABLE MATERIALS are substances derived from trees, plants, animals or ecosystems that have the ability to regenerate. A renewable material may be produced over and over again (e.g wood used to make paper renewed by reforestation). The renewable materials can, in principle, be produced indefinitely with benefits to the environment.

RECYCLED MATERIALS are obtained by reusing materials benefited as raw material and transformed into a new product. The concept of recycled material is directed only to materials that can return to the original state and be transformed again into a product equal in all its features.

REUSED MATERIALS are obtained by reusing materials benefit as raw materials and processed into a new product, however, the new material does not return all the properties of the initial material. It is obtained a new product with different characteristics.

DEGRADABLE MATERIALS are materials that undergo significant changes in chemical structure under certain environmental conditions, resulting in a loss of some properties that can be measured using standard methods suitable and applied in a determined period of time, determining its classification (based on ASTM D 5247-92).

BIODEGRADABLE MATERIALS are materials in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae (based on ASTM D 6002-92).

COMPOSTABLE MATERIALS are materials capable of undergoing biological decomposition in a compost site as part of an available program, such that the material is not visually distinguishable and breaks down into carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials (ASTM D 6002-92).

COMPOSTING is an aerobic process designed to produce compost. Compost is an organic soil conditioner obtained by biodegradation of a mixture consisting principally of vegetable residues, occasionally with other organic material, and having a limited mineral content (ISO 14855-1:2012).

AEROBIC BIODEGRADABILITY is a process that occur the breakdown of an organic compound by microorganisms in the presence of oxygen into carbon dioxide, water and mineral salts of any other elements present (mineralization) plus new biomass (ISO 14851:1999).

ANAEROBIC BIODEGRADABILITY breakdown of an organic compound by microorganisms in the absence of oxygen to carbon dioxide, methane, water and mineral salts of any other elements present (mineralization) plus new biomass (ISO 15985:2004).

GREEN HOUSE GASES (GHG) are gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of infrared radiation emitted by Earth's surface, the atmosphere and clouds (ISO/DIS 14067:2013).

CARBON DIOXIDE EQUIVALENT (CO_2e) is the unit for comparing the radiative forcing of GHG to carbon dioxide.

CARBON FOOTPRINT is a weighted sum of greenhouse gas emissions and greenhouse gas removals of a process, a system of processes or a product system, expressed in CO_2equivalents (ISO/DIS 14067:2013).

PRODUCT CARBON FOOTPRINT is a carbon footprint of a product system (ISO/DIS 14067:2013).

GLOBAL WARMING POTENTIAL (GPW) is a factor describing the radiative forcing impact of one mass-based unit of a given GHG relative to an equivalent unit of carbon dioxide over a given period of time (ISO/DIS 14067:2013).

ECO-DESIGN is a tool to reduce the impact during the life cycle of products that has evolved primarily through engineering and Life Cycle Assessment (LCA) (Muñoz, 2013).

ECO-LABELLING is a "certification" and manifestation of the environmental aspects of a product or service (Muñoz, 2013).

ECOLOGICAL FOOTPRINT is the metric used to calculate the human pressure on the planet and come up with facts (Muñoz, 2013).

LIFE CYCLE ASSESSMENT (LCA) is a compilation and evaluation of the input, outputs and the potential environmental impacts of a product system throughout its life cycle (ISO/DIS 14067:2013).

LIFE CYCLE INVENTORY (LCI) is a phase of life cycle assessment involving the compilation and quantification of inputs and outputs for a product throughout its life cycle (ISO/DIS 14067:2013).

3. Leather

3.1. Definition and classification

Leather, is the material that results from tanning animal's hides or skins. There are several tanning processes however all of them convert the raw hides and skins in materials that:

- Resist to putrefaction, even after wetting and heating;
- Remain workable, after drying.

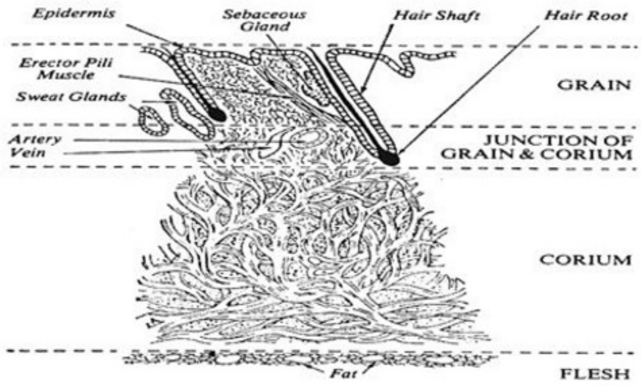
The type of tanning process is important for the final properties of leather materials, namely, softness, hardness, tightness and stretching.

A definition of leather is "a material which is resistant to putrefaction and enzymatic destruction and after repeated wetting-drying cycles returns back to its former soft characteristics." However, there are many other definitions, namely: "a material formed from a network of collagen fibres of hides and skins, treated by appropriate chemical and physical processes to obtain the properties necessary for its final use". Tannage therefore has to change the properties of collagen, either by chemical reaction or by covering the fibres against outside influences.

The classification of leather depends on its conservation process, animal type, processing stage, tanning process, type of finishing and final quality based on physical-mechanical and aesthetic properties.

3.1.1. Hides and skin structure

The composition of fresh hides or skins is manly water, protein, fatty materials and some mineral salts, being the proteins the most important for leather making. The collagen is the protein that originates leather and keratin is the main constituent of hair, wool, horn and epidermal structure. The following figure shows a cross section of skin.



F2. **Cross section of skin (sharphouse, 1983).**

The skin can be divided in the following layers:

1. **Epidermis** – surface of the skin, which consists of the hair and the loose connective tissues. This layer is removed, partly by chemical means (liming) and partly by mechanical means (dehairing and fleshing machines).
2. **Dermis** – fibrous part of the skin which is used for leather. The dermis is composed by the grain layer, containing the hair follicles, the fat and the sweat glands, and by the corium, which consists of a network of collagen fibres very intimately woven and joined together. The corium is generally the strongest part of the leather.
3. **Subcutaneous tissues** – the fibres are mainly horizontal and adipose tissue could be found.

The hides and skins can be distinguished as the follow:

- **Hide** is the outer covering of a mature or fully grown large mammal (e.g. cattle, horse, camel elephant and whale).
- **Skin** is the outer covering of small mammals (sheep and goats) or of immature mammals of the larger species (e.g. calves and colts). It is also used for the covering of reptiles, birds and fish.

3.1.2. Types of hides and skins

Leather materials can be produced from a wide range of animal types, namely:

Bovine

Bovine hide is the most used on the footwear industry and could be divided in four categories:

1. bull - hides of full-grown male animals;
2. cow - hides of full-grown female animals;
3. veal's - skins of young animals;
4. calf – skin of the youngest animals.

Characteristics:

- The size and age of the animal's hides is very important for the quality of leather products. Small skins of calf present better grain quality and a compact fibre structure, while hide of large animals certainly present a loose fibre structure and an overall low grain quality.
- Youngest animals allow to get better quality leather materials, with less defects and consequently, with more usable area.

Goatskin

The goatskin can be divided in three categories, namely:

- chevreaux;
- chevrettes;
- goats.

Characteristics:

- Fresh goatskin has a structure which is similar in some aspects to calfskin and in others to sheepskin but the total structure is typical in character.
- The hair side shows both large and fine hair, the latter resembling the wool of sheep.
- Goatskins are tougher and more tightly-fibred than sheep and have a very hard-wearing grain and their fat content is usually lower.
- The chevreaux, and chevrettes result in flexible leather with open pore.
- The goatskin has less elasticity and resistance.
- The leather of goatskin is used in the manufacturing of lady shoes.

Ovine – Sheepskin

Sheepskin can be used in the production of wool-on sheepskin or dewooled leather products.

Characteristics:

- Wool skins are primarily of importance in respect to the nature of the wool which is produced.
- Most sheepskins produce wool fibre oval in shape, other wool fibres are straight cylinders such as found on the hair-sheep variety.
- The widely differing characteristics of sheepskins depend on the breed of which are many. Their skins vary from about three to twelve square feet each, and amount of wool can weight more than twice as much as the skin proper.
- The sheepskins are characterized to have a high percentage of fat and to lose the fibre structure with the age of the animal.
- Normally, the sheepskins are used on the manufacturing of clothing, footwear, upholstery and leather goods.

Reptile

The reptile skins, in place of the hair and epidermis of mammalian, have a keratinous layer of scales, which is removed in the lime yard.

Characteristics:

- The weave of the fibre of these cold-blooded animals is much more horizontal and dense, resulting in a very tough thin skin, less soft or supple than mammal skins.
- These skins are normally used in high quality footwear products.

Pigskin

Characteristics:

- The pigskin is mainly used to produce leather for shoes lining.
- Pigskins have a distinctive grain structure, the hair penetrating through the usable grain layer leaving holes with a peculiar pattern pig. In general, presents low mechanical resistance.

Other

Other skins can be used in production of shoes, namely:

- Crocodile skins
- Horse hides
- Fish skins
- Ostrich skins
- Deer hides

3.1.3. Sources and types of conservation of hides and skin

Hides and skins are by-products of the meat industry. Leather industry recycles approximately 25-30% by weight of these high organic content residues to produce a high-value material, the leather.

Raw material can be conserved by different processes when removed from the animal and before being subjected to tanning process:

FRESH – Skins or hides removed from the animals that are not subjected to any type of conservation process. These skins or hides have to be used within few hours to prevent their natural degradation.

WET-SALTED – The cold, flayed is spread out, flesh side up, on a concrete floor and well sprinkled with salt (sodium chloride). Then a second hide is placed over the first one sprinkled with salt.

BRINING – The hides are cleaned by hosing with water and are then hung in pits or run in large paddles in a very strong salt solution. This gives very good and uniform salt penetration for heavy hides.

DRY-SALTING – The flayed skin is salted by either, or both, methods (wet-salted or brining) and is then hung up to dry. This reduces the weight and the cost of transport, but care must be taken to do a gradually and evenly drying process and when the skin has to be tanned, it must be soaked in water until it has taken up as much water as it had on flaying.

DRYING – This technique is practised in countries with hot and dry climates. In this case the hides could be by simply spread out on a bed of twigs or stone or hung or lair over poles, ropes or wires in the sun. In this case occurs a better ventilation and quicker drying, but may result in heat damage and pole or rope marks, showing as hard creases down. The hide could also be dried in an open-sided covered shed, to keep off the direct heat of the sun and allow a good ventilation. Dried hides and skins require careful packaging or bailing for transport or storage and are susceptible to insect attack, so precautions need to be taken.

FREEZING TECHNIQUES - are relatively expensive and also involve problems in transport and subsequent de-freezing in the tannery. The hide is likely to be heavily contaminated with farmyard dirt and bacteria and its hair or wool gives an insulating resistance to rapid temperature changes. Formation of ice crystals within the fibre structure may cause micro distortion, resulting in leather which is softer and looser than normal.

In the following table are presented the main sources and types of conservation of hides and skins.

Cattle hides	Europe, North and South America, Australasia	Wet salted, brined
	South America, Central America, India, Africa, Asia	Sun dried, dry-salted
Calf, Veals, kips, and smaller hides	Europe, America, Australasia	Wet salted, brined
	India, Asia	Dry, dry-salted, rough-tanned
	Africa	Dry and dry-salted
Sheep wool types	Europe, America, New Zealand	Usually pickled
Sheep hair types	Cape, Abyssinia, North Africa	Dry-salted or pickled
	India, Nigeria	Rough-tanned
Goat	Europe	Wet-salted
	India, Middle East, Brazil, Nigeria	Dry and dry-salted
	India, Nigeria	Rough tanned

T1. Main Sources And Types Of Conservation Of Hides And Skins.

Recommendations for lower environmental impact:

- If possible, using fresh is the most environmental friendly option. Because there is no need to re-hydrate the skin and eliminate the conservation salt. However, this option is possible if the hide or skins are used in few hours after being removed from the animal.
- The country of origin and transportation process are also crucial for carbon foot print (less impact: boat, train; medium impact: well-planned truck; higher impact: plane.
- Hides or skins of European origin are, normally, of good quality.

3.2. Leather manufacturing

Leather is one of the oldest goods of mankind and most likely the first natural material chemically modified by man. Leather is made by converting animal skins or hides by tanning that consists of various mechanical and chemical operations. Production of leather is a long and complicated process, and certainly not one which can be embarked upon successfully without specialized skills.

Tanning is the process of converting unstable raw hides into leather, with adequate strength properties and resistance to various biological and physical agents. This process is based on the introduction of additional crosslink into collagen, which binds the active groups of the tanning agents to functional groups of the protein (COO^- and NH_3^+).

The tanning process leads to changes in appearance, handling and touch of the skin and other tissues. The skin becomes rougher and loses transparency drying. Compared with the wet state, there is a loss of flexibility but at the same time acquires a certain porosity.

The raw materials exceptional amounts of fibres and bundles of fibres and their irregular and interlaced three-dimensional structure coupled with the adequate tanning and finishing processes lead to materials with outstanding properties.

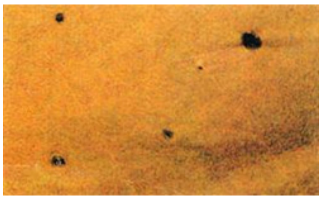
Leathers are characterized for having, in general, good tear and tensile strength, elasticity, breathability, air and vapour permeability, thermal insulation and water resistance, shape retention as well as the maintenance of these properties under varying temperature and moisture conditions.

3.2.1. Raw material defects

The following table summarizes the possible defects that can be associated to the animal life and after death to the beginning of stabilization process based in salting. Materials acquisition needs to ensure adequate surface quality (e.g. defects) to minimize materials solid wastes.

LIVE ANIMAL	DEAD ANIMAL
Fire marks Stains ink marking (marking) Insect bites Worms and parasites Scratches (Barbed Wire) Eczema Damage by freezing mark Sagging skin Damage by excrement and urine Transport Warts Others	Knife cuts Spots of blood Bacterial attack Acid stains Putrefaction Skin heating Salt spots

T2. Animal skin and hides defects.


WARTS


HORN SCRATCHES


FAT FOLDS


DUNG MARKS


CLOSED SCARS


VEINS


INSECT BITES


SALT STAINS


CURRY-COMB SCRATCHES


GOAD MARKS

T3. Example of animal defects.[1]

3.2.2. Production Stages

Leather making involves complex timing consuming processes performed over several stages, and in which a large variety of chemicals are used. Leather manufacturing process frequently includes three phases, namely the beamhouse (preparation of hides or skins), tanning (in the tanyard) and finishing (in post tanning area). The various stages of the process are can be systematized and shortly described as follow.

F3. Stages of tanning process.

• Soaking

Soaking consists in restore the moisture lost during the preservation and storage of hides and skins and elimination of globular proteins contained within the fibrous hide structure. Water also serves as a vehicle for the penetration and removal of chemical into fibrous structure for the most subsequent processes.

• Unhairing and liming

Unhairing and liming is used to remove the hair or wool, epidermis and inter-fibrillary proteins (to some degree), prepare the hide or skin for the removal of flesh and fat and give the final leather an attractive appearance. Normally, sodium sulphide and hydrated lime are used to destroy the keratinous material of the epidermis and hair or wool. By increasing the pH the fats are hydrolysed and the skin structure swollen due to water entrance into the fibre network, forming a material with open structure, translucent and a jelly-like aspect.

To minimize liquid effluents organic matter leathers made by processes in which the hair is removed not dissolved are to be preferred.

• Fleshing and Splitting

Fleshing is a mechanical operation used to cut away the flesh layer, normally, using rapidly rotating knives. The corium has a firm structure suitable for knives work on. In this stage the hides or skins can be split into two or more layers, i.e. a grain layer and one or more flesh layers. The number of layers depends on the hide thickness.

The splitting operation can be also done after tanning.

• **Deliming and bating**

Deliming operation is a simple acid treatment used to neutralize and remove the calcium ions from the pelt. During this process the pH inside the collagen network should be regulated and the bath buffered; the swelling of pelt reduced to the expected degree; fibres separated by washing out the matrix and products of protein degradation removed from pelt.

Bating is an enzymatic processes applied to remove non-collagenous hide or skin components, keratin degradation products, globular proteins, elastin and cells structure residues. In the bating operation it is necessary to control the enzymatic processes. An excessive removal of proteins from the pelt; due to their prolonged action, over dosage or temperature increase; may result in an empty leather and loose of grain. An insufficient bating can produce a leather stiff or even brittle.

• **Pickling**

Pickling is another operation used to prepare the skin or hides for tanning. In this operation the enzymatic bating is stopped and the acidity and pH of the hide or skin adjusted. Acidification of skins or hides also prevents their swelling under the action of acid.

Pickling is responsible for the deeper penetration of tanning agents avoiding their bonding to external pelt layers.

• **Tanning**

Tanning is the process responsible to convert unstable hides or skins into leather, with suitable strength properties and resistance to various biological and physical agents. During this process the tanning agent is introduced into the hide or skin, and crosslinked with collagen, these links are responsible for the binding of active groups of the tanning agents to functional groups of the protein (collagen).

There are several types of tanning processes to convert the skin or hides in leather material. These may be divided in mineral tanning (e.g. chromium, aluminium, zirconium, iron or titanium salts) and organic tanning (e.g. vegetable extracts, aldehydes or synthetic resins).

Actually, chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterized by top handling quality, high hydro-thermal stability, user-specific properties and versatile applicability. Waste containing chrome resulting from leather manufacturing and footwear manufacture and use, however, poses a significant disposal problem.

• **Neutralization**

Neutralization increases the pH and chemical are used to reduce the stringency of the leather to anionic chemicals such as retaining agents, dyes and fatliquors.

• **Retaining, Dyeing and Fatliquoring**

Normally, tanned leathers (or pretanned) are treated with additional tanning agents in order to get a material with the desirable properties. The aim of retaining process is to better stabilize the leather materials, lighten the colour of the leather, produce a feeling of fullness and facilitate the penetration of dyes, fatliquoring's and finishing agents.

Leather dyeing contributes to give the material the desired colour and prepares for finishing. The total penetration of dye through leather thickness depends on the chemicals and the processes used and properties required for final leather materials. In some leather materials surface dye is sufficient, reducing the consumption of chemicals/dyestuffs. This process affects the chemical properties of leather.

Fatliquors are added to confer to leather fullness, softness and flexibility properties. At these stage water repellent products may be used to produce water resistance leather.

The wet-phase of leather manufacturing process occur mainly in drums (see Figure 4).

F4. Wet phase drum.

• Drying

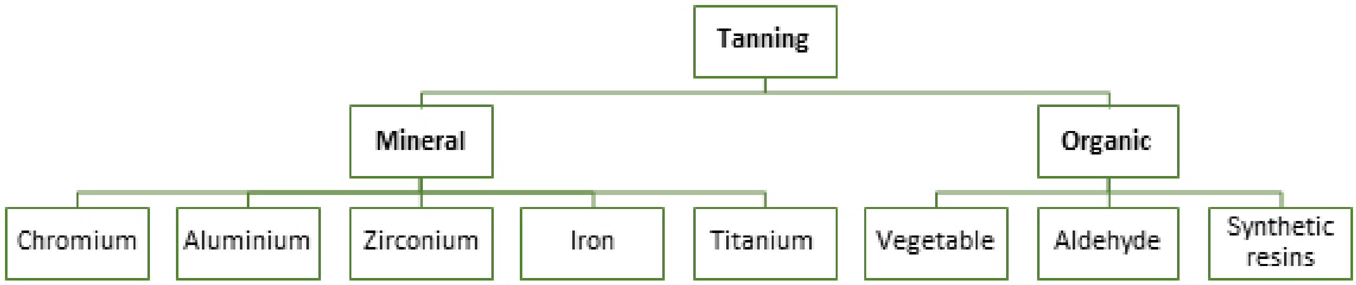
After the described processes, leather is washed and dried before the finishing stages. Excess of water may be removed from the leather using a samming machine. Several processes can be used to dry the leather materials, which can be combined, such as vacuum drying, overhead drying, tuner drying and toggle drying.

• Finishing

Finishing process is responsible for the final aspect of leather materials. The finish process could be used to hide defects, increase the leather beauty properties and to confer fashion effects. During this stage could be used resins, pigments, dyes, handle modifiers, fillers and other products that are applied by spraying guns, roller coating systems, curtain-coating systems or by hand. Other machines like heated hydraulic or roller presses are used to produce smooth or patterned leathers.

3.2.3. Leather tanning

The tanning process applied confers the final leather and footwear products distinctive characteristics. Currently, leather production is dominated by three processes: Chrome, Vegetable and Aldehyde and their combinations.



F5. Tanning processes.

• Chromium tanning

The most common tanning agents used to produce leather materials are chromium salts, such as the chromium (III) sulphate, which may crosslink and stabilise the collagen molecules within the fibrils.

This tanning process results in light, cost attractive, high thermal and bacterial resistance leathers. A great variety of leather materials can be produced based on chrome tanned leather.

The chrome tanned leather has a shrinkage temperature higher than 100 ºC, which is of great importance from the point of view of leather stability and footwear production process. During the shoe production the leather material can be subject to high temperatures. However, these materials are not easily biodegradable (e.g. composting, aerobic, anaerobic) and the presence of chromium limits the production wastes and used footwear valorisation options, thus rendering the overall sustainability of the material often questionable.

Chromium VI

Inevitably, when mentioning about Chromium tanned leather rings the bell of hexavalent chromium and all associated negative connotations. The hexavalent chromium oxidation state, Cr(VI), may be considered allergenic and carcinogenic and is restricted namely in the EU (detection limit 3 mg/kg).

As mentioned, trivalent chromium sulphate is commonly used for leather tanning. In this way, leather contains Cr (III), which is mostly bound to collagen and in minor amount could be free. The Cr (VI) is not used for tanning in modern mixtures, however can be formed in leather under particular conditions.

Chromium VI in leather is often determined using the method described on EN ISO 17075 after extraction. To simulate the effect of ageing, leather can be submitted to different conditions namely a temperature of 80 ºC during 24 hours before Cr (VI) determination.

Recommendations to avoid the oxidation of Cr (III) to Cr (VI)

1. Carefully degrease the raw hides.
2. Avoid or reduce the quantity of bleaching agent used prior to the tanning process; never use bleach after tanning process.
3. Use chromium (VI)-free tanning agents and chemicals.
4. Neutralise down to the lowest-possible pH value; avoiding pH peaks during neutralisation.
5. Preserve wet blue sufficiently with biocides approved for the purpose. Avoid the formation of mould over the entire process.
6. Use 1 – 3% vegetable re-tanning agents (e.g. 1 – 2% Tara tanning agent).
7. Replace polyunsaturated fatliquors by oxidation-resistant fatliquors.
8. Avoid ammonia or other chemicals containing ammonia when neutralising, and when purging or dyeing; use dispersing syntans instead.
9. End the wet finishing at low pH values (pH 3.5 – 4). Conduct additional washing processes.
10. Check the leather after prolonged storage for chromium (VI) presence.

Aluminium (Al) salts combine only weakly with collagen when used by itself (solution pH 2). Al interaction becomes similar to chromium salts as they become more basic by the addition of alkalis. Aluminium salts are not much used in the tanning industry due to regulatory pressure and the perception of toxicity.

The use of titanium as a tanning agent by itself is only moderately effective, since large quantities are required to achieve the highest shrinkage temperatures (> 95 ºC), that are lower than the achieved by chrome tanning. An overfilled and soft leather is obtained in that conditions. In the following table are compared the Al(III) and Ti (IV) tanned materials properties.

PROPERTY	Al (III)	TI (IV)
Tanning effect	Weak	Weak
Stability to hydrolysis	Good	Good
Filling Effect	Poor	Poor
Optimum tanning effect	4	4

T4. Comparison between the properties of al (iii) and ti (iv) tanning agents (Covington, 1997).

The use of zirconium (IV) as a tanning agent is more recent. Normally, zirconium (IV) is used in combination with other tanning agents because of its indifferent effectiveness on shrinkage temperature increase; the acidity of salts and the vulnerability to hydrolysis, meaning that they must be applied at high concentration and at pH < 1, therefore running the risk of osmotic swelling in the hide.

In the following table are summarized the benefits and limitations of introducing another metal salts different from chromium salts.

BENEFITS	LIMITATIONS
• Improve the efficiency of chrome uptake by reducing offer; • The rate of chrome uptake can be improved by the presence of another mineral tanning agent, applied as a pre-treatment (demonstrated in case of aluminium (III)).	• Shrinkage temperature decrease; • Modification of leather properties due to the presence of other mineral tanning agent; • Aluminium (III) salts may change the leather handle in terms of collapsing the fibre structure; • Titanium (IV) or Zirconium (IV) salts may change the leather handle in terms of filling the fibre structure; • Leather become more cationic and, consequently more surface reactive to anionic reagents; • The leather colour may change (as with iron salts). • Decrease of hydrothermal stability of leather materials.

T5. Benefits and limitations of metal tannings (based on Covington, 2008/2009).

• **Vegetable tanning**

Vegetable tanning uses vegetable extracts of wood, shells, leaves, routes, among others (chemically are a complex mixture of polyphenols). To be used as a tannin the molecular mass must be between 500 – 3000. Tannins presenting lower molecular mass fractions are classified as non-tans and those with higher molecular masses as gums.

Traditional vegetable tanning process is done in pits over a prolonged period of time (slow penetration of large reactive molecules). Today vegetable tanning, normally, requires about 3 weeks. However, this tanning process can be prolonged until a period of up to 6 months, depending on the type of leather required.

Modern vegetable tanning, especially for sole, is still conducted in pits and the procedure retains some of the traditional elements.

A leather produced exclusively by vegetable due to their properties (less flexible and with lower thermal stability) is used in the production of soles, belts, furniture, lining and bags.

Vegetable extracts may be used in the retanning phase to confer specific aesthetic, touch and functional attributes to materials pretanned with aldehydes or tanned with chromium. In the last case is proven that certain vegetable extracts, namely Tara contributes to minimize chromium(III) oxidation to chromium(VI).

• **Aldehydes**

Formaldehyde

In formaldehyde tanning the shrinkage temperature can typically be raised up to 80-85 ºC. However, the crosslinking is relatively inefficient probably because the formaldehyde species are not monomeric.

The use of formaldehyde as tanning agent is nowadays relatively limited, to prevent emissions of free formaldehyde, thus minimizing health and safety problems.

Glutaraldehyde

In glutaraldehyde tanning the shrinkage temperature achieved is typically around (82 – 87) ºC.

The glutaraldehyde can interact with the collagen peptide links by hydrogen bonding resulting in a spongy and hydrophilic character leather.

Glutaraldehyde tanning results in yellow-orange colour leather, which may be undesirable.

The impact of glutaraldehyde on health and safety is being evaluated.

Glutaraldehyde tanned leather shows adequate appearance and physical properties. However, may often present little fastness to light and yellowing problems.

• **Oxazolidine**

The use of oxazolidine alone as tanning agent confers to leather a shrinkage temperature below 75 ºC.

The combination of oxazolidine with synthetic or vegetable tanning agents allows to achieve higher shrinkage temperatures and obtain leathers with quality comparable to mineral tanned leather.

Oxazolidine tanned leather (as well as other aldehyde tanned materials) may need a final conditioning treatment to minimize/avoid the presence of free formaldehyde in the final leather material. This could be done intensifying the final washing steps, using formaldehyde-free syntans and "natural" vegetable tanning agents.

The use of oxazolidine promotes the fixation of chrome on leather.

• **Syntans**

Synthetic resins were more recently introduced as tanning agents. These synthetic resins are classified into three types according to their primary properties, namely:

• Auxiliary syntans (normally based on naphthalene), that promote the penetration of vegetable tannins, solubilise the aggregated phlobaphenes of condensed tannins, disperse acid dyes and reduce the leather reactivity to dyeing, increasing the colouring. Another function of these compounds is to act as non-swelling acids for pickling to low pH, to avoid osmotic swelling.

  The auxiliary syntans are characterized by their low tanning power.

• Combination or retaining syntans, usually consists on simple phenolic compounds. These products are more complex than the auxiliary syntans, having higher molecular masses and may be crosslinked in two dimensions.

  Combination or retaining syntans confer hydrothermal stability and more filling effect, but a weak tanning power. They are best used a retanning agents.

• Replacement syntans, can used to replace vegetable tannins due to an increase of the tanning power. They can be used by itself as tanning agents because their properties are similar to plants polyphenols.

  The leather produced by replacement syntans is similar to the produced by vegetable tannins, including the shrinkage temperature of about 80-85 ºC. The leather is more lightfast than vegetable tanned leather.

Due to the superior properties achieved by chrome tanned leathers to substitute it in footwear related applications would probably involve the development of a process that could achieve the following properties:

• High hydrothermal stability, $T_s > 105$ ºC;

• No metal salts;

• White or pale coloured base leather, dyeable in a wide range of colours;

• Lightfast;

• Lower environmental impact;

• Comparable cost.

3.3. Finishing and categorization

The finishing of leather surface assumes great importance on the final footwear surface aesthetics and properties, namely:

• Protection from contaminants (water, oil and soiling);

• Colour, homogenise or intensify the colour provided by the dyes;

• Improve the feel, floss and physical performance of leather;

• Confer aesthetic and fashion final aspect;

• Improve leather quality by disguising surface defects.

In the following table are summarized different types of leathers by type of finishing.

LEATHER	DESCRIPTION
Aniline	Aniline leather is the most natural leather with unique surface characteristics of the hide remaining visible. This leather is coloured with dye and not with a surface coating. A light surface coating may be applied to enhance its appearance and offer slight protection against spillages and soiling.
Semi-Aniline	Semi-aniline leather is more durable than aniline, maintaining a natural appearance. The application of light surface coating containing a small amount of pigment usually increases stains resistance.
Pigmented leather	Pigmented leather is the most durable leather and is frequently used in furniture and car upholstery. A polymer surface coating containing pigment confers a higher durability.
Full grain pigmented leather	Leather with surface coating applied in the intact grain surface. Any imperfection existent on hide (e.g. veins, cuts) will be visible in the finished leather.
Corrected grain pigmented leather	Leather with a decorative grain pattern embossed into the grain surface. The procedure "correcting the grain" can be used to correct/minimize the visual effect of scar marks, wire scratches and growth marks. This procedure contributes to higher leather surface usage (otherwise higher amount of waste could be generated during the footwear production).
Finished split leather	Leather of the middle or lower section of a hide with a polymer coating applied and embossed to mimic a grain leather.
Antique grain (two-tone or rub-off)	Leather with a special surface effect created to mimic the unique "worm" appearance of traditional leathers. A contrasting top-coat is applied unevenly or partially rubbed off to reveal a paler underlying colour.
Pull-up/waxy/oily pull-up	Leather with a natural appearance with lightens in colour when stretched during wear to produce unique worn-off effect with time.
Nubuck	Aniline dyed leather which has been lightly abraded on the grain surface to create a velvety finish or nap.
Suede	A split which has been abraded to create a distinctive nap.
Nappa	Full grain leather drummed to give a soft and comfortable feel.
Patent	Patent leathers have a surface coating of PVC or polyurethane to give a very gloss finish.
Waterproof	Leather with water resistance properties
Transfer Coat	A foil is hot pressed (pressure and temperature) onto leather surface and a coating transferred to the leather surface.
Engraved leather	Laser machines could be used to engrave leather materials surface and produce very aesthetic and fashionable materials.
Printed leather	Printing machines could be used to print on leather materials surface.

T6. Leather finishing's.[2]

The finishing process and amount of finishing product depends on the leather quality and the final footwear product requirements.

Higher quality hides could be used to produce more natural leather, which need less finishing processes. As a result, lower environmental impact, is achieved. However, footwear could be more affected by the use (e.g. more prone to stains, changes of colour).

On the other hand, more intense coatings can be applied to valorise hides of lower quality. The resulting footwear products may have adequate and interesting surface functionalities and fashion appeal even though less "natural" look.

3.4. Environmental impact of leather Industry

The raw materials used in the production of leather materials are by-products of the animal-based food chain. The conversion of hides and skins into leather allows to get added value materials and products and valorise a potential waste.

The overall tanning process converts raw hides or skins into stable flexible materials (leather) that can be used in a wide variety of applications, such as shoes.

Environmental issues/emissions associated with this process include:

- Wastewater;
- Air emissions;
- Solid waste;
- Hazardous materials.

To guarantee that leathers are sustainably produced, namely regarding environment impact, the tanneries need to control all the stages since the hides/skins acquisition until its finishing and delivery to the clients. The tanning process comprises the processing of considerable amounts of chemicals and volumes of water and may generate pollution loads. Normally, the pre-tanning and tanning processes are responsible for about 90% of the total pollution of a tannery.

To design and produce more sustainable eco shoes, footwear technicians need to select and use leathers with a sustainable footprint, produced by more environmentally friendly processes.

Wolf defined four elements that should be considered in the production of leather to provide a sustainable footprint (Wolf, December 2013/January 2014), namely:

1. **Carbon footprint** – Reduction of CO_2 emission by the process and products in tannery and reduction of impact on climate change.
2. **Water footprint** – Reduction of water consumption and wastewater treatment by using new technologies and chemicals to get more efficient processes.
3. **Resource Footprint** – Upgrade of low-quality leather and increase the efficiency of hide utilization, decreasing the waste generated during the cutting; Increase the efficiency of chemicals use.
4. **Toxicological Footprint** – Avoid the use of harmful substances legal restrictions and ensure the product Stewardship.

The leather carbon footprint evaluates the impact of process design, chemicals, energy, management and waste usage. An important issue and contribution for carbon footprint is related with the durability of leather products and properties, safety of the products and ecological/natural properties. In this way the labelling of leather materials is important to ensure to consumers that the leather and leather consumer goods are safe and were produced in an ecological and responsible way.

3.5. More sustainable leather for footwear

Recommendations for lower environmental impact

- Select leather from companies that accomplish ecological criteria and requirements; sustainable processes and good environmental practices.
- Select leather companies that use skin raw material from countries in close proximity to decrease the transportation carbon footprint.
- Use of more natural leather without too much finishing products applications.
- Use high quality and durable leather.
- Use of leather without restricted and hazardous substances.
- Use thinner leather materials.
- Good use of leather area during the cutting process to reduce the leather waste

3.6. New Leather Materials

3.6.1 Chrome-free leather compostable and disintegrable: BiOnature

BiOnature is a compostable disintegrable leather material developed in the framework of Portuguese R&D project, Be Nature. This material is commercialised by Portuguese tannery, António Nunes de Carvalho., S.A.[3]

Figures 9 shows the disintegration of leather shoe in composting conditions along of 21 days of laboratory tests.

F6. Evolution of leather disintegration in composting conditions.

3.6.2. Chrome-free leather with water resistance properties: hydroOak

The water resistance properties of leather materials is one of the limitation of chromium-free leather when compared with chromium leather. However, in the last years several studies and developments were conducted to improve the water resistance of chromium free leather and considerable positive results were obtained, despite the performance being still far from the chromium leather.

hydroOak leather is a chrome free leather with water resistance properties developed in a framework of Portuguese R&D project, NEWALK. This material is commercialized by Portuguese tannery, António Nunes de Carvalho, S.A.

The hydroOak leather was tested for Bally Penetrometer test achieving a penetration time higher than 420 minutes and a water absorption of 13% after 420 minutes. For the Maeser Penetrometer test the leather resisted more than 25 000 cycles and a water absorption of 8% (warming sound).

F7. Hydrooak water resistant leather

3.6.3. Chrome-free leather: BioLeather

The Bioleather material is tanned with tannin extracted from some trees, in particular Mimosa, Acacia, Quebracho, among others, and with polymeric resins. In this leather material appear only traces of iron, copper, zinc, lead, cadmium, nickel, cobalt, pesticides and chromium elements. This material is commercialized by Portuguese tannery, Curtumes Aveneda, LDA.

F8. Bioleather.[4]

3.6.4. EcoLife™

Green Hides® Company developed a leather material called EcolikeTM based on chrome-free tanning, solvent-free finishing - and even avoids salt treatments and conserves water by using the freshest hides.[5]

3.6.5. Organic Leather: Organio Leather

Organio Leather is free from chrome, metal, formaldehyde, sodium sulphide, glutaraldehyde and sulphuric acid which are all usually found in regularly tanned leathers and tanneries.

Their tanneries only use natural materials to cure, preserve and tan leather, these are all natural biodegradable tanning materials such as bark tannins, plant tannins, lime or smoke which allows us to keep this process 100% environmentally friendly, so much so that the run off from one of the tannery's we work with goes straight out on to a read bed and then to the fields where they raise their sheep. The natural tanning process takes anywhere form 5 weeks to 12 months (regular chrome tanning takes less than a week). It is still hard to find people willing to put in the time and effort to do this, but the numbers are growing and the word is spreading.[6]

3.7. Quality control and requirements

Leather is a noble material used in the production of shoe quality products, that can be used as a fashion "accessorize" (fashion shoe) or as a personal protective equipment (safety shoes).

The properties and quality of leather depends on the raw materials (hides or skins quality) and manufacturing process, since the beamhouse stage to finishing. The manufacturing process of leather is designed considering the desired requirements for shoe in terms of aesthetic, physical and chemical properties, without forget the associated costs.

Leather quality control is essential to guarantee the quality of shoe products in terms of physical resistance and comfort, as well as to avoid the presence of hazards substances that can be prejudicial or are forbidden for people and environment. As the requirements depends on the shoe final application.

3.7.1. Leather for upper

The leather for shoe upper should comply with the following properties:

- **Flexible and with tear strength**.

  Leather is subjected to flexion and stretch during the shoe manufacturing and wear, being essential to guarantee a suitable flex resistance and tear strength, considering the handling and final application, to avoid the break of finishing and material itself. Normally, the leather has good physical resistance properties, unless that has been subjected to an inappropriate chemical process during tanning or by a great reduction of thickness.

- **Elasticity and plasticity properties**

  The elasticity property of leather is important to mould the 2D material in a 3D construction and get a permanent shape, even after the last is removed. On the other hand, during wear the shoe is constantly subjected to flexion and should recover its original shape when it is removed from the foot. In this way it is necessary combine in a proper way the elasticity and plasticity properties to get a suitable shoe product.

- **Delamination resistance**

  The delamination during wear should be avoided by a good adhesion of finish to leather surface.

- **Bondability and seam strength properties**

  To ensure a good adhesion between the upper and sole and resistance during the stitching process and wear.

- **Colour fastness and abrasion resistance**

  To prevent the loss of colour and maintain the original aspect of leather. If the shoe has not lining material, it is necessary prevent the staining of socks or users' feet.

- **High temperature resistance**

  During the shoe manufacturing process, leather is subjected at high temperatures, so the leather has to have resistance to these temperatures to prevent the shrinkage and break during the drying operations.

- **Water vapour permeability and absorption**

  The comfort depends on the humidity inside the shoe during the wear due to transpiration, so the leather should be capable to release the water vapour to the outside. The finishing applied on leather surface can prejudice the breathable properties that characterize leather materials.

- **Water resistance**

  The water resistance is a property required in special applications, such as protective footwear.

- **Low water soluble substance content**

  To prevent salts migration to the surface.

- **Absence of hazardous substances to human and environmen**t (e.g. REACH, CADS list; critical sustances)

3.7.2. Leather for lining, insocks and insoles

The lining and insock materials are in direct contact with feet and very influent for the footwear comfort. In general, lining materials should present physical resistance properties, but normally with less demanding requirements than the established for leather upper. The main properties of lining materials are:

- **Colour fastness to transpiration and abrasion**

  To prevent the staining of socks or feet during wear.

- **Water vapour permeability and absorption and water absorption capacity**

  To promote the breathability and thermal comfort of shoe.

- **Absence of hazardous substances to human and environment** (e.g. REACH, CADS list; critical sustances)

3.7.3. Leather for outsoles

Leather outsole is mostly used in high quality shoes. Normally, leather outsole is manufactured by vegetable tanning process, due to its characteristics, such as moldability and higher rigidity. These properties are essential for the comfort and physical resistance required to outsoles. The main properties of leather outsoles are:

- **Flexibility and dimensional stability**

  To avoid the breaking and stability during use.

- **Tear strength and abrasion resistance**

  To guarantee physical resistance and performance during use.

- **Bondability and needle tear strength**

  To guarantee the linkage between the upper part and the sole.

- **Water resistance**

  To prevent water penetration through sole.

- **Absence of hazardous substances to human and environment** (e.g. REACH, CADS list; critical sustances)

4. Textiles and Synthetics

4.1. Origin and Classification

Textile materials refers to materials that are susceptible of being transformed in yarns and posterity in woven. These materials are, essentially, all types of fibres of **natural** origin (vegetable, animal or mineral), **chemical** origin (obtained from natural and synthetic polymers) or **metallurgical** origin (obtained from inorganic substances by metallurgical technology).

The textile materials properties depend on several factors, namely:

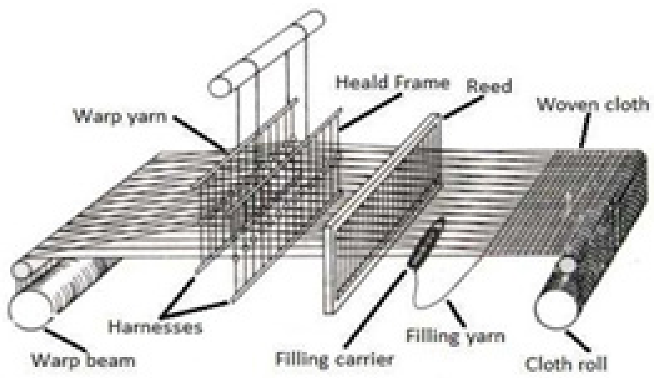
- Type of fibre;
- Fibre dimension;
- Type of yarn;
- Fibre diameter;
- Construction method of textile;
- Type of finishing.

Textile materials should be functional and meet the requirement of their end use. A proper balance between its technical and functional characteristics is need.

Textile fabrics are most commonly woven but may also be produced by knitting, felting, lace making, net making, nonwoven processes and tufting or a combination of these processes. Most fabrics are two-dimensional but an increasing number of three-dimensional woven textile structures are being developed and produced.

Usually, woven fabrics are based on two sets of yarns that are interlaced and lie at right angles to each other. The threads that run along the length of the fabric are known as warp ends whilst the threads that run from selvedge to selvedge, that is from one side to the other side of the fabric, are weft picks. Frequently they are simply referred to as ends and picks. In triaxial and in three-dimensional fabrics yarns are arranged differently.

The properties of woven textiles, such as strength, thickness, extensibility, porosity and durability, can be different and depend on the weave used, the thread spacing (number of threads per centimetre) and the raw material structure (filament or staple), linear density (or count) and twist factors of the warp and weft yarns. Woven fabrics can achieve higher strengths and greater stability when compared to any other fabric structure using interlaced yarns. By using different structures is possible to produce fabrics with widely different properties in the warp and weft directions.



F9. Basic structure of a loom.[7]

The weave structures that can be produced practically in an unlimited number. In the following table we will briefly describe the basic structures.

WEAVE STRUCTURES	DESCRIPTION
Plain weave	It is produced alternating lifting and lowering one warp thread across one weft thread. Plain weave is good for linings of vamps because the threads are interlaced the maximum number of times causing the threads to crimp.
Rib fabrics and matt weave fabrics	Produced by lifting two or more adjoining warp threads and/or two or more adjoining picks at the same time. It results in larger warp and/or weft covered surface areas than in a plain weave fabric.
Twill fabrics	In the weaving twill fabrics one warp thread crosses over two weft threads and then under two. The next warp thread has similar interlacing but on subsequent weft threads. A diagonal line on the cloth is produced in this pattern of weaving. In some fabrics this line is accentuated by interlacing a larger number of weft threads with a smaller number of coarser warp threads. This weft faced twill are unsuitable for shoe linings because of low warp stretch and very high weft stretch.
Drill weave: Jean and florentine	Jean has the warp crossing over two weft threads. Florentine has the warp crossing over three weft threads and under one weft thread.
Satin weave	In the simplest satin weave or satin finish, the warp threads interlace over four weft threads and under one. Warp faced satin weaves may have warp ends interlaced over eight or more weft picks and under one. In all such weaves the warp threads show on the face of the fabric. If, the warp threads cross under four weft threads, then the weft threads will show on the face of the cloth and a sateen weave or finish is made.
Triaxial weaves	In triaxial fabrics the three sets of threads form a multitude of equilateral triangles. The triaxial fabrics have superior tear resistance and bursting resistance properties because strain is always taken in two directions and excellent shear resistance because intersections are locked, when compared with the standard fabrics

T7. Weave structures[7]

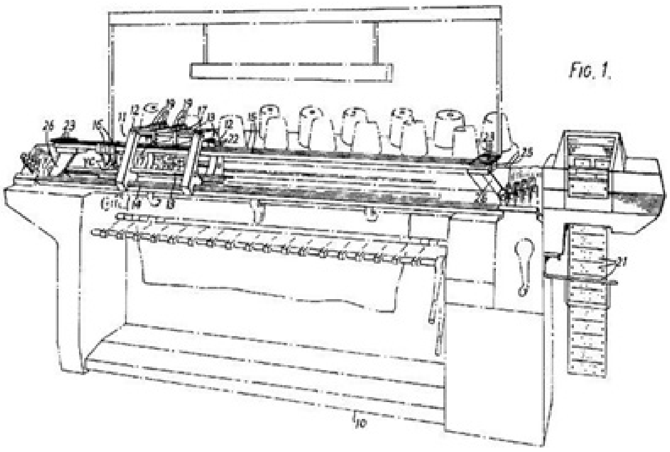
The most important fabric specifications are:

- cloth width;
- threads per centimetre in the warp and weft directions;
- linear density (count) and type of warp and weft yarns (raw material, filament or staple construction, direction of twist and twist factors);
- weave structure and finish.

There are two principal categories of machines knitting (weft and wrap knitting) that consists of a series of interlaced loops. The horizontal rows of loops are called courses, and the vertical lines are called wales.

KNITTED STRUCTURES	DESCRIPTION
Warp knitting	Is a method whereas weft knitting depends on the formation of lateral loops as the yarn travels horizontally, warp knitting forms stitches or chains of loops in each yarn in the warp direction. It is the fastest method of converting yarn into fabric, when compared with weaving and weft knitting.
Weft knitting	Is a method, in which the loops are formed, as in hand knitting, by the fabric being made (one loop at a time) as the yarn travels across the face of the machine. Each new row of loops hangs on the previous row loops in the fabric. This method is the more versatile of the two in terms of the range of products produced as well as the type of yarns utilised. Example: single jersey fabric and double jersey fabric (non-jacquard or jacquard).

T8. Knitted structures.

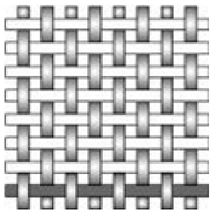


F10. Flat weft knitting machines with sequential stitch formation in a row of stitches. [8]

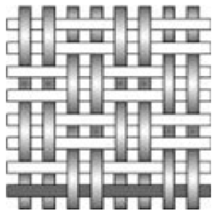
The footwear industry uses more warp-knitted than weft-knitted fabrics. The more important warp-knit structures are:

- tricot, characterized by its soft handle and good grape and elasticity is used for linings laminated to other fabrics.
- locknit, a smooth face materials and good resistance to laddering.
- satin, a back smooth surface material and good lustre.

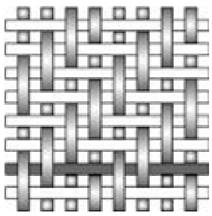
The warp-knitted are more stale and have less stretch when compared with the weft-knitted fabrics. However, all the knitted fabrics have a high degree of stretch that limit their use in footwear production.



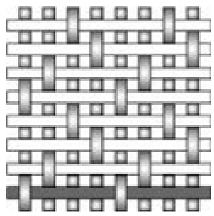
Plain weave



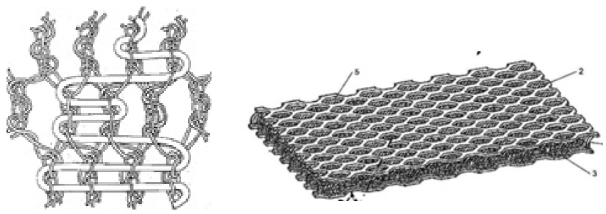
Structure of basket weave fabric



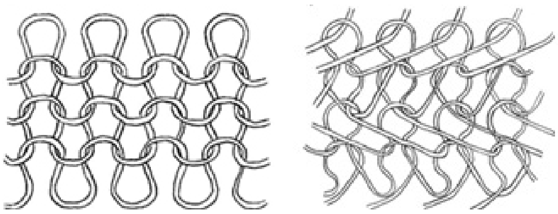
Twill weave



Satin weave



Mesh Fabrics



Knitted Fabrics (plain knit made on a weft or filler knitting machine and a single-warp tricot knit)

T9. EXAMPLES OF CONSTRUCTIONS. [9,10,11]

The non-woven textile are structures made from fibre webs, deposited in a targeted manner, and compacted by mechanical, thermal, chemical or solvent means and combinations thereof. In a simple way a non-woven is defined as a fabric that can be produced by a variety of processes other than weaving and knitting. These structures may be applied alone or in combination with other textile or non-textile materials such as meshes, woven fabrics, reinforcing wires, foam layers and metal sheets. This type of structure is very important to combine the ease of production with low cost.

The first non-woven material production is attributed to Garnett in 1850 in West Yorkshire (United Kingdom). Garnett designed a special kind of cards, for recovering waste textiles, giving them new fibrous form and are presented in the form of blanket. This material was used mainly as filler cushions and upholstery. The Garnett card type would have a very important role in the development of existing non-woven, obtained by the dry process.

The great development of a non-woven production occurred in Weinheim, Germany, in 1936, by the Freudenberg company, using Drylaind process and commercialized in 1948 as Vliesline (linings for clothes) and Vilela (cleaning windows).

The fibres most used in the production of non-woven are:

- Cellulosic natural fibres (wood fibres);
- Animal fibres (wool and silk);
- Chemical fibres, cellulose derivatives (viscose and Rayon)
- Chemical fibres, from oil (polyester, polyethylene, polypropylene, etc).
- Mineral fibres (glass fibres).

The properties of non-woven fabrics depend on the following properties, namely:

1. The choice of fibres;
2. Technology used to produce the non-woven, that determines the arrangement of fibres;
3. The bonding process and bonding agent.

The production of web is the first stage of the manufacturing process of non-woven and another is "bonding of web by using several methods. Some of those binding methods are felting, adhesive bonding, thermal bonding, stitch bonding, needle punching, hydro-entanglement and spin laying.

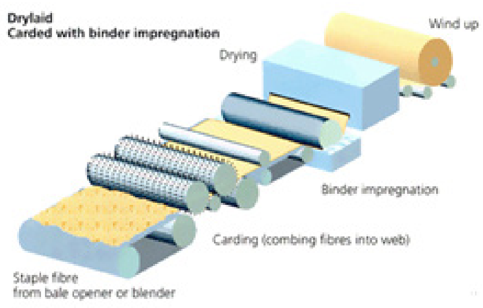
The manufacturing of non-woven is normally based on the following technologies:

- Drylaid
- Airlaid
- Spunlaid/Meltblow
- Wetlaid

The following table describes briefly each of the technologies used to manufacture the non-woven materials.

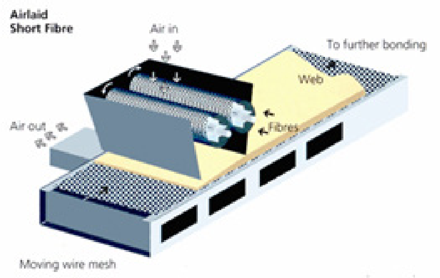
DRYLAID

Carding is a mechanical process, which starts with the opening of bales of fibres which are blended and conveyed to the next stage by air transport. The fibres are then combed into a web by carding machine, which is a rotating drum or series of drums covered in fine wires or teeth. The precise configuration of cards will depend on the fabric weight and fibre orientation required. The web can be parallel-laid, where most of the fibres are laid in the machine direction, or they can be random-laid. Typical parallel-laid carded webs result in good tensile strength, low elongation and low tear strength in the machine direction and the reverse in cross direction. Relative speeds and web composition can be varied to produce a wide range of properties.



AIRLAID

The second method of dry laying is airlaid. In airlaid, the fibres, which can be very short, are fed into an air stream and from there to a moving belt or perforated drum, where they can form a randomly oriented web. Compared with carded webs, airlaid webs have a lower density, a greater softness and an absence of laminar structure. Airlaid webs offer great versatility in terms of the fibre blends that can be used.



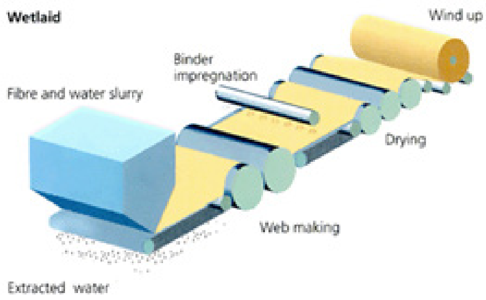
SPUNLAID/MELTBLOWN

In this process polymer granules are melted and molten polymer is extruded through spinnerets. The continuous filaments are cooled and deposited on to a conveyer to form a uniform web. Some remaining temperature can cause filaments to adhere to one another, but this cannot be regarded as the principal method of bonding.

The spunlaid process (sometimes known as spunbonded) has the advantage of giving nonwovens greater strength, but raw material flexibility is more restricted.

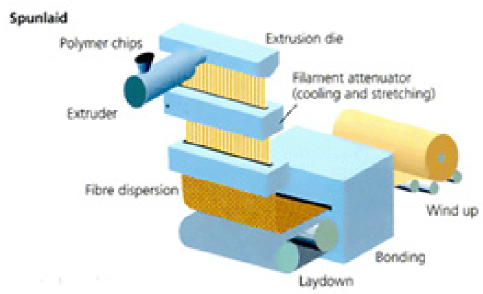
Co-extrusion of second components is used in several spunlaid processes, usually to provide extra properties or bonding capabilities.

In meltblown web formation, low viscosity polymers are extruded into a high velocity air stream on leaving the spinneret. This scatters the melt, solidifies it and breaks it up into a fibrous web.



WETLAID

Dilute slurry of water and fibres is deposited on a moving wire screen and drained to form a web. The web is further de-watered, consolidated, by pressing between rollers and dried. Impregnation with binder is often included in a later stage of the process. Wetlaid web forming allows a wide range of fibre orientations ranging from near random to near parallel. The strength of the random oriented web is rather similar in all directions in the plane of the fabric. A wide range of natural, mineral, synthetic and man-made fibres of varying lengths can be used.



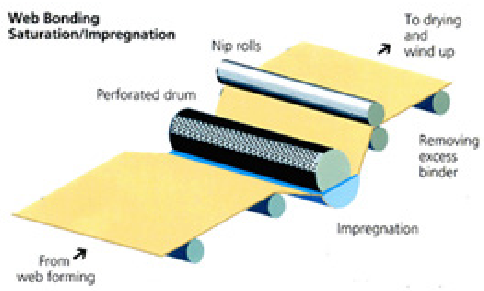
T10. Non-woven technologies production.[12]

There are three basic types of bonding:

- Chemical
- Thermal
- Mechanical

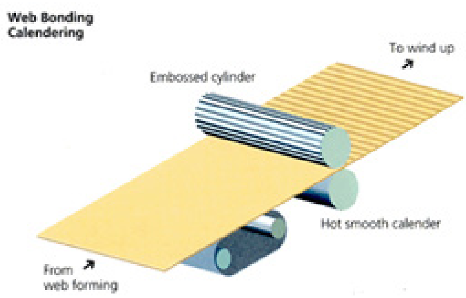
CHEMICAL

Chemical bonding mainly refers to the application of a liquid based bonding agent to the web. Three groups of materials are commonly used as binders, acrylate polymers, styrene-butadiene copolymers and vinyl acetate copolymers. Water based systems are the most widely used but powdered adhesives, foam and in some cases organic solvent solutions are also found.
There are many ways of applying the binder. It can be applied by impregnating, coating or spraying or intermittently, as in print bonding. Print bonding is used when specific patterns are required and where it is necessary to have the majority of fibres free of binder for functional reasons.



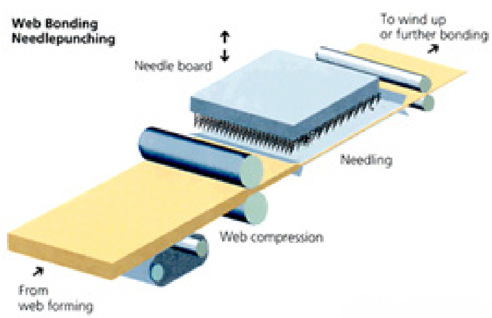
THERMAL

This method uses the thermoplastic properties of certain synthetic fibres to form bonds under controlled heating. In some cases, the web fibre itself can be used, but more often a low melt fibre or bi-component fibre is introduced at the web formation stage to perform the binding function later in the process.
There are several thermal bonding systems in use.
Calendaring uses heat and high pressure applied through rollers to weld the fibre webs together at speed.
Through-air thermal bonding makes bulkier products by the overall bonding of a web containing low melting fibres. This takes place in a carefully controlled hot air stream.
Drum and blanket systems apply pressure and heat to make products of average bulk.
Sonic bonding takes place when the molecules of the fibres held under a patterned roller are excited by high frequency energy, which produces internal heating and softening of the fibres.



MECHANICAL

In mechanical bonding the strengthening of the web is achieved by inter-fibre friction as a result of the physical entanglement of the fibres. There are two types of mechanical bonding: needle punching and hydro-entanglement.
Needle punching can be used on most fibre types. Specially designed needles are pushed and pulled through the web to entangle the fibres. Webs of different characteristics can be needled together to produce a gradation of properties difficult to achieve by other means.
Hydro-entanglement is mainly applied to carded or wet laid webs and uses fine, high pressure jets of water to cause the fibres to interlace. Hydro-entanglement is sometimes known as spun lacing, as the arrangement of jets can give a wide variety of aesthetically pleasing effects. The water jet pressure used has a direct bearing on the strength of the web, but system design also plays a part.



T11. Web bonding.[12]

4.2. Fibres

4.2.1. Natural Fibres

Natural fibres are made from plant, animal and mineral sources. The natural fibres can be classified into three chemical classes:

- Cellulosic, which are the fibres obtained from various parts of plants, such as the stems (bast fibres), leaves and seeds.
- Protein (keratin) fibres, which are the fibres obtained from wool and hair and silk.
- Mineral (the only naturally occurring mineral fibre is asbestos but its use is banned in many countries because of its toxicity).

Table 12 summarizes the natural fibres by origin: vegetable, animal and mineral.

NATURAL FIBRES						
VEGETABLE			ANIMAL			MINERAL
Bast Fibres Flax Jute Hemp Ramie Nettle Bamboo	**Leaf Fibres** Sisal Manilla Raffia Abaca henequen	**Seed Fibres** Cotton Coir kapok	**Wool Fibres**	**Hair Fibres** Cashmere Camel Mohair Alpaca Angora	**Silk Fibres**	Asbestos

T12. Natural fibres.

Textile fibres are characterised by their fineness, length and thickness. There are several fibrous structures, however they have to be able to be converted into yarns for textile fabrics manufacturing. Most of the natural fibres, ranging from 2–50 cm in length and 10–40 mm in cross-section. Staple fibres are converted into yarns by spinning process that requires some degree of surface roughness to allow the adhesion to one another in the yarn.

• Flax

Flax fibres are obtained from the stem of the plant (of the species *Linum usitatissimum*). Flax fibre is called "linen", once it is spun into a yarn, then woven or knitted into a fabric. The best quality flax fibres are obtained from the coastal regions of northern France, Belgium, and Netherlands. Smaller quantities are produced in Poland and the Czech Republic. China and Russia are responsible for the production of a significant quantity of flax. The flax fibres can be very long in comparison with cotton fibres. The purity of flax fibres is lower than cotton in terms of cellulose content, they contain about 60% of cellulose. This composition also contains hemicellulose, lignin, proteins, waxes, pectin's and natural colouring materials.

F11. Natural fibres.[13]

• Jute

Jute is obtained from the stem of the jute plant. Jute is mainly produced in producing India, Bangladesh and China, with lesser quantities being produced in Myanmar and Thailand. Jute fibres are relatively cheap because they don´t need fertilizers or pesticides. However, cultivation is labour intensive because the plants are harvested by manual cutting, as common in Asian countries that pay low salaries.

In footwear, jute is mainly used for the ethnic look. However, this material has a poor abrasion resistance for footwear applications. Jute fabrics are normally strong, with low extensibility, coarse and hair fibres could be irritating. However, jute has less rotting and shrinkage problems when compared with cotton.

F12. Jute[14]

• Hemp

Hemp is a bast fibre obtained from the stem of the plant. These fibres are much lower in cellulose content than cotton, but contains hemicellulose and lignin. The presence of lignin confers a harsher handle than cotton and make the fibres stiffer and brittle. The physical and chemical properties are similar to flax properties. Some hemp fibres are relatively bright and lustrous, but others are darker which detracts from their appearance. It is difficult to dye these fibres, contrary to its eco-friendly characteristics. Hemp is characterized to be strong, durable and absorbent and to have food resistance to UV radiation.

The main producing countries of hemp fibre are China, Spain, Korea and Russia, and the plant is very tolerant of varying climatic conditions.

F13. Hemp.[15]

• Bamboo

Bamboo fibres composition is about 61% cellulose and 32% lignin. This fibre is characterized by its absorbency and coolness, together with a very soft handle.

Bamboo fibre is a regenerated cellulosic fibre and derived from a renewable resource. However, its extraction is done by chemically aggressive process with significant implications for the environmental. Alternatively, the woody stalks could be crushed mechanically and subjected to retting process, in which the natural enzymes break down the cell walls and the separate the bamboo fibres. The fibres are smooth and round and are ideal for skin that is sensitive to allergies or irritable materials.

• **Leaf fibres**

The use of leaf fibres is limited because they are coarser then bast fibres. These fibres are normally obtained from the leaves by mechanically scraping away the non-fibrous material, washed and dried.

• **Cotton**

Cotton is made of long chains of natural cellulose. The length of the chains determines the ultimate strength of the fibre. The unique physical and aesthetic properties of the fibre, combined with its natural generation and biodegradability, are reasons for its universal application.

Cotton is used mainly in knitted and woven fabrics of most weights. The advantageous for footwear applications are: availability; easily dye; can be raised, woven, knitted or braided; easily bonded and results in strong fabrics. As disadvantageous of cotton fabrics are associated to the shrink and rot if they are not properly treated and can also have poor stretch and abrasion resistance.

F164. Cotton.[16]

• **Wool**

Wool availability is lower and the cost is higher when compared with cotton fibres. However, its use is important. The wool fibre is a natural product of the sheep made of keratin. Keratin (protein) in the wool fibre has a helical rather than folded chain structure with strong inter- and intrachain hydrogen bonding which are believed to be responsible for many of its unique characteristics. The location, origin and animal growth conditions are important for the characteristics of the materials.

The overall high extensibility of wool, its natural waviness and ability to trap air has a coordinated effect of comfort and warmth, which also make it an ideal insulating material. The sophisticated dual morphology of wool produces the characteristic crimp which has also been an inspiration for the development of some highly technical synthetic fibres. Wool fibre used in footwear production is usually limited to specific applications and products, mainly and lining or decorative parts.

F15. Wool.[17]

4.2.2. Man-Made Fibres

The man-made be sub-divided into three broad groups:

- 'Regenerated' fibres, which are fibres derived from natural sources comprising organic polymers by chemical processing to both extract the fibre-forming polymer and to impart novel characteristics to the resulting fibres.
- Synthetic fibres that are produced from non-renewable sources.
- Inorganic fibres, such as ceramic and glass fibres.

Table 13 summarizes the man-made fibres by origin: natural, synthetic and inorganic.

MAN-MADE FIBRES				
NATURAL POLYMERS			SYNTHETIC	INORGANIC
Cellulose Rayan Vicose Cupro Modal Lyocell	**Cellulose esters** Acetate triacetate	**Others** Rubber Alginate Collagen Casein Soya Starch (PLA)	Polyvinyl alcohol (PVA) Polyvinyl chloride (PVC) Polyacrylonitrile (PAN) Polytetrafluoro ethylene (PTFE) – Teflon Polyamida (PA) – nylon 6, nylon 66, aramids Polyester (PET) Polypropylene (PP) Polyetheylene (PE) Polyurethane (PU) – elastane (e.g. Lycra) Special Fibres - (e.g. polybenzoxazole and polybenzimidazole)	Carbon Glass Metal

T13. Man-made fibres.

- **Viscose**

The cellulose present in pine or beech wood is the raw materials to produce viscose. These fibres are quite inexpensive, but the production processes imply ecological limitations.

The manufacture of viscose integrates the following steps:

- Isolation of cellulose from the wood;
- Transformation of cellulose by chemical treatment;
- Spinning process.

The main properties of viscose fibre are:

- Relatively low strength;
- Fairly extensible and stretches more in wet conditions;
- Low recovery from stretching
- Very good resilience
- Low retention of heat
- Loses strength on exposure to sunlight.
- When burning, viscose fibre burns quickly and leaves a very small amount of ash.

More recently, are produced special viscose fibres, that are stronger, more resistant to wear and less absorptive.

In footwear production viscose (depending on the type) is used as:

- Fabric for surface components;
- Laces;
- Linings and interlinings
- In blends with fibres from synthetic polymers.

• Cupro

Cellulose fibre obtained by the cuprammonium process.

The fabric is commonly known by the trade name "Bemberg", owned by the J.P. Bemberg Company.

There are main properties of cuprammonium rayon are:

- Very fine
- Produce a soft silk like handle
- Has same properties as cotton except the average degree of polymerisation is lower, and a larger part of this fibre is occupied by amorphous region.
- It burns rapidly and chars at 180 ºC.
- On ignition, it leaves behind ash containing copper

• Modal

Modal is a type of high wet modulus rayon that has a very precisely defined strength. Modal can be defined as a cellulose fibre that has a high breaking force and a high wet modulus. The breaking force in the conditioned state and the wet modulus required to produce an elongation of 5 %. The Modal fibre is mainly used, often blended with cotton, to produce garments worn next to the skin, such as lingerie, and for home textiles, such as towels, bath robes and bath mats. It is also used for fashion knitwear.

• Lyocell Fibres

Lyocell fibres can be defined as cellulosic fibres obtained by an organic solvent spinning process. It is understood that:

1. an "organic solvent" means essentially a mixture of organic chemicals and water, and
2. "solvent spinning" means dissolving and spinning without the formation of a derivative.

The main properties of Lyocell fibres are:

- Greater tenacity and greater wet strength than viscose fibres, due to their structural characteristics;
- Small diameters can be produced (fineness to the touch);
- Propensity to fibrillate that could be positive or negative depending on the final use.
- Claimed to be a natural hygienic fibre that inhibits the bacterial growth because has a great capacity to absorb moisture and perspiration from the body.

Tencel® is a cellulosic fibre produced from wood being classified as a renewable resource and biodegradable. Two important characteristics from the environmentally-friendly point of view.

• Cellulose Acetate Fibres

Acetate is a cellulose acetate fibre in which less than 92 %, but at least 74 %, of the hydroxyl groups are acetylated.

Triacetate is a cellulose acetate fibre in which at least 92 % of the hydroxyl groups are acetylated.

The general properties of these cellulose acetate fibres are:

- not very crystalline fibres, in comparison with starting cellulosic material, being less stronger fibres;
- superb handle; silk-like quality and smooth.

4.3. More sustainable textiles and synthetics for footwear

Sustainable textiles and synthetics should be environmentally friendly and respect social and environmental quality, preventing or controlling the level of pollution. Additional, should take in account the Restricted Substances Lists (RSLs) that connect the production ecology to human ecology. The Restricted Substances Lists promote the safer use of chemicals and the verification of materials cleaner production.

Recommendations for lower environmental impact

Textiles/synthetic:

- Without all carcinogenic or potentially carcinogenic chemicas and dyes;
- With biodegradable materials in substitution of aggresive chemicals;
- Without or with minium amount of active chloride and other active halogen compounds;
- Without or with minium amount of formaldehyde compounds;
- Without dyestuffs containing heavy metal ions;
- Sustainable fibres: Biodegradable, recyclable and reycled;
- More natural materials;
- More durable and light materials.

Production processes that:

- Recycle, purify and reuse chemicals;
- Use dyestuffs with maximum exhaustion, reducing the waterwater pollution;
- Reduce the dye-to-liquor ratio, water, energy, chemical and dyestuff consumption;
- Reuse heat and water, saving energy and water and reducing the environment pollution level.

CLASS	ECO-FRIENDLY FIBRES
Organic	Organic cotton, organic wool, organic silk
Man-made	Corn/soya bean, lyocell, pineapple, milk weed
Recycled	Recycled cotton, recycled polyester
Natural	Naturally coloured cotton

T14. Eco-friendly textile fibres.[16]

4.4. New materials

4.4.1. New eco-friendly fibres and process

Seacell[18] - this fibre is derived from wood pulp and seaweed (algae) and diffuses its protective and anti-inflammatory properties into the skin, stimulating the metabolism.

Lenpur[19] - this biodegradable fabric is made from white pine tree clippings, and "offers the comfort of silk, the touch of cashmere and the lightness of linen." Lenpur's website states that it's a cut above the other cellulose fibres due to its softness, its absorption capacity and ability to release dampness, and its ability to sustain a higher thermal range —thus keeping you cooler in the summer and warmer in the winter.

SoySilk[20] - this lesser known 100% biodegradable eco-friendly fabric is made from tofu-manufacturing waste. Soy protein is liquefied and then stretched into long, continuous fibres that are cut and processed like any other spinning fibre. Because soy has high protein content, the fabric is very receptive to natural dyes, so there's no need for synthetic dyes.

STINGplus Nettle Fabric[21] - The fabric is woven from the stinging nettle, which "produces a uniquely strong, soft and naturally fire retardant textile fibre" and, blended with pure new wool, it is "the ultimate environmental upholstery solution."

Organic cotton[22] - More than 25 percent of the world's pesticides are used in conventional cotton production. Organic cotton is grown without toxic, synthetic chemical inputs. Look for natural dyes or coloured cotton to further reduce the amount of chemicals dumped into our ecosystem.

Recycled polyester[22] - This fibre is made from cast-off polyester fabric and soda bottles, resulting in a carbon footprint that is 75 percent lower than virgin polyester. Recycled polyester contains toxic antimony, but some companies are working on removing it from their fabrics.

Soy cashmere/silk[22] - This fabric is made from soy protein fibre left over after processing soybeans into food. The soy may be genetically engineered unless noted on the label.

Organic Wool[22] - Wool is renewable, fire-resistant and doesn't need chemical inputs. Look for chlorine-free wool from humanely-treated animals. Organic wool is increasingly becoming available: it is produced using sustainable farming practices and without toxic sheep dips.

EVO by Fulgar[23] – Fulgar, a leader in the synthetic fibre market, has developed EVO, an innovative high-performance fibre made of a biopolymer derived entirely from castor oil seed. Castor oil has traditionally been used as a laxative and in many other applications ranging from soaps and lubricants to paints and dyes.

Even these choices are not clear-cut, says The Nature Conservancy. These types of fabric represent positive change, but have drawbacks. Textiles production in general has environmental impact, including:

- **Energy** - It takes agricultural energy to produce natural fibres and mining or processing for synthetic fabrics. Energy also is needed for production, processing and shipping of the fabric and finished product.
- **Toxic chemicals** - Pesticides, dyes and bleaches and chemical processing are used for fibres like bamboo or rayon.
- **Land/natural resources** - Natural fibres can require large areas for production and synthetic ones typically require petrochemicals.
- **Water** - Nearly all fabrics require some water use during production, with cotton requiring the most.

The way we use textiles can make an enormous environmental difference - as much as the type of fabric. Since all textile manufacturing has a fairly hefty impact, wearing what we already have for a longer time is one of the best and easiest things you can do to make your clothing more eco-friendly. Other ways include buying used clothes, recycling what doesn't fit and repairing damaged clothes rather than throwing them away.[24]

4.4.2. New footwear products

- **Vegan Footwear** [25, 26]

Vegan footwear, refers to footwear made without leather or any animal ingredients. Originally touted by hippies and the vegetarian and vegan communities, vegan shoes have now spread to the fashion world.

BEYOND SKIN
Based in Brighton in the United Kingdom, Beyond Skin creates its faux-suede footwear using a microfiber called Dinamica, which is made in Italy from 100 percent post-consumer recycled plastic bottles.

BOURGEOIS BOHEME
Bourgeois Boheme began as an online marketplace and retail showroom in London's Notting Hill district, but the vegan enclave soon expanded to create its own wares from handpicked, non-exploitative factories that oppose child labour.

CRI DE COEUR
Founded by Parsons The New School of Design graduates Gina Ferraraccio and Julie Dicterow, Cri de Coeur clads its kicks in premium, cruelty-free materials such as low-VOC polyurethane, 100 percent recycled Ultrasuede (derived from post-industrial polyester), and reclaimed wooden soles.

FORM & FAUNA
Form & Fauna handcrafts its critter-friendly shoes in the United States from biodegradable Italian synthetic leathers, organic cotton and hemp fabrics, and second-generation scrap wood for its heels, wedges, and platforms. Water-based glues cobble everything together, while an open cell-rubber lining adds comfort and durability.

KAILIA
Designed in Italy and fairly handmade in small, family-owned factories across Europe, Kailia's vegan boots, pumps, and flats abide by strict environmental standards, including the eschewal of toxic polyvinyl chloride and a preference for vegetable-dyed organic linen and cotton linings, pre-consumer recycled footboards, and water-based glues.

MOHOP
Designed to provide infinite interchangeable options, Mohop's American-crafted sandals feature sustainably harvested cherrywood from Pennsylvania, black soles derived from natural rubber and rice husks, and padded footbeds made from faux leather.

NEUAURA
Produced in a green, union-run facility in Brazil that runs on hydroelectricity and recycles its waste, Neuaura's eco-conscious shoes are completely devoid of fur, leather, silk, or wool. Plus, the company donates a portion of its annual sales to charities that work to improve animal welfare and the environment, including the Wildlife Conservation Society for 2011.

NOHARM
Noharm bears the stamp of approval from no less than Britain's Vegan Society, along with an ethos that opposes child labor and worker exploitation. Its dapper men's oxfords, loafers, and boots are ethically handcrafted in Italy, where they're packaged in biodegradable boxes printed with environmentally friendly inks.

NOVACAS
Novacas —named for the Spanish and Portuguese word for "no cow"—manufactures its vegan, PVC-free men's and women's shoes in worker-friendly factories in Portugal that align with European Union labor standards. It uses nontoxic, 100 percent biodegradable uppers whenever the opportunity presents itself, along with high-quality synthetics that stretch, breathe, and wear just like the genuine article.

OLSENHAUS
In addition to nontoxic, environmentally preferable synthetics—including a microfiber derived from recycled televisios – Olsenhaus plies its wares with sustainable materials such as organic cotton, linen, and cork. All its shoes are fairly handmade in Central America, where production is kept as local as possible to minimize its footprint.

ELIZABETH'S KIND CAFE
Handmade in the United States, derived from recycled plastic bottles, and completely animal-free, Elisabeth Katzman's nascent shoe line is a triple threat to reckon with. Bonus: a portion of every sale benefits People for the Ethical Treatment of Animals and 1% for the Planet.

VEGETARIAN SHOES
It all started with a simple lace-up shoe, but Vegetarian Shoes has come a long way since 1990. Two decades later, its extensive range of men's and women's styles are made to order in factories across the United Kingdom and Europe, including England's oldest co-op, which was first established in 1881.

ZOE & ZAC
From the unlikely quarters of Payless ShoeSource comes an affordable line of green footwear derived from faux leathers, organic cotton, linen, natural hemp, recycled rubber, and water-based glues. Zoe & Zac is a collaboration between the footwear giant and model-entrepreneur Summer Rayne Oakes, who lends her unerring eye to the ongoing collection.

OLANTHE
Perfect for vegan brides and bridesmaids, Olanthe's matrimonially minded satin flats and heels hail from the south of France, where they're crafted in a family-owned factory that has been making shoes for 100 years.

MACBETH
Macbeth isn't exclusively vegan, but its range of cruelty-free sneakers and hi-tops is so extensive that we would be remiss if we left it out. Although the shoemaker manufactures overseas, Macbeth only works with factories that abide by strict labor laws relating to minimum age, wage and overtime regulations, employee housing, and workplace safety.

KEEP
An animal-friendly shoe and clothing company based in Los Angeles, Keep uses a third-party auditor to ensure ethical working conditions in its factories in China, Brazil, and Vietnam. "A Keep team member is on the line for every single production," it says

FREERANGERS
Not only is every pair of Freerangers handmade to order in the United Kingdom, but it also bears the Vegan Society insignia as a guarantee of excellence. Your purchase also includes a full refurbishing service, so your clodhoppers stay in tip-top shape for years to come.

CHARMONÉ
Beautiful, luxurious, sexy shoes that are also sustainable and cruelty-free. Every shoe incorporates European design and quality while using only animal-free, eco-friendly materials. We believe no one should sacrifice their style conscious just to serve their social conscience. Charmoné is focused on compassionate design: compassion for animals; compassion for planet and compassion for people.

- **Biodegradable shoes**

Biodegradable shoes is related to footwear that uses biodegradable materials with the ability to compost at the end-of-life phase. Such materials include natural biodegradable polymers, synthetic biodegradable polymers, and biodegradable blends. The use of biodegradable materials is a long-term solution to landfill pollution that can significantly help protect the natural environment by replacing the synthetic, non-biodegradable polymers found in athletic footwear.

OATSHOES
OAT claims made the world's first biodegradable sneakers that grow flowers when you plant them. We developed the first biodegradable leather shoes, bags that grow sunflowers and even baby shoes with seeds to grow your baby's Tree of Life.

T17. Pat biodegradable shoe.[27]

- **Recycled Shoes**[28]

Recycle shoes are obtained by reusing materials benefited as raw material and transformed into a new product.

SIMPLE SHOES[29]
All of their shoes use recycled materials. The simple shoes integrate the following recycled (or organic) materials:

- Bamboo
- Silk
- Recycled Plastic
- Hemp
- Recycled carpet padding
- Organic cotton
- Recycled car tires
- Coconut
- Eco-certified leather and suede
- Wool
- Recycled inner tubes
- Natural crepe rubber
- Cork
- 100% post-consumer recycled paper

4.5. Requirements and Quality Control

The quality control for textiles used in footwear, must be basically the same as that used for the leather. The characteristic of uppers, insoles, insocks and linings, in the shoe must maintain the properties, regardless of the material, namely:

- **Flexible and with tear strength.**

  Textile/synthetic is subjected to flexion and stretch during the shoe manufacturing and wear, being essential to guarantee a suitable flex resistance and tear strength, considering the handling and final application, to avoid the break of finishing and material itself.

- **Elasticity and plasticity properties**

  The elasticity property of textile/synthetic is important to mould the 2D material in a 3D construction and get a permanent shape, even after the last is removed. On the other hand, during wear the shoe is constantly subjected to flexion and should recover its original shape when it is removed from the foot. In this way it is necessary combine in a proper way the elasticity and plasticity properties to get a suitable shoe product.

- **Delamination resistance**

  The delamination during wear should be avoided by a good adhesion of finish to textile/synthetic surface.

- **Bondability and seam strength properties**

  To ensure a good adhesion between the upper and sole and resistance during the stitching process and wear.

- **Colour fastness and abrasion resistance**

  To prevent the loss of colour and maintain the original aspect of textile/synthetic. If the shoe has no lining material, it is necessary prevent the staining of socks or users' feet.

- **High temperature resistance**

  During the shoe manufacturing process, textile/synthetic is subjected at high temperature, so the material has to have resistance to these temperatures to prevent the shrinkage and break during the drying operations.

- **Water vapour permeability and absorption**

  The comfort depends on the humidity inside the shoe during the wear due to transpiration, so the textile/synthetic should be capable to release the water vapour to the outside. The finishing applied on material surface can prejudice the breathable properties that characterize leather materials.

- **Absence of hazardous substances to human** (e.g., azo-dyes, chromium VI, DMFU, formaldehyde, heavy metals, organic tin, etc).

5. Soles and Midsoles

The sole is one of the most important part of footwear. It´s first function is to prevent the damage of the floor could make to the feet. The footwear sole also provides the absorption of energy during the walking, protects the feet from heat and cold and can be extremely important for supporting certain activities, like running, hiking, walking, etc. The sole, can be a distinguish factor for footwear, its design and special features, formulation and composition contributes for specific function.

5.1. Classification

The kind of sole depends on such factors as demands, fashion, ease of manufacture, price, durability, and a satisfactory source of supply. There are many types of procedures and technologies associated to the production of types of soles. The sole and midsole materials could be based in several material that could be divided by:

- Natural origin materials;
- Synthetic origin materials

5.2. Natural origin materials

Natural origin materials, are the ones that have origin in nature, like leather, wooden, cork, natural rubber.

• Leather

Leather is the oldest / traditional sole material. This kind of soles has been modified and improved by tanners so that a high quality leather sole is now light, flexible, waterproof and still retains breathability. The main advantage of leather soles is their ability to absorb dampness and to improve the comfort. In other side the disadvantages are their low lifetime, usually lower slip resistance and high price. Nowadays this kind of soles is mainly used for formal shoes and classic dance shoes, where the leather soles support turning and spinning on the dance floor.

• Wooden

This kind of soles are very rare nowadays, and only used for clogs or fashionable summer sandals. This soles are very rigid (low flexibility) and have low slip resistance.

• Cork

Cork is a natural product and is used for numerous components but is mainly incorporated into wedges/ and platforms. Depending on the aesthetic requirements or quality (roughness) of cork or cork agglomerate platform may be a requirement of applying an insock. Cork is:

- Environmental friendly; Natural and recyclable;
- Light (90% of its weight is air);
- Good thermal isolation;
- Good indentation: prevents the rough surface of the ground is transmitted to the foot;
- Good shock absorber;
- Good plantar pressure distribution;
- Permeable: allows the foot to breath and absorbs the humidity of the foot;
- Impermeable: Prevents the foot to moist;
- Good slip resistance;
- Good resistance to wear.

Some negative aspects are the low flexibility and the crack of the material.

T18. Cork insoles[30]

• **Natural / crepe rubber (NR)**

Natural rubber is, made by coagulating latex from rubber tree. This soles are very high wear resistant, have good heat insulation properties and are flexible. They have been gradually replaced by vulcanized rubbers, because of price. NR is constituted by Polyisoprene and has good abrasion resistance and flex cracking.

F19. Extraction of natural rubber.[31]

5.3. Synthetic materials

Synthetic sole and midsoles materials are polymer based and are produced and processed by man.

The word polymer means a material produced by the chemical joining together of many small units to form much larger on in the form of long chain-like chemical structures. The polymers physical properties result from the interaction of hundreds of millions of these chains intertwined with another like the interangled structure of wire wool.

The small units used for making the links of the long chains are called monomers, meaning single units.

Polymerisation – the linking together of the monomer pieces to form a polymer is carried be a process called polymerization. In case of rubber, there's natural rubber obtained by latex and synthetic natural rubber produced by chemistry industry. Both processes are made by converting monomer Isoprene into polymer polyisoprene.

Various rubber polymers are used for soles, and natural rubbers is just one. Note that natural rubber is the only soling rubber produced by nature. All the other rubbers used in soles are man-made.

Copolymerisation – two or more different monomers in differing proportions may be linked together into a chain-like polymer structure. In these cases, the result polymer is called copolymer. As an example, nitrile rubber is therefore a copolymer rubber produced by the polymerisation of a mixture of acrylonitrile and butadiene monomers.
The proportions of the two monomers used to form the copolymer are variable according to the end of use.

Cross-linking – this chemical term means that the intertwined long chain molecules can be linked together chemically where they cross over or are close to one another. The actual nature of the cross-links can be varied so that they are permanent or semi-permanent.

The more relevant materials used in footwear are the following:

• **Styrene-butadiene rubber (SBR)**

SBR is a synthetic rubber, with properties very similar to the natural one (the version developed by Goodyear is called Neolite that has a greater content of styrene 50 to 85%). The styrene/butadiene ratio influences the properties of the polymer: with high styrene content, the rubbers are harder and less rubbery.

• **Synthetic polyisoprene (IR)**

This is a synthetic rubber with the same chemical constitution as natural rubber, and it closely resembles natural rubber and its physical properties. Because of differences in molecular weight and shape, however, it tends to have better flow characteristics.

- **Polybutadiene (BR)**

Synthetic rubber with a great resilience than natural rubber. It is most used in blends with NR or SBR either to improve the quality of compound or to reduce the overall cost by allowing more extender oil to be added.

- **Nitrile rubber (NBR)**

NBR is an acrylonitrile-butadiene copolymer and is the rubber most commonly used, either by itself or blended with PVC. It has very good abrasion resistance.

- **Polychoroprene (CR)**

Neoprene is a brand name of this synthetic rubber .Such rubbers are used mainly for their oil and weathering resistance and they are superior to the NBR in weather resistance.

- **Thermoplastic Rubber (SBS / TR)**

Styrene-Butadiene-Styrene (SBS) copolymers are a versatile family of compounds which combine a high strength, a comprehensive range of hardness and a low viscosity for the thermoplastic melt processing. The wear resistance and physical resistance is variable (depending on composition). Mostly used for common footwear. TR may vary according to the type of process used, presenting itself in the form of compact TR or TR expanded. The compact TR normally presents densities between 0.90 and 1.20 g / cm^3. The expanded TR normally presents densities between 0.60 and 0.80 g / cm^3.

- **Styrene-Ethylene/Butylene-Styrene (SEBS)**

These copolymers are a family of compounds with a high resistance to UV radiation, good resistance to high temperature and good processing stability. This material is widely used in the handles, cables, thermoplastic modifiers of impact properties and medical applications.

- **Acrylonitrile-butadiene-styrene (ABS)**

ABS resins are a dispersed phase of rubber, constituted by a matrix of styrene -acrylonitrile copolymer and styrene- butadiene. These are thermosetting plastic with good resistance to solvents and elevated temperatures polystyrenes. It is usually used in the production of heels, shoe heel of high fashion.

- **Polyvinyl chloride (PVC)**

PVC it is normally used in its thermoplastic form. It is a hard polymer, colourless solid resin and melts at temperatures between 170-180 ° C. Its thermal instability can be problematic due to breakage of the PVC to release HCl, which can be harmful.

Often have a reasonable / good wear resistance. For the processing of PVC plasticizers are used to increase flexibility, stabilizers products to prevent temperature degradation, lubricant products to help the processing, loads to lower the price and pigments for colouring.

Nowadays, PVC is considered not to be suitable for soles. PVC is used only on children shoes, where it's relatively high density is not so shown. On adult shoes is only used in work footwear, because of its resistance to environment with animal fats. Besides this PVC has high heat conductivity, heating the feet and becoming uncomfortable to the wearer. Environmentally PVC soles are nowadays considered as unfriendly plastic, which liquidation and burning can create carcinogen dioxins. PVC needs to be softened and this is achieved by adding phthalates, which are considered to be harmful (they must not be used by children under 3 years old).

- **Ethylene vinyl acetate (EVA)**

EVA is produced by co- polymerization and can be used in the production of soles in its thermoplastic form and crosslinked. Typically presents in its expanded form (microcellular), however, can be used in its compact form). Mostly used in sports because it is a very light material (low density). It is possible to foam in different degree and its easy workability are major advantages. The biggest disadvantages of EVA soles are the permanent deformation and lower wear resistance.

• **Polyurethane (PU)**

PU is different compare to other plastics because PU soles flexibility is reached by gas saturation rather than plasticizers. A PU sole is made by metering the necessary chemical ingredients in liquid form into a mixing chamber, mixing them, and transferring the mixture into a mould. While they are still in the mould, the liquids react to form a polyurethane.

Pu soles are soft with high level of comfort and thermal isolation, are lighter than most of plastics. This soles present good resistance to oils, abrasion, slip, energy absorption, flexibility. As disadvantages, are the environmental factors, as the use of fluorohydrocarbons and isocyanates and the high quantity of waste generated.

• **Thermoplastic Polyurethane (TPU)**

TPU appeared in the nineties. Its advantage is the use of no waste technology and the easier procession and relativity good utility properties. Slip resistance is better than PU soles.

5.4. Soles and midsoles processing processes

The most used materials for the production of soles, heels and midsoles are Vulcanized Rubber, Thermoplastic Rubber (TR), Polyvinyl Chloride (PVC), Thermoplastic Polyurethane (TPU) and Polyurethane (PU) with several compositions and expansion states.

The technologies, equipment, raw materials used for their production are summarized in following table.

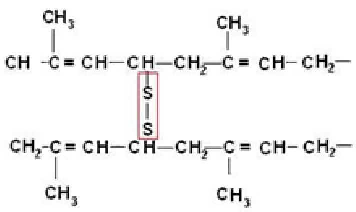
PRODUCTS	TECHNOLOGY	MAIN EQUIPMENT	RAW MATERIALS
Soles and heels made of vulcanized rubber	Compressing shaping	Mixing equipment for preparing the rubber compounds. Vulcanization presses.	Rubber, charges, plasticizers, additives, several.
Soles of TR, PVC, TPU compact and expanded	Injection shaping	Injection presses of thermoplastics	TR – Thermoplastic Rubber PVC - Polyvinyl Chloride
PU soles	Casting shaping	Casting presses of polyurethane	Liquid system Polyol/isocyanate

T15. Technologies, equipment, raw materials for soles production.

- **Vulcanized rubber**

Several different rubber polymers are used for shoe soles. Each polymer has its own combination of properties, and the polymer is chosen according to the end use. The two main polymers used are natural rubber (polyisoprene) and styrene-butadiene rubbers (SBRs). There are also synthetic polyisoprene, polybutadiene, nitrile, and polychloroprene (neoprene) rubbers.

Actually, most of the used rubber in footwear is vulcanized. During vulcanization, the macromolecules are reticulated by transversal bonds (most frequently through the sulphur molecules). The process of vulcanization can be influenced by temperature, pressure and the application time of temperature and pressure.



F20. Process of vulcanization.[32]

The compounds used for manufacturing vulcanized rubber soles result from mixing several raw materials. The most important are:

- Polymers (rubbers) – Natural rubber (NR), Synthetic Rubber (Styrene-butadiene rubber (SBR), Polybutadiene (BR), Nitrile rubber (NBR) and Polyisoprene (IR);
- Reinforcing fillers - Silica and carbon black;
- Plasticizers – Mineral oils and synthetics;
- Sulphur;
- Protective agents.

To produce soles, the compound is put in a mould and heat (150-170 ºC). During shaping time (6-12 minutes) occurs a chemical reaction – vulcanization, the chemical connection between the polymers molecules.

The main parameters in the process are the temperature and vulcanization time.

This process includes the following steps:

1. Raw materials weight;
2. Compost mixture;
3. Preform cutting;
4. Moulding and vulcanization;
5. Deburring;
6. Finishing (Chemical carding or mechanics, painting, etc.)
7. Packing

In table 16 are presented some of typical characteristics of vulcanized rubbers.

PROPERTIES	SBR	IR	BR	NBR	CR
Polymer density	0.92 to 0.99	0.91 to 0.93	0.91 to 0.93	0.96 to 1.01	1.23 to 1.24
Hardness shore A	30-95	15-100	40-95	20-100	20-95
Tensile properties, MPa	7-21	15-25	3.5-21	7-21	7-21
Elongation at break, %	600	1000	600	600	600
Tear resistance	excellent	excellent	excellent	good	good
Impact resistance	excellent	excellent	excellent	good	good
Residual deformation, (%)	10-30	10-30	10-30	10-20	20-60
Abrasion resistance	excellent	excellent	excellent	excellent	excellent
Minimum temperature service (ºC)	- 45	- 50	- 60	- 30	- 45
Maximum temperature service (ºC)	85	80	90	125	100
Resistance to ozone	moderate	weak	moderate	moderate	good
Resistance to weathering, sunlight and UV	good	weak	moderate	moderate	good
Gases impermeability	moderate	moderate	moderate	good	good
Water resistance	good	good	good	moderate	good
Resistance to diluted acids and basis	good	good	good	good	good
Resistance to concentrated acids and basis	weak to moderate	weak to moderate	weak	weak to moderate	very weak
Resistance to oils	very weak	very weak	very weak	excellent	good
Average life	3-5 years	2-5 years	3-5 years	3-10 years	5-15 years

T16. Typical characteristics of vulcanized rubbers.[33]

- **Thermoplastics**

The compounds of TR, PVC and TPU are received in granular form already formulated.

The compounds of TR are usually polymers of Styrene-Butadiene-Styrene (SBS) or styrene-isoprene-styrene (SIS).

The compounds of TR, PVC or TPU may already be incorporated with expansion agents that release gases when heated. These gases are responsible for the air bubbles formation in soles, reducing their weight.

To produce the soles, the compost is heated into a paste that is injected into the mould. By cooling the compost solidifies. The main parameters of the process are the injection temperature (140-190ºC), the injected volume and the cooling time (2-6 minutes).

This process includes the following steps:

1. Injection and shaping;
2. Finishing (mating process, painting, etc.);
3. Packing.

The main advantages of thermoplastics are:

1. Good relation price / quality;
2. Looks and feel likes rubber;
3. Low price;
4. Easy processing;
5. Wide range of hardness;
6. Good physical properties (abrasion resistance, flexibility at low temperatures, thermal isolation among others).

Thermoplastics are lighter and better satisfy the requirements of fashion point of view, presenting a more efficient production process that the rubber. They have a lower temperature and resistance to solvents. Thermoplastics don't require vulcanization, they just need to be shaped and when the cooling happens they acquire the shape of the mould.

Their hot melt characteristics allow them to be reheated and re- embedding the shaped and their residues in the initial formulations.

• **PU soles**

The Polyurethane used for soles is formed by the reaction of two liquids, the Polyol and the Isocyanate. The two basic PU compounds are polyester and polyether.

The liquids are mixed immediately prior to being poured into the mould. The chemical reaction for the PU formation occurs after the mixture of the two liquids. These gases released from this reaction are responsible for the tinny air bubbles formation in PU soles, reducing their weight.

When mixtures of cork with PU are made, the cork is added at the mix time of Polyol and the Isocyanate.

This process includes the following steps:

1. Mix and casting;
2. Moulding;
3. Deburring;
4. Finishing (painting, milling, etc.);
5. Packing.

Belong is presented a summary table 16, with the most relevant polymeric materials used in soles.

Latex / Crepe Not vulcanized natural rubber, compact, lower density (0.85-0.95 g / cm^3) and less stiff. Good slip resistance properties.	**Natural Rubber (NR) – Polyisoprene** Sole material with good properties of resistance to abrasion and flexing.	**Polyisoprene (IR)** Synthetic rubber with same constitution of natural rubber.
Polybutadiene (BR) Synthetic rubber with high resilience, abrasion and flexion resistance. Very used in mixture with NR and SBR to improve its properties or to reduce production costs.	**Styrene-butadiene rubber (SBR)** Similar characteristics of natural rubber (can be mixed). Density between 1.10 and 1.25 g / cm^3 and a hardness between 60 and 80 Shore A. Good abrasion resistance, good physic-mechanical properties and resistance to slip.	**Nitrile rubber (NBR)** Acrylonitrile- butadiene copolymer. Density between 1.10 and 1.25 g / cm^3 and hardness Shore A of 60 to 80. It can be blended with PVC to improve resistance to oil and temperature. Good properties of resistance to abrasion and slip.
Polychoroprene (CR) Corresponds to the neoprene brand. It is normally used when superior properties of resistance to oils and conditions are required.	**Neolite** The base polymer is styrene - butadiene copolymer, but with a greater styrene content (50 to 85 %). High hardness (88 Shore A) and the density of 1.25 1.40 g / cm^3. Low tensile strength and flexing. Normally used in classic shoe (soles and / or covers).	**SEBS (Styrene-Ethylene/Butylene-Styrene)** High resistance to UV radiation, good resistance to high temperature and processing stability. Mostly used in hospital footwear.

Rubber Thermoplastic (SBS) Copolymers of styrene -butadiene- styrene. High strength, a large range of hardness and low viscosity. Compact RT: density between 0.90 and 1.20 g / cm^3. TR expanded: density between 0.60 and 0.80 g / cm^3.	**Acrylonitrile-butadiene-styrene (ABS)** Thermosetting plastics with good resistance to solvents and more elevated temperatures than polystyrenes Typically used in the production of heels, shoe heel of high fashion.	**Polyvinyl chloride (PVC)** Used in its thermoplastic form. It is a hard polymer, colourless solid resin and melts at temperatures between 170-180 ° C. Its thermal instability can be problematic due to breakage of the PVC to release HCl, which can be harmful. Often have a reasonable / good wear resistance
Polyurethane (PU) There are two types of polyurethane used in soles: base polyester and polyether. Density may vary from 0,06 to 1.25 g / cm^3. It can present in expanded form and compactly (TPU). The expanded PU soles have properties such as lightness, flexibility, and softness, good resistance to frost and good slip resistance. PU components based on polyester have superior properties of use and stamina, but are more expensive and difficult to process.		**Ethylene Vinyl Acetate (EVA)** Can be used in its expanded form (microcellular) or compact (less usual). Lightweight (low density). Some compounds (more extended) can be slippery, low tear resistance and wear resistance and low recovery (after compression). Used mostly in sports shoes.

T17. Polymeric materials used in soles.

5.5. More sustainable sole materials for footwear

Recommendations for lower environmental impact

- Use of materials from natural and renewable resources (e.g. cork, natural rubber, wood).
- Use of recycled and/or recyclable polymeric materials.
- Use of biodegradable polymers (e.g. PU; PLA, PCL, etc.).
- Minimization/elimination of hazardous and restricted substances from materials formulation.
- Produce durable and light sole components.
- New concepts of soles that facilitate the separation of components at the use enf of life of footwear.

5.6. New materials

Increased awareness of the need to honour the earth in all areas, including clothing and footwear manufacturing, has spurred high consumer demand for shoes that are eco-friendly in materials, processing, and packaging—green shoes, if you will.

The ecological part weighs increasingly on the shoe-making worldwide, and there is already a lot of companies focusing on recyclable materials, particularly for the soles. "More than 60% of the soles used today seem rubber are actually made of thermoplastic and recyclable materials. Even when using rubber tries always to be also recycled."

Also, customers in search of earth-friendly footwear now have an extensive array of options: recycled footwear (most are made from old tires), hemp shoes, vegan shoes (no animal products are involved in the process or packaging), and more. A quick Internet search reveals many truly creative, innovative, and earth-friendly solutions that different manufacturers are offering:

- Companies that make the soles—or the entire shoe—from recycled tires, or recycled foam and rubber from factory floor droppings. Some implement shoe recycling programs by which they re-use materials or donate used shoes. These old goods are then converted to items like tracks or playground flooring.
- Companies that take it a step further and integrate ultra-sustainable ingredients such as hemp and bamboo, which utilize fast-growing plant crops.
- Companies that offer biodegradable baby footwear made of natural latex rubber that dissolves when baby grows out of it.
- Companies that focus their efforts on fair trade and fair factory labour practices.
- All of the creative practices footwear makers are coming up with help to green the process from start to finish, making shoes a more sustainable industry for the earth.

Nowadays, new materials are becoming available for the use for several companies that pretend to innovate and create new concepts in footwear industry.

APX™ is a virgin rubber compound using a patented process produced by Austin Rubber Company LLC ("Austin Rubber"). The system converts recycled tires and other scrap rubber compounds into a less expensive substitute for virgin rubber compound, which can be used in a variety of new products.[34]

Greenboots is a company that produces recyclable soles. The company produces the "SOLA TIRE", Made in recycled and reused tire rubber, more Sustainable, never forgetting the comfort and durability. [35]

Rice Rubber™ is a unique sustainable, eco-friendly product featuring a combination of natural rubber and natural rice husks that delivers durability, slip and abrasion-resistant properties. [36]

Hevea Natural Latex, is the latex Patagonia company uses in soles comes from the milk of hevea trees. Hevea natural latex provides a natural cushion underfoot which helps us to tread lighter and be more comfortable doing so. [37]

EcoTPU developed by Resimol is polyester-based TPU that contains 44% of renewable material of vegetable origin, i.e. not based on petroleum. It has got very similar properties to a petrol-based TPU. [38]

BioMoGo is a midsole that biodegrades 50 times faster than conventional athletic shoe midsoles, making it one of the most significant sustainable technologies to hit the running footwear market. BioMoGo midsoles include a non-toxic, natural additive that exponentially increases the rate of biodegradation by encouraging anaerobic microbes to break down nutrients into reusable by products. [39]

5.7. Requirements and Quality Control

The properties and quality of soles and midsoles depends on the raw materials and manufacturing process.

Sole quality control according to its end of use, is essential to guarantee the quality of shoe products in terms of physical resistance and comfort, as well as to avoid the presence of hazards substances that can be prejudicial or are forbidden for people and environment.

Vulcanized Rubber	Vulcanized Rubber Soles are a kind of material that is very temperature resistance e with a wide range of proprieties. This soles are applicable in fashion footwear, comfort footwear and safety footwear.
Thermoplastic	Light materials with a touch feeling like vulcanized rubber. Very used material in day to day footwear. The expanded forms can be used for all sole or midsole with trace of compact TR. This soles are applicable in fashion footwear and comfort footwear. Many composts are made for safety footwear.
PVC	This material presents a large range of properties, mainly controlled by hardness. The possible mixtures with nitrile rubber allows its use in safety footwear.
TPU	High durability material and resistance to flexion. Provides an excellent definition of surface. The expanded types combine lightness with good durability and excellent aesthetics. As compact form TPU can be used as midsole.
PU	Very light material, flexible, comfortable and durable. Special kinds can be used in safety footwear. Can be used as midsole in vulcanized rubber soles or TPU soles. With cork in its composition is great material for insoles.

T18. Most used materials in soles production and its use in footwear.

In a general way, soles should comply with the following properties:

- **Flex resistance**
To avoid the breaking and stability during use

- **Tear strength and abrasion resistance**
To guarantee physical resistance and performance during use

- **Slip resistance**
To avoid slip and falls (ceramic floor and water and detergent)

- **Delamination resistance or slip tear (only for multilayer soles)**
The delamination during wear should be avoided by a good adhesion of multilayer soles

- **Dimensional stability**
To guarantee the dimensions on soles.

- **Compression energy**
To guarantee that there's a good heel energy absorption

- **Bondability (only for sewn footwear)**
To guarantee the linkage between the upper part and the sole.

- **Water soluble substances content**
To prevent salts migration to the surface.

- **Water resistance**
To prevent water penetration through sole.

- **Needle tear strength.**
To prevent objects penetration through sole.

- **Resistance to oils**
To prevent sole degradation when in contact with oils.

- **Flame resistance**
To guarantee flame protection of user during use.

- **Antistatic or conductive properties**
To guarantee electrical protection of user during use.

- **Absence of hazardous substances to human**
Heavy metals, organic tin, phthalates, DMFU, etc.

6. Miscellaneous components and accessories

6.1. Components and accessories

Components and accessories in footwear have a fundamental part in footwear, although they are less "visible". The components and accessories of footwear include, toe puffs, stiffeners, heels, and shanks, which, while less apparent, are nonetheless important.

6.1.1. Toe Puffs and Stiffeners

Toe puffs and stiffeners are reinforcing materials incorporated in the uppers of shoes during manufacture so as to preserve the last shape and original appearance of the shoe. Toe puffs reinforce the toe end of the shoe upper, and stiffeners retain shape and provide support at the back of the shoe. The wide range of footwear, from lightweight fashion shoes to heavy work boots, demands a correspondingly wide range of reinforcements to satisfy practical and aesthetic needs.

Furthermore, a wide range of materials is necessary as a result of the differences in manufacturing techniques, with their different demands on the properties of shoe components. Indeed, as more and newer materials become available, innovations will continue, with the aim of producing the most acceptable reinforcement of toes and backs at the lowest prices.

The most used materials for toe puffs and stiffeners are thermoplastics sheets. These materials present:

- Strong glutinosity, well bonding;
- High tensile, good breaking and peeling resistance;
- Good in toughness, deflection and flexibility;
- Very Competitive Price.

F21. Stiffener in thermoplastic material. [40]

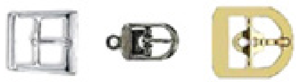
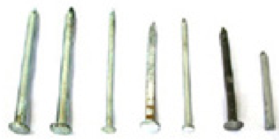
There are also toe puffs and stiffeners made of non-woven materials.

Nowadays most materials used in toe puffs and stiffeners are recyclable (100% recycled fibres), natural (e.g. cellulose fibres) and some do not use dyes making it viable economic and ecological.

6.1.2. Metallic components

The metallic components used in footwear manufacture are shanks, midsoles, protection against crushing (toe and plant of the foot), protection against wear (toe and heel), grommets, dowels, buckles, zippers, studs (spikes), nails and screws.

In the next board, are present the main **metallic components** presented in footwear manufacture.

	
Shanks	Buckles
	
Toe Puffs	Zippers
	
Midsoles	Spikes
	
Eyelets	Adornments
	
Dowels	Buttress

T19. Metallic components (examples). [41]

6.1.3. Laces, touch and close fasteners

Laces, touch and close fasteners are many times the system to fit the footwear to the foot. Laces and touch and close fasteners can be made with textile materials, like nylon, polyamide among others. They can also be made of leather, used more in classic footwear.

6.1.4. Heels

Although the function of heel in footwear design is difficult to justify, heels have been an important part of footwear since the 16th century. Heels have adorned shoes in a variety of shapes and sizes, from short and chunky to tall and slim, from wedge shaped to square shaped.

Many different heel types are used in modern footwear. The most common type for women's shoes is injection moulded plastic, although turned wood heels and built heels are still used. Built heels, however, are used mainly on men´s shoes.

- **Chunky Heels**

The most common materials used for this type of heels are polystyrene, ABS, polypropylene and expanded plastic. Nearly all chunky heels used nowadays are moulded from high impact, toughened polystyrene and are either white or self-coloured.

ABS heels are harder than most grades of polystyrene, and so heel attaching pins require greater pressure for insertion. Consequently, its pin-holding strength is greater.

Polypropylene has been used only on a limited scale for chunky heels because it is more difficult to mould than polystyrene and is resistance and doesn't became brittle.

Although expanded plastic would appear to be a good choice for covered chunky heels because of its inadequate pin-holding strength, it is not recommended unless a solid insert is used in the seat to take the attachment grindery.

- **Stiletto Heels**

For stiletto heels, the most widely used plastic is polystyrene, but other materials used include ABS, polypropylene, polyacrylate, nylon, and expanded polystyrene.

Most of the strength of a stiletto heel is in its steel reinforcement. Nerveless, a plastic compound with adequate impact and fatigue resistance must be used to prevent stem breakage. Breakage in wear occurs in two ways – either by a sudden sharp impact or wrench, such as in stepping off a bus or getting caught in a grating or kerb edge, or else by fatigue built up be the repeated small impacts of normal walking. To avoid this situation stiletto heels must have good fatigue resistance.

- **Built Heels**

Traditionally, heels were produced using all leather lifts, but since the development of fibre board, heels are now mainly made of a combination of leather and fibreboard or, sometimes all board.

- **Plastic Heels bases**

Plastic heel bases, are extensively used in men's footwear as an alternative to leather and board lifts. Made from low density polyethylene by conventional injection moulding, they are competitively priced and satisfactory in production and wear.

Plastic heel bases cannot match the appearance of leather heel finishes that highlight the individual lifts, but they compare favourably with leather and board when an opaque colour is required.

• **Heel attachment**

The faulty attachment of a heel to a shoe is one of more serious causes of wear complaint because it can lead to personal injury. The heel must be secure in the finished shoe.

Two methods of attaching heels are used:

- Inside method – nails, staples, or screws are inserted from the inside of the shoe. More used in fashion and high heels;
- Outside method – the heel can be attached in a number of ways, but in each case, the nails are inserted into the insole from the outside, often clenching over a last plate. Used for shoes with low board heels.

6.1.5. Top Piece

The part of the heel that comes in contact with the ground. Made of a durable material that helps maintain friction with the ground.

According to the type of footwear, the toe pieces can be of TPU, PU, rubber or leather. Classic footwear, normally uses leather, but fashion stiletto uses more TPU or PU. Toe pieces must have good abrasion resistance, must be well attached to heels, and help prevent the slip resistance.

6.1.6. Adhesives

During the various operations that take place in the shoe industry, specifically in the shoe manufacture are many and diverse adhesives that can be used. These can be classified considering various aspects of which may be related to the way by which they are applied.

According to the way the adhesives are applied, there are four main groups, namely:

- First group – Solvent based adhesives. These glues are polymers dissolutions, such as Natural rubber, Polychloroprene and Polyurethane.
- Second group – water based adhesives. These group include the aqueous dispersions of homopolymers and copolymers of various polymeric compositions such as polyurethanes, polychloroprenes, latex, etc.
- Third group - this group includes the hot-melt, reactive and non-reactive, whose base composition is polyamide, polyesters, ethylene vinyl copolymers, PU, etc.
- Fourth group - this group includes the reactive liquid adhesives, in which the reaction (polymerization) begins when mixed (epoxy resins, polyurethanes) or when initiating cure.

The three first adhesives mentioned are the most relevant for footwear industry.

• **Solvent based adhesives**

This group is the most commonly used, with glues based on polychloroprene, polyurethane, which find wide application in bonding shoes.

The polychloroprene based glues use mixtures of solvents, as toluene, light hydrocarbons, methylethylketone (MEK), among others.

The polyurethane based glues use as solvent acetone or MEK, and other solvents as toluene, ethyl acetate, which may be added to improve their properties.

With this kinds of glues may also be added isocyanates (curing agents), which combined with improved adhesive properties, thereby enabling them to achieve better bonding with high difficulty.

Although these two types of glue (polychloroprene and polyurethane) present a great performance in bonding materials used in the construction of the shoe, they present a danger to the health of everyone involved in the manufacturing process of footwear because of the release of VOCs (volatile organic compounds). This bonding process also contributes to environmental pollution.

• **Water based adhesives**

Within this group, the most important adhesives are the polyurethane and polychloroprene dispersion, existing as in the case of solvent based adhesives, important differences in the power of bonding of these two types.

Water based polyurethane adhesives consist of natural or synthetic rubber dispersed in water. These adhesives have high application in seams works.

Water based adhesives, because of their water composition don't have the dangers to health and environment as the solvent based adhesives.

• **Hot-melt adhesives**

These adhesives are solids, so they don´t use solvents. It's mainly applicable in sewing operations and in footwear assembly. These adhesives react with air humidity and allow to obtain bonding results comparable with the solvent based adhesives, eliminating solvents and drying operations in working atmospheres and outdoor environment.

These adhesives don't have the risks associated with solvent based adhesives, but has the disadvantage of requiring specific equipment to apply. It is quite viscous, has low penetration in porous surfaces and a high cost.

6.1.7. Products containing volatile organic compounds environmental issues

The evaporated solvents from glues and other solvents used in the footwear industry contaminate the working atmosphere, and its emission into the atmosphere contributes significantly to environmental pollution. In order to minimize the risks associated with flammability and toxicity of these products are auxiliary systems for extraction and recovery of VOCs.

As the trend of environmental legislation at a global level to take increasingly stringent measures and tightened the control of pollution in the emissions of volatile organic compounds (VOCs) have been increasingly being reported is of great interest to the industry the adoption of practices which enable it to competitive way to address such restrictions.

In a global way there are two things can be made:

• Replace the products by others without solvents;

• Retain or destroy the solvents vapours.

Being economically penalizing the use of auxiliary exhaust systems, retention and disposal of solvents is more viable to replace toxic products with less hazardous.

6.2. More sustainable miscellaneous components and accessories for footwear

Recommendations for lower environmental impact

• Reduce to essential the number of components and acessories in footwear;

• Use components from natural and renewable origin.

• Use components and accessories based on biodegradable materials;

• Use components and accessories based on recycled and/or recyclable materials.

• Use materials in no hazardous or restricted substances.

• Use of water based adhesives.

• Use of adhesives based on biodegrable polymers.

• Reduce the amount of adhesives in footwear production.

• Reduce the number of metallic pieces.

6.3. Requirements and Quality Control

In a general way, the components and accessories for footwear should comply with the following properties:

6.3.1. Toe puffs and stiffeners

• **Bondability**
Bondability to upper and lining materials.

• **Mechanical characteristics**
Shape retention and collapsing load.

6.3.2. Metallic components

• **Corrosion resistanc**e
The metallic components tests, normally involves the analyses of corrosion. The corrosion of metallic materials occurs due to contamination by atmospheric pollution or to corrode due to the action of salt water. The resistance to corrosion is related with the propensity of metal surface to either change visually due to atmospheric pollution (spots of sulphides) or by contact with salt water.

• **Absence of hazardous substances to human**
Testing the Nickel release from metallic accessories can also be made, once about 5-13% of worldwide population is allergic to this metal.

6.3.3. Laces and touch and close fasteners

• **Abrasion resistance**
Laces and touch and close fasteners are tested to evaluate the abrasion tests evaluate when rubbed with an abrandant fabric or by action of a mechanical machine.

• **Flex resistance**
Flex and fatigue tests of Laces and touch and close fasteners, heels simulate the use conditions of materials to evaluate its suitability to be applied on footwear.

• **Absence of hazardous substances to human**
Heavy metals, organic tin, phthalates, DMFU, etc.

6.3.4. Heels

• **Impact resistance**
The impact heels can also be analysed and the damage at the end of the test will be analysed.

6.3.5. Top pieces

• **Slip resistance**
To avoid slip and falls (ceramic floor and water and detergent)

• **Abrasion resistance**
To guarantee physical resistance and performance during use

7. Eco labelling and eco certification of materials and footwear products

7.1. EU footwear ecolabel

EU Ecolabel is a mark awarded by European Community (EU) to producers who voluntarily employ verifiable measures that significantly reduce the harmful effects of their processes and products. This EU Ecolabel covers a wide range of product groups, from major areas of manufacturing to tourist accommodation services. In the following figures is shown the symbol of EU ecolabel.

F22. **The eu's flower eco-label.** [42]

Every four years on average, the criteria are revised to reflect technical innovation such as evolution of materials, production processes or in emission reduction and changes in the market. Because of this, you and your customers can be sure that EU Ecolabel continues to stand for the highest environmental performance.

The "User's manual for Ecolabelling of Footwear" describes the procedure for applying the EU Ecolabel. The aim of the "Application Form" is to give guidance for companies that want to draw up an application for an Ecolabel for footwear. The application also describes the procedures for controlling continuous compliance with the criteria, once the Ecolabel has been granted.

The ecological criteria for footwear (Decision 2009/563/EC) are in some cases process related (i.e. emissions from the production of material, use of Volatile Organic Compounds during final assembly). In other cases they are related to the use of certain materials or substances and in other cases they are related to the final product. These criteria aim in particular at limiting the levels of toxic residues and the emissions of volatile organic compounds, and at promoting a more durable product. Appropriate test ensure that the product is conform to fitness for use.

The products covered by this European Ecolabel are: "All articles of clothing designed to protect or cover the foot, with fixed outer sole which comes into contact with the ground, footwear shall not contain any electric or electronic components".

European Footwear Ecolabel complies with the restricted substances in the shoe and packaging, as well as complying with ecological requirements during the various material and shoe manufacturing operations and duration its use.

For further information and revision of the data here after presented please see: http://ec.europa.eu/environment/ecolabel/products-groups-and-criteria.html

Environmental impact and life cycle analyses considered by European Footwear Ecolabel are:

- Limited water pollution during production;
- A reduction of emissions of volatile organic compounds during production;
- The exclusion of substances harmful for the environment and health;
- Limited residues of metals and formaldehyde in the final product;
- Energy consumption;
- The use of recycled packaging;
- The careful control of different aspects of durability.

In the following table are presented the ecological criteria and the requirements.

#	ECOLOGICAL CRITERIA	REQUIREMENTS
1	Dangerous substances in the final product	(a) For shoes made of leather, there shall be no Chromium VI in the final product. (b) There shall be no Arsenic, Cadmium and Lead in the materials used for the product assembly or in the final product.
		(c) The amount of free and hydrolysed formaldehyde of the components of the footwear shall not exceed the following limits: • Textile: not detectable • Leather: 150 ppm
2	Reduction of water consumption (only for the tanning of hides and skins)	The following limits to water consumption for the tanning of hide and skin (1) shall not be exceeded: • Hides: 35 m3/t • Skins: 55 m3/t
3	Emissions from the production of material	(a) If the waste waters from leather tanning sites and from the textile industries are released directly into fresh waters the content of: • COD shall not exceed 250 mg COD/l of water discharged. • If the waste waters from leather tanning sites are released into a municipal waste water treatment plant/facility, then this criterion shall not apply, as long as it can be demonstrated: • that the discharge of waste water from the tanning site into the municipal waste water supply is authorised and, • that the municipal waste water treatment facility is operational and that the subsequent discharge of treated water into the fresh water system is in line with minimum Community requirements according to Council Directive 91/271/EEC (2). (b) Tannery waste water after treatment shall contain less than 1 mg Chromium (III)/l.
4	a) Use of hazardous substances (up until purchase) PCP & TCP	Pentachlorophenol (PCP) and Tetrachlorophenol (TCP) and its salts and esters shall not be used.
	(b) Use of hazardous substances (up until purchase) Azo Dyes	No azo dyes shall be used that may cleave to any of the following aromatic amine: 4-aminodiphenyl (92-67-1) / benzidine (92-87-5) / 4-chloro-o-toluidine (95-69-2) 2-naphthylamine (91-59-8) / o-amino-azotoluene (97-56-3) /2-amino-4-nitrotoluene (99-55-8) / p-chloroaniline (106-47-8) /2,4-diaminoanisol (615-05-4) / 4,4´-diaminodiphenylmethane (101-77-9) / 3,3´-dichlorobenzidine (91-94-1) / 3,3´-dimethoxybenzidine (119-90-4) / 3,3´-dimethylbenzidine (119-93-7) / 3,3´-dimethyl-4,4-diaminodiphenylmethane (838-88-0) / p-cresidine (120-71-8) / 4,4´-methylene-bis-(2-chloraniline) (101-14-4) / 4,4´-oxydianiline (101-80-4) / 4,4´-thiodianiline (139-65-1) / o-toluidine (95-53-4) / 2,4-diaminotoluene (95-80-7) / 2.4,5-trimethylaniline (137-17-7) / 4-aminoazobenzene (60-09-3) / o-anisidine (90-04-0)

#	ECOLOGICAL CRITERIA	REQUIREMENTS
	(c) Use of hazardous substances (up until purchase) Nitrosamines	The following N-Nitrosamines shall not be detected in rubber: N-nitrosodimethylamine (NDMA) / N-nitrosodiethylamine (NDEA) / N-nitrosodipropylamine (NDPA) / N-nitrosodibutylamine (NDBA) / N-nitrosopiperidine (NPIP) / N-nitrosopyrrolidine (NPYR) N-nitrosomorpholine (NMOR) / N-nitroso N-methyl N-phenylamine (NMPhA) N-nitroso N-ethyl N-phenylamine (NEPhA)
	(d) Use of hazardous substances (up until purchase) C10-C13 Chloroalkanes	C10-C13 chloralkanes shall not be used in leather, rubber or textile components.
	(e) Use of hazardous substances (up until purchase) Dyes	No dyes meeting the criteria for classification as carcinogenic, mutagenic toxic to reproduction, hazardous/ dangerous to the environment with the following R-phrases R40, R45, R49, R50, R51, R52, R53, R60, R61, R62, R63 or R68 (or any combination), shall be used. (Classification rules as according to Council Directive 67/548/EEC (1) or Directive 1999/45/EC of the European Parliament and of the Council. Alternatively, classification may be considered according to Regulation (EC) No 1272/2008 of the European Parliament and of the Council (1). In this case no substances or preparations may be added to the raw materials that are assigned, or may be assigned at the time of application, with the following hazard statements (or combinations thereof): H351, H350, H350i, H400, H410, H411, H412, H413, H360F, H360D, H361f, H361d H360FD, H361fd, H360Fd, H360Df, and H341.
4	f) Use of hazardous substances (up until purchase) APE & PFOS	Alkylphenol ethoxylate (APE), and Perfluorooctane sulfonate (PFOS) shall not be used.
	g) Use of hazardous substances (up until purchase) Dyes (R43)	No dyes meeting the criteria for classification as sensitising to skin (R43) shall be used. (Classification rules as according to Directive 67/548/EEC or Directive 1999/45/EC).
	h) Use of hazardous substances (up until purchase) Phtalates	Only phthalates that at the time of application have been risk assessed and have not been classified with the phrases (or combinations thereof): R60, R61, R62, R50, R51, R52, R53, R50/53, R51/53, R52/53, in accordance with Directive 67/548/EEC, may be used in the product (if applicable). Additionally, DNOP (di-n-octyl phthalate), DINP (di-isononyl phthalate), DIDP (di-isodecyl phthalate) are not permitted in the product.
	i) Use of hazardous substances (up until purchase) Biocides	Only biocidal products containing biocidal active substances included in Annex IA of the Directive 98/8/EC of the European Parliament and of the Council (2), and authorised for use in footwear, shall be allowed for use.

#	ECOLOGICAL CRITERIA	REQUIREMENTS
5	Use of volatile organic compounds (VOCs) during final assembly of shoes	VOCs are any organic compound having at 293,15 K a vapour pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use. The total use of VOCs during final footwear production shall not exceed, on average, 20 gram VOC/pair.
6	Energy Consumption	The energy consumption at the manufacturing stage shall be declared.
7	Packaging of the final product	Where cardboard boxes are used for the final packaging of footwear, they shall be made of 100 % recycled material. Where plastic bags are used for the final packaging of footwear, they shall be made of, at least, 75 % recycled material or they shall be biodegradable or compostable, in agreement with the definitions provided by the EN 13432 (3).
8	Information on the packaging	(a) User Instructions The following information (or equivalent text) shall be supplied with the product: • "These shoes have been treated to improve their water resistance. They do not require further treatment." (This criterion is applicable only to footwear that has been water-resistant treated) • "Where possible, repair your footwear rather than throw them away. This is less damaging to the environment." • "When disposing of footwear, please use appropriate local recycling facilities where these are available." (b) Information about the eco-label The following text (or equivalent text) shall appear on the packaging: "For more information visit the EU Ecolabel website: http://www.ecolabel.eu" (c) Information to consumers An information box in which the applicant explains its approach to environmental sustainability should be put on the packaging. Assessment and verification: the applicant shall provide a sample of the product packaging and of the information supplied with the product, together with a declaration of compliance with each part of this criterion.
9	Information appearing on the eco-label	Box 2 of the eco-label shall contain the following text: • low air and water pollution, • harmful substances reduced. Assessment and verification: the applicant shall provide a sample of the product packaging showing the label, together with a declaration of compliance with this criterion.

#	ECOLOGICAL CRITERIA	REQUIREMENTS
10	Parameters contributing to durability	Occupational and safety footwear shall carry the EC mark (in accordance with Council Directive 89/686/EEC (2)). All other footwear shall meet the requirements indicated in the table overleaf. Assessment and verification: the applicant shall provide a test report corresponding to the parameters indicated in the table overleaf, using the following test methods: • EN 13512- Upper - Flex resistance / EN 13571 - Upper - Tear strength, • EN 17707 - Outsoles - Flex resistance / EN 12770 - Outsoles - Abrasion resistance, • EN 17708 - Whole sole - Sole adhesion / EN 12771 - Outsoles - Tear strength, • EN ISO 17700 - Test methods for uppers, linings and in socks — Colour fastness to rubbing.

T20. Ecological criteria and requirements.

To be updated with the revision that is in course at EU level.

7.2. Other ecolabels

BIOCALCE – Is a Portuguese certification that guarantees comfort and quality, strength and durability in shoes that use exclusively materials free of toxic substances to the user and the environment.[43]

STeP - Sustainable Textile Production is a certification system for brands, retail companies and manufacturers from the textile chain who want to communicate their achievements regarding sustainable production to the public in a transparent, credible and clear manner. Certification is possible for production facilities of all processing stages from fibre production, spinning mills, weaving mills, knitting mills to finishing facilities and manufacturers of ready-made textile items. [44]

OEKO-TEX STANDARD 100 This standard assesses the chemical usage and handling, water usage and disposal, exhaust air production, dust and noise generation, energy usage, general workplace conditions and requires an environmental management system to be in place. Oeko-tex 100 standard is now mandatory in several European countries.[44]

GOTS is now a Global Organic Textile Standards which resulted when a number of certification and standard bodies formed a working group. For more information visit www.global-standard.org. This group is working towards bringing their respective labels under one umbrella, thus making it less confusing for the consumer. [45]

ECO MARK is an environment labelling program operated according to ISO 14020 abd –uso 14024 and considers whole lifecycle of products. [46]

BLUESIGN STANDARD® indicates all the input streams from raw materials to chemical components and resources used are assessed on their ecological impact. It is essentially a label that helps identify fabric and apparel producers that have analysed their manufacturing chain and are constantly investing in research and development in an active effort to reduce their ecological footprint. Labels that meet the standards of the sign include Nike, prAna, and Lululemon Athletica. [47]

COTTON MADE IN AFRICA indicates that the cotton is sustainably grown by African farmers in collaboration with the Aid by Trade Foundation. This initiative is meant to provide African cotton farmers with the knowledge and practices for sustainable cotton farming, and to improve their quality of life as farmers. The initiative works with retailers that are demanding sustainably produced cotton.[48]

CRADLE-TO-CRADLE certified indicates a product that is either completely recyclable or biodegradable, and made with the lowest impact manufacturing processes that are not harmful to people or the environment in any way. The certification program applies to materials, sub-assemblies and finished product and is a chance for companies to demonstrate eco-intelligent design. Textiles from Pendleton Woolen Mills, Greenweave Fabrics and Sunbury Textile Mills have received this prominent certification. [49]

FAIR TRADE symbol indicates that the product has met certain social, environmental and economic criteria that support the sustainable development of small-scale producers and agricultural workers in the poorest countries in the world. The Fair Trade organization essentially gives consumers the opportunity to help reduce poverty and instigate change by purchasing Fair Trade cotton and several certified food items.[50]

GLOBAL RECYCLE STANDARD indicates that the product contains recycled content of some sort. This is often in the form of recycled polyester or rPET, which is often found in sportswear and cotton/rPET fabric blends. Members of the GRS include Patagonia, Nike, Adidas, H&M, Levi Strauss, Volcom and many more large name brands.[51]

MADE-BY's blue button sign is a label that indicates a fashion company's environmental responsibility and fair labour practices throughout the entire supply chain. The Made-By organization works with brands that use organic cotton and work with sewing factories with enforced social codes of conduct. Partner brands include G-Star Raw, Jackpot and Komodo.[52]

SCS certification measures the amount of recycled content that has been diverted from the waste stream in a certain product. The SCS organization also grants certification to companies the meet certain criteria for in-house recycling schemes. [53]

USDA Certified Organic is often recognized for food labelling, but accounts for all agricultural crops. These include cotton, wool and other natural fibres that come from animals who have not been given antibiotics or growth hormones and receive organic feed, and plants that have not been grown with pesticides, synthetic fertilizers or ionizing radiation. All products that are labelled as USDA certified organic have to meet the standards whether or not the raw material was grown in the U.S. or somewhere else. [54]

Zque certification indicates responsibly manufactured and environmentally safe wool. Wool with this accreditation has been produced in an environmentally, socially and economically sustainable manner, to high animal welfare standards, and is traceable back to its source. Most Zque wool is merino wool raised and produced in New Zealand. [55]

8. Quality Control and Requirements

Footwear and footwear components properties are fundamental to understand footwear behaviour and quality. Test is essential to guarantee the footwear final performance.

This chapter describes briefly the most relevant tests dedicated to footwear and footwear properties.

8.1. Physical Properties

• **Abrasion**

Abrasion is the property related with the resistance that a material can addle, when it is subject to friction. Most all footwear materials can be tested and their abrasion resistance recorded.

The abrasion tests evaluate the surface resistance of uppers, linings, insocks, insoles, outsoles, laces and eyelets when rubbed with an abrandant fabric or by action of a mechanical machine, according to the applicable method.

F23. Abrasion martindale.

• **Adhesion**

Adhesion is the property that determines the strength of adhesion between two surfaces. It can be evaluated in whole shoe, in several coatings and its bases, in finishing's, lacquers, upper/outsole and sole interlayer.

F24. Adhesion resistance.

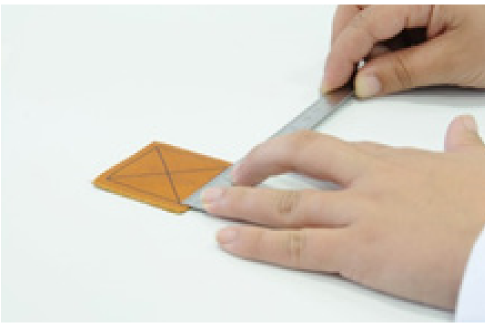
• **Colour fastness**

Colour fastness is the persistence of colour. Several tests can be made to simulate use and evaluate the colour fastness in several conditions. This property can be evaluated by several means and in diverse materials. It can be evaluated by simulating human perspiration or by water contact and rubbing for analyses of the maintenance of the material's colour.

F25. Colour fastness to cycles of to-and-for rubbing.

• Dimensional stability

Dimensional stability is the method that determines the dimensional stability of insoles, irrespective of material, for example swelling and increase in size after immersion in temperature and shrinkage after temperature.



F26. **Dimensional stability.**

• Flex and fatigue resistance

Flex and fatigue resistance tests simulate the use conditions of materials to evaluate its suitability to be applied on footwear. There are several tests, which include evaluation of uppers, linings, outsoles and heels in several materials in order to assess the suitability for the end use in footwear.

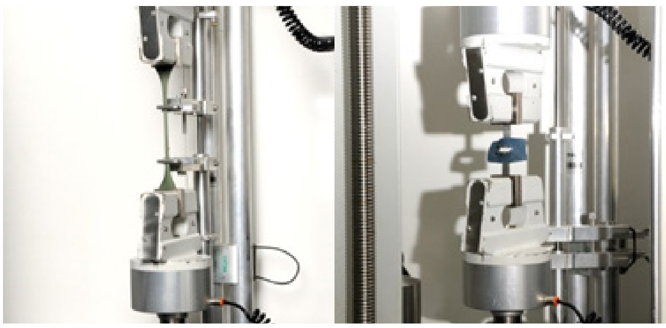
F23. **Flex and fatigue resistance.**

• Tear strength

Tear strength is the force required to tear a material. There are many tests for materials applied in uppers, lining, insocks, outsoles and even it is possible to evaluate the tear strength of seam stitches.

• Tensile properties

Tensile properties are properties related to the force required to break a test specimen. The procedures may include transverse or elongation strength in diverse materials applied in footwear. These materials can be applied as uppers, outsoles, insoles, eyelets, decorative pieces and other materials. There are different methods for this test that are done according to its use.



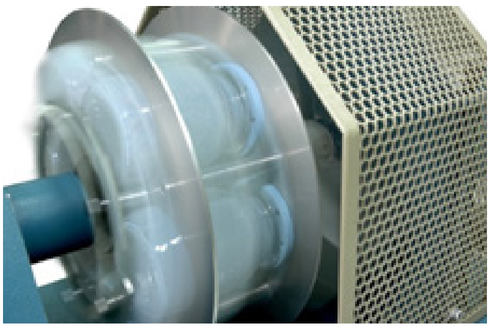
F27. **Mechanical properties, using dynamometer.**

• Water absorption and desorption

Water absorption and desorption is related with material capacity has to absorb and desorbs water. This property is important to remove humidity from foot skin surface and promote a higher comfort.

• Water vapour permeability

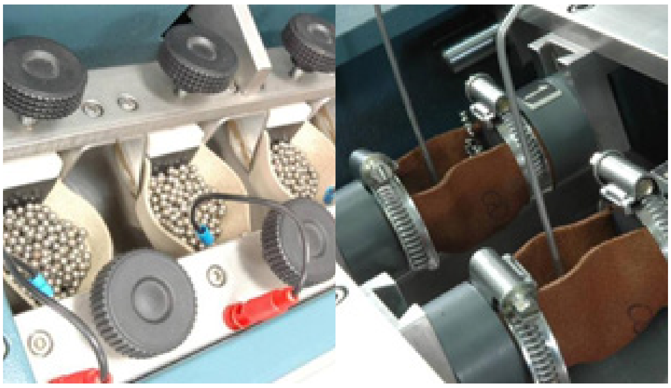
Water vapour permeability is related with materials breathability, in other words, its capacity in the passage and absorption of water vapour. It's necessary to assure a good breathability of materials in footwear to promote the feet comfort.



F29. **Water vapour permeability.**

• **Water resistance**

This property is related to the penetration of water in footwear and the associated materials. It can be tested leather for uppers and whole footwear.



F30. Maeser and permeability water permeability.

F31. Determination of resistance to water for whole footwear.

• **Thermal insulation**

Thermal insulation is a measure of the rate at which heat passes through a material or through a series of layers of different materials. High thermal insulation means that heat travels very slowly through the material, causing the temperature to build up on the side of heat source. Methods are available to evaluate the resistance of footwear to the passage of heat and cold when placed in hot and cold surfaces, respectively. A method to measure the thermal insulation of upper, lining and insocks is available.

• **Slip resistance**

Slip resistance is related to the coefficient of friction between soles and the floor in which the footwear it's in use. The item of footwear to be tested is put on a surface, subjected to a given normal force, and moved horizontally relative to the surface (or the surface is moved horizontally relative to the item of footwear). The frictional force is measured and the dynamic coefficient of friction is calculated.

F32. Slip resistance.

• **Cushioning and shock absorption**

Cushioning and shock absorption are related with contact of footwear in ground during walking. These properties can be assessed in insocks, midsoles, whole shoes, uppers and in seat region and in materials intended for cushioning.

F33. Shock absorption.

• Longitudinal and Torsional stiffness of footwear

The test of longitudinal stiffness determines the force required to flex the footwear to an angle representing a 50º flex of the foot or the maximum angle that can be achieved without exceeding a critical bending moment.

F34. Longitudinal stiffness of footwear.

8.2. Chemical Properties

• pH determination

pH measurement determines the pH value and the difference figure of an aqueous leather extract. In this test is prepared an aqueous extract from a test portion of leather or textiles, or an aqueous dispersion in case of adhesives and electrometrically measurement of the pH-value at room temperature by means of a glass electrode. A low pH value can promote the deterioration of footwear components and result in allergic reactions.

F35. pH measurement.

• Chromium VI determination

Evaluates the quantity of chromium salts that are used for tanning agent mostly used in leather tanning process due to the properties that conferee to the final product. The use of chromium salts, as a tanning agent gives a softer, flexible, with higher physical resistance and stability. The chromium normally present in the leather is Cr (III), however by external conditions, sunlight and humidity the Cr (III) could oxidise to Cr (VI). The chromium (VI) can cause cancer and is environmental prejudicial.

F36. Chromium VI determination B UV-VIS.

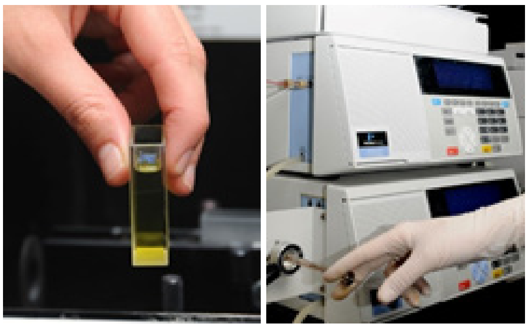
• **Heavy metals**

Heavy metals are extremely reactive and bioaccumulative, which means that organisms cannot eliminate. The determination of arsenic, mercury, antimony, selenium, nickel, copper, cadmium, lead, barium and silver by atomic absorption technique, after acid digestion, it's very important because occurs many reactions of skin in presence of these metals. For example, nickel is now the most frequent cause allergy in Europe, and 10-20% of female population is allergic to nickel. Skin absorption of nickel ions, which are released from some nickel-containing materials in direct and prolonged contact with the skin causes sensitivity. Further exposure to soluble nickel salts results in allergic contact dermatitis.

F37. Determination of heavy metals, using flame atomic absorption.

• **Formaldehyde**

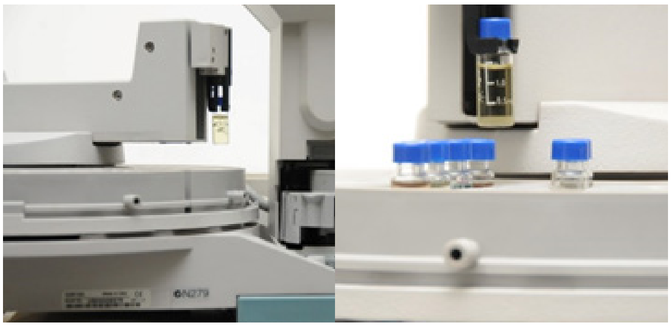
Formaldehyde is toxic and irritable substance. Its presence is normally due to the use on tanning (of leather), preserving and finishing products. The associated techniques for the determination of formaldehyde content are colorimetric and HPLC method.



F38. UV-Vis spectrophotometer. (a) and hplc (b).

• **Penta (PCP), tri (TCP) and tetrachlorophenols (TeCP)**

Chlorophenols are mostly in gaseous form, can irritate the skin, eyes and skin. The amount of chlorophenols, its salts and esters, can be determined on leather and textiles after water extraction followed by n-hexane phase transfer and followed by acetylation with acetic anhydride. The ortophenilphenol (OPP) is a preservative agent added to leather to protect against microbiologic attack. The acetates of PCP, TCP and TeCP and OPP are analysed by gas-chromatography.



F39. GC-Chromatograph.

• **Azo colourants**

Azo colourants are very important once they may release certain aromatic amines. The aromatic amines are highly toxic and are responsible for vesicular irritation and tumors. The azo colourants may be determined in dyed leathers and textiles (with or without polyester).

• **Organotin compounds**

Organotin compounds are identified and quantified in rubber materials. These compounds are very pollutant for the environment and can be introduced in outsoles by the pigments. These compounds after extraction are determined by gas chromatography-mass spectrometry (GC-MS).

• **Phthalate**

Phthalates are chemical compounds used as plasticizers in outsoles to conferee more flexibility. These compounds are extractable using suitable methods and the analysis is performed by gas chromatography.

• Dimethyl fumarate (DMF)

DMF is a powerful desiccant agent. However, is responsible for allergies extremely serious that could result in hospital internment. This chemical agent is applied directly in any footwear raw material (leather, textile and outsole) or placed inside the package.

• Allergic Dyes

Allergic Dyes are a range of "disperse dyes" that can cause allergic reactions to come into direct contact with skin. Allergic Dyes are basically used in certain products of polyester, acetate and polyamide so in tinted and patterned textiles, as in dyed accessories such as buttons.

• Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA)

PFOS and PFOA are polymers used promptly in textile and leather articles provide greater resistance to grease, oil and water. PFOS may be present in waterproof textiles and / or stain treatments (hydrophobic and oil repellent) in apparel products, home textiles and footwear, mainly.

• Polycyclic aromatic hydrocarbons (PAHs)

PAHS are naturally occurring substances in fossil fuels and may be formed during incomplete combustion of organic materials. Oils contaminated with PAHs may be used as softeners or extenders in rubber and plastic. PAHs also may be formed by thermal decomposition of recycled materials during reprocessing and may be present as impurities in carbon black pigments and dyestuff. Naphthalene is often present as an impurity from raw materials used as intermediates in the production of textile dye dispersing agents and may be found in textiles. Some PAHs can be very toxic to aquatic organisms and above certain exposure levels may cause long-term adverse effects in the aquatic environment. Above certain levels, long-term exposure to some PAHs may result in the development of particular cancers. Some PAHs, above certain exposure levels, may impair human fertility or cause harm to unborn children.

• Corrosion of metallic materials

Corrosion of metallic materials occurs due to contamination by atmospheric pollution or to corrode due to the action of salt water. The resistance to corrosion is related with the propensity of metal surface to either change visually due to atmospheric pollution (spots of sulphides) or by contact with salt water.

F40. Metallic pieces for corrosion test.

8.3. REACH Regulation

REACH (EC 1907/2006) aims to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. This is done by the four processes of REACH, namely the registration, evaluation, authorisation and restriction of chemicals. REACH also aims to enhance innovation and competitiveness of the EU chemicals industry.

No data no market": the REACH Regulation places responsibility on industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database in the **European Chemicals Agency (ECHA)** in Helsinki. The Agency is the central point in the REACH system: it manages the databases necessary to operate the system, co-ordinates the in-depth evaluation of suspicious chemicals and is building up a public database in which consumers and professionals can find hazard information.

The Regulation also calls for the progressive substitution of the most dangerous chemicals (referred to as "substances of very high concern") when suitable alternatives have been identified.

One of the main reasons for developing and adopting the REACH Regulation was that a large number of substances have been manufactured and placed on the market in Europe for many years, sometimes in very high amounts, and yet there is insufficient information on the hazards that they pose to human health and the environment. There is a need to fill these information gaps to ensure that industry is able to assess hazards and risks of the substances, and to identify and implement the risk management measures to protect humans and the environment.

Having entered into force in 2007, REACH provisions are being phased-in over 11 years. Companies can find explanations of REACH on the Internal Market, Industry, Entrepreneurship and SMEs or ECHA websites, and can contact national helpdesks.

Websites to visit:
http://ec.europa.eu/environment/chemicals/reach/reach_en.htm

http://echa.europa.eu/

http://ec.europa.eu/growth/sectors/chemicals/reach/index_en.htm

http://echa.europa.eu/web/guest/support/helpdesks/national-helpdesks/list-of-national-helpdesks

• Restricted List

The list of restrictions is the Annex REACH and includes all the restrictions adopted in the framework of REACH and the previous legislation, Directive 76/769/EEC. Each entry shows the substance or group of substances or the mixture, and the consequent restrictions conditions. The latest consolidated version of REACH presents the restrictions adopted until that date. Subsequent changes are included in the amending Commission regulations.

The restricted substances (on their own, in a mixture or in an article) are substances for which manufacture, placing on the market or use is limited or banned in the European Union.

The Restricted substance table has been prepared by the European Chemicals Agency (ECHA) to facilitate the searching of restricted substances in the Annex XVII of the REACH Regulation.

The table contains:

- EC and CAS numbers; please note that not all the entries in Annex XVII of the REACH Regulation have these numbers;
- Consolidated text: page of the entry in the latest updated consolidated version of Annex XVII to REACH Regulation;
- Appendices: links to appendices concerning certain restricted substances. Please note that searching with CAS or EC numbers is not yet possible for substances restricted under Appendices 1-6 (CMR substances);
- New amendments (EU Regulation): the subsequent amendments of REACH Regulation after the latest consolidated version;
- Q&A: the relevant question(s) from the latest updated Q-A document and FAQ on ECHA's website;
- Standards: links providing information on standards, where available (links to the CEN search engine for the European standards, or to the international standards' pages).

Websites to visit:
http://echa.europa.eu/pt/addressing-chemicals-of-concern/restrictions/list-of-restrictions

• Candidate List

Candidate List is a list published by the E.C.H.A (European Chemicals Agency) in accordance with Article 59(10) of the REACH Regulation, which contain some substances very high concern (SVHC). These substances are object of special evaluation by the E.C.H.A. It is possible to find information regarding the candidate list on the web site of E.C.H.A.

In the framework of REACH, companies in footwear and allied industry can assume simultaneously several roles (downstream user, importer or manufacturer). For each of these roles are associated different obligations, so the first step to prepare REACH should be the definition of company role. As producers of goods (footwear, leather, soles, and textiles) should ensure that their products do not contain substances that cause very high concern in concentrations higher than 0.1% (m / m).

Producers and suppliers of articles are obliged to transmit to the recipient of the articles the information to enable safe use of articles. This obligation is only applied in the case of articles containing substances of very high concern in a concentration above 0.1% (w / w).

In view of the obligations under REACH is necessary exchange of information along the downstream supply chain (from supplier to customer) and upstream (from client to supplier).

All supply chain actors should compile and keep available all the information required to comply with the obligations under REACH for at least ten years after the date of manufacturing, importing, supplying or used for the last time the substance or preparation.

Companies should require the raw materials Safety Data Sheet from to guarantee the compliance with legislation. Another option to inform the suppliers of REACH requirements could be the signature of a conformity declaration.

Websites to visit:
http://echa.europa.eu/candidate-list-table

• **Authorisation List**

The Annex XIV, overseen by the ECHA (European Chemicals Agency), is a list of substances subject to authorization, substances of very high concern (SVHC). To include the substances in the Annex XIV is following procedure is used:

1. A European member state shall propose it to ECHA.
2. ECHA inform all the members' state and a first enquiry is done in order to include the substance to the candidate list of Annex XIV.
3. After the agreement of the member's state, ECHA includes the substances in the candidate list to Annex XIV. As soon as a substance has been included in the candidate list, it should be taken into account exactly as a SVHC.
4. ECHA prioritizes the substances from the Candidate List to determine which ones should be included in the Authorisation List (Annex XIV of REACH) and therefore, subject to authorization. ECHA regularly submits recommendations to the European Commission, who will decide on the substances to be included in the Authorisation List.

Following the evaluation of the Annex XIV substances, ECHA can take the decision to restrict the substances. This restriction may take the form of an authorization for use, an authorization only for specific applications in specified fields or, in some cases, a complete ban on the use of the substance.

During the evaluation process, these chemicals are not forbidden or limited in use. The regulation requires that the user shall be informed if one or more of these substances are present in any part of the article in quantity over 0,1 % by weight.

The Technical Report **CEN/TR 16417:2016**, recently published, shows which of these chemicals may be present in footwear materials and the footwear industry in order to help shoe manufacturers to collect mandatory information from suppliers regarding the content of these chemicals and, at same time, allow them to provide accurate information to their customers.

8.4. CADS - List of Restricted substances in shoes

CADS – Cooperation at DSI – deals with the subject of hazardous substances in shoes and actively seeks to prevent their use. The association's objectives are the generation and dissemination of knowledge for manufacturing and marketing shoes and shoe materials without hazardous substances as well as for environmentally compatible production.

Specifically, these are:

- Pool and forward knowledge about hazardous substances as well as current and future statutory regulations;
- Develop prevention strategies and actively implement consumer protection
  Run a public awareness campaign;
- Commission scientific research for analyzing the potential hazards of substances used in shoes;
- Develop replacement substances and processes or commission their development
  prepare and publish studies about hazardous substances;
- Promote theses and dissertations that deal with hazardous substances in shoes and their prevention;
- Implement measures suitable for manufacturing and marketing environmentally compatible shoes without hazardous substances.

CADS integrates a group substances regulated by law, considering only European Limits, (Group 1) and critical substances (group 2). The group of substances considered by CADS are:

- Azo Dyes
- Biocide
- Chlorinated phenols
- Dyestuffs classified as allergens
- Dyestuffs classified as carcinogenic
- Heavy Metals;
- Organic Tin compounds;
- Other chemicals residues;
- Other phenols;
- Phthalates;
- Polycyclic aromatic hydrocarbons (REACh);
- Polycyclic aromatic hydrocarbons (EPA)
- Volatile Organic Compounds

Websites to visit:
www.cads-shoes.com/en/documents.html

8.5. Footwear Critical Substances

The Technical Report ISO/TR 16178, "Footwear - Critical Substances potentially present in footwear and footwear components", establishes a list of a critical chemical substances present in footwear and footwear components.

The ISO/TR 16178 describes the critical chemical substances, their potential risks, the materials where they could be found and the test methods that can be used for quantification. This Technical Report does not include the requirements.

This technical report defines 5 categories of critical substances, namely:

- **Critical substances category 1 -** substances with proven dangerous effect on the wearer. These substances are restricted by regulation at European level;
- **Critical substances category 2** - substances with dangerous effect on the wearer. These substances are restricted by regulation at national level in some countries.
- **Critical substances category 3** - substances with environmental impact. These substances are mentioned in European Ecolabel.
- **Critical substances category 4** - substances that are highly suspected to have an effect on the wearer. Possibly, these substances are not restricted by regulation at the time of publication of this Technical Report.
- **Critical substances category 5** - substances that are suspected to have an effect on the wearer

In the annex 1 are defined critical substances that should be tested in footwear material.

8.6. Footwear Performance requirements

The following technical reports establish the performance requirements for the footwear components, in order to assess the suitability for the end use and/or fitness purpose. It also establishes the test methods to be used to evaluate the compliance with the requirements.

- ISO/TR 20879 – "Footwear – Performance Requirements for components for footwear – Uppers";
- ISO/TR 20882 – "Footwear – Performance Requirements for components for footwear – Lining and insocks";
- ISO/TR 20881 – "Footwear – Performance Requirements for components for footwear – Insoles";
- ISO/TR 20880 – "Footwear – Performance Requirements for components for footwear – Outsoles".
- ISO/TR 22648 – "Footwear – Performance requirements for components for footwear – Stiffeners and Toe Puffs".
- ISO/TR 20573 – "Footwear – Performance requirements for components for footwear – Heels and Top Pieces".

In annex 1 are presented the requirements by type of component and type of shoe.

The following standards establish the test methods and the requirements that should be used on Personal protective equipment evaluation properties and or the CE marking, namely:

- ISO 20344: 2011 – "Personal protective equipment — Test methods for footwear";
- ISO 20345: 2011 – "Personal protective equipment – Safety Footwear";
- ISO 20346: 2014 – "Personal protective equipment – Protective Footwear";
- ISO 20347: 2012 – "Personal protective equipment – Occupational Footwear".

9. Test of knowledge

Choose the correct option:

Q1.	**Natural materials are:**

- ○ Products or physical matter from plants, animals or soil.
- ○ Products that may be produced over and over again (e.g wood used to make paper renewed by reforestation).
- ○ Products obtained by reusing materials benefited as raw material and transformed into a new product.

Q2.	**Substances derived from trees, plants, animals or ecosystems that have the ability to regenerate are:**

- ○ Renewable materials.
- ○ Recycled materials.
- ○ Reused materials.

Q3.	**Biodegradable materials are:**

- ○ Materials that undergo significant changes in chemical structure under certain environmental conditions
- ○ Materials in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.
- ○ Substances derived from trees, plants, animals or ecosystems that have the ability to regenerate.

Q4.	**Life cycle assessment (LCA) is:**

- ○ The metric used to calculate the human pressure on the planet and come up with facts.
- ○ A phase of life cycle assessment involving the compilation and quantification of inputs and outputs for a product throughout its life cycle.
- ○ A compilation and evaluation of the input, outputs and the potential environmental impacts of a product system throughout its life cycle

Q5.	**Skin can be divided in the following layers:**

- ○ Epidermis and subcutaneous tissues;
- ○ Epidermis, Dermis and subcutaneous tissues;
- ○ Epidermis and Dermis;

Q6.	**Fresh, wet salted, brining, dry-salting and drying are:**

- ○ Tanning processes of skin
- ○ Freezing processes of skin
- ○ Conservation processes of skin

Q7. Tanning process can be divided in:

○ Mineral and natural tanning

○ Mineral, organic and inorganic tanning

○ Mineral an organic tanning

Q8. Mineral tanning processes:

○ Chromium, Aldehyde, Zirconium

○ Aluminium, Synthetic resins, Chromium

○ Iron, Titanium, Chromium

Q9. Zdhc means:

○ Zero Discharge Hazardous Contribution

○ Zero Discharge Hazardous Chemicals

○ Zero Discharge High Chemicals

Q10. Bioleather material is a leather:

○ tanned with tannin extracted from some trees and with polymeric resins

○ without tanning

○ tanned with minerals

Q11. Aniline is:

○ The most natural leather with unique surface characteristics of the hide remaining visible.

○ A split which has been abraded to create a distinctive nap.

○ Full grain leather drummed to give a soft and comfortable feel.

Q12. Carbon footprint in the production of leather can be defined as:

○ Reduction of water consumption and wastewater treatment by using new technologies and chemicals to get more efficient processes.

○ Reduction of CO2 emission by the process and products in tannery and reduction of impact on climate change.

○ Avoid the use of harmful substances legal restrictions and ensure the product Stewardship.

Q13. Textile materials are made of fibres. There are three types of fibres:

○ Natural, organic, chemical

○ Natural, chemical and metallurgical

○ Natural, organic and inorganic

Q14. Drylaid, airlaid, spunlaid/meltblow and wetlaid are tecnologies used in production of:

○ Organic fibres

○ Mineral fibres

○ Non-woven;

Q15. Bounding can be:

○ Chemical, Thermal, Natural

○ Chemical, Thermal, Mechanical

○ Chemical, Physical, Mechanical

Q16. Natural fibres can be divided in to:

○ Vegetable, animal and mineral

○ Organic, inorganic and mineral

○ Vegetable and animal

Q17. Viscose is a man-made fibre from:

○ Inorganic substances

○ Natural polymers

○ Synthetic polymers

Q18. Polyvinyl alcohol (PVA) is a:

○ Natural polymer

○ Inorganic fibre

○ Synthetic fibre

Q19. Some examples of eco-friendly textile fibres are:

○ Organic silk, recycled polyester

○ Silk, polyester

○ Silk, polyester, wool

Q20. The definition of vegan footwear is:

○ Made of biodegradable materials

○ Made without leather or any animal ingredients

○ Made without leather

Q21. Soles for footwear can have natural or synthetic origin. As examples of natural materials for soles, we can mentioned:

○ Cork, wood, TR

○ Cork, wood, NR

○ Cork, wood, SBR

Q22. Polymerization is:

○ The linking together of the monomer pieces to form a polymer

○ The formation of man-made rubber

○ c. The formation of new polymers

Q23. The polymer ethylene vinyl acetate (EVA), because of its lightweight (low density) is most used for:

○ Safety footwear

○ Lady's footwear

○ Sports footwear

Q24. Production of thermoplastics include:

○ Vulcanization, finishing and Packing.

○ Injection and shaping, vulcanization and Packing.

○ Injection and shaping; Finishing and Packing.

Q25. For safety footwear, is necessary to test antistatic or conductive properties, this is tested for guarantee:

○ Footwear is high quality

○ Electrical protection of user during use

○ Footwear is the right one for electricians

Q26. Toe puffs and stiffeners have a fundamental part in footwear, although they are less "visible". These components are:

○ Reinforcing materials incorporated in the uppers

○ Reinforcing materials incorporated in the soles

○ Reinforcing materials incorporated in the midsoles

Q27. Top pieces are the part of the heel that comes in contact with the ground. So, they need to present:

○ Low toxicity values and good abrasion resistance

○ Good values of durability and good abrasion resistance

○ Flexibility and good abrasion resistance

Q28. During the various operations that take place in the shoe industry, specifically in the shoe manufacture are many and diverse adhesives that can be used. The solvent based adhesives are the group most commonly used in footwear industry, because they are the:

○ Most efficient

○ Cheaper

○ Most environmental friendly

Q29. VOCs means:

○ Volatile organic compounds

○ Volatile organic compounds sustainable

○ Volatile organic compost

Q30. The healthy problems associated with vocs are related with:

○ Water based adhesives

○ Hot melt adhesives

○ Solvent based adhesives

Q31. Metallic components of footwear in contact with skin should be tested for nickel release because:

○ Environmental issues

○ 5-13% of worldwide population is allergic to this metal

○ It can be solved in water

Q32. EU Ecolabel is a:

○ An environmentally friendly footwear brand

○ Mark awarded by European Community (EU)

○ Mark awarded by National authorities

Q33. AZO DYES and NITROSAMINES are:

○ Adhesives used in footwear industry

○ Substances that cause the release of vocs

○ Substances that are referred in ecological criteria

Q34.	**Biocalce, oko tex and gots are ecolabels. When this labels are in products, means:**

○ They are all natural products

○ Products with higher quality

○ Products have an ecological concern

Q35.	**Abrasion, tear strength and adhesion are some tests can be performed in footwear and footwear components. These properties are related with:**

○ Physical properties

○ chemical properties

○ Physical and chemical properties

Q36.	**Testing materials in footwear industry is very important. Colour fastness testing in lining is important to realize the:**

○ Persistence of colour

○ Sweeting of feet

○ Release of metals from lining

Q37.	**Is very important to perform quality control in footwear materials. A low ph value in footwear materials can promote:**

○ Change of colour of footwear materials

○ Deterioration of footwear materials

○ Stability of footwear materials

Q38.	**The chromium normally present in the leather is CR (III), however by external conditions, sunlight and humidity the CR (III) could oxidise to CR (VI). The chromium (VI) is related with**

○ Cancer and is environmental prejudicial

○ Release of VOCs

○ High levels of pollution

Q39.	**The meaning of echa is:**

○ European Chemical Agency

○ European Carbon Agency

○ European COVs Agency

Q40. REACH (EC 1907/2006) aims to improve the protection of human health and the environment through the

○ High quality control in products

○ Better and earlier identification of the intrinsic properties of chemical substances.

○ Limitation of Chromium VI

Q41. Annex XVII to REACH integrates the:

○ Restricted List

○ Candidate List

○ Authorisation List

Q42. The technical report ISO/TR 16178 "footwear - critical substances potentially present in footwear and footwear components" categorizes the critical substances in:

○ 3 categories

○ 4 categories

○ 5 categories

Q43. The meaning of SVHc is:

○ Substances of Very High Chemical Content

○ Substances of Very High Concern

○ Substances of Very High Carbon Content

Q44. The standard ISO 20345: 2011 – personal protective equipment is applied to:

○ Safety footwear

○ Occupational footwear

○ Protective footwear

Q45. According to candidate list:

○ As producers of goods (footwear, leather, soles, and textiles) should ensure that their products do not contain substances that cause very high concern in concentrations higher than 1% (m / m).

○ As producers of goods (footwear, leather, soles, and textiles) should ensure that their products do not contain substances that cause very high concern in concentrations higher than 0.1% (m / m).

○ As producers of goods (footwear, leather, soles, and textiles) should ensure that their products do not contain substances that cause very high concern in concentrations higher than 10% (m / m).

Answer Key:

Q1.	Products or physical matter from plants, animals or soil.
Q2.	Renewable materials
Q3.	Materials in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae
Q4.	A compilation and evaluation of the input, outputs and the potential environmental impacts of a product system throughout its life cycle
Q5.	Epidermis, Dermis and subcutaneous tissues
Q6.	Conservation processes of skin
Q7.	Mineral an organic tanning
Q8.	Iron, Titanium, Chromium
Q9.	Zero Discharge Hazardous Chemicals
Q10.	tanned with tannin extracted from some trees and with polymeric resins
Q11.	The most natural leather with unique surface characteristics of the hide remaining visible
Q12.	Reduction of CO2 emission by the process and products in tannery and reduction of impact on climate change
Q13.	Natural, chemical and metallurgical
Q14.	Non-woven
Q15.	Chemical, Thermal, Mechanical
Q16.	Vegetable, animal and mineral
Q17.	Synthetic polymers
Q18.	Synthetic fibre
Q19.	Organic silk, recycled polyester
Q20.	Made without leather or any animal ingredients
Q21.	Cork, wood, NR
Q22.	The linking together of the monomer pieces to form a polymer
Q23.	Sports footwear
Q24.	Injection and shaping; Finishing and Packing
Q25.	Electrical protection of user during use
Q26.	Reinforcing materials incorporated in the uppers
Q27.	Good values of durability and good abrasion resistance
Q28.	Most efficient
Q29.	Volatile organic compounds
Q30.	Solvent based adhesives
Q31.	5-13% of worldwide population is allergic to this metal
Q32.	Mark awarded by European Community (EU)
Q33.	Substances that are referred in ecological criteria
Q34.	Products have an ecological concern
Q35.	Physical properties
Q36.	Persistence of colour

Answer Key:

Q37.	Deterioration of footwear materials
Q38.	Cancer and is environmental prejudicial
Q39.	European Chemical Agency
Q40.	Better and earlier identification of the intrinsic properties of chemical substances
Q41.	Restricted List
Q42.	5 categories
Q43.	Substances of Very High Concern
Q44.	Safety footwear
Q45.	As producers of goods (footwear, leather, soles, and textiles) should ensure that their products do not contain substances that cause very high concern in concentrations higher than 10% (m / m)

10. Annex

Property	Test Method	Sports	School	Casual	Men's town	Cold weather	Women's town	Fashion	Infants	Indoor
Flex resistance	ISO 17694	dry 100 000 cycles wet 20 000 cycles coated leather, at -5ºC, 20 000 cycles (w.v.d.)		dry 80 000 cycles wet 20 000 cycles coated leather, at -5ºC 20 000 cycles (w.v.d.)		dry 100 000 cycles wet 20 000 cycles coated leather, at -20ºC, 30 000 cycles (w.v.d.)	dry 50 000 cycles wet 10 000 cycles Coated leather, at -5 ºC 20 000 cycles (w.v.d)	dry 15 000 cycles without visible damage		
Tear Strength	ISO 17696	≥ 40 N average tear force						≥ 30 N average tear force		
Colour fastness	EN ISO 17700	Inside stain: if unlined footwear, ≥ 2/3 after 50 cycles with perspiration solution (method A)								
		Outside surface color and staining: ≥ 3 (grey scale) after 150 cycles dry and 50 cycles wet (method A) ≥ 3 to 4 (grey scale) after 512 cycles and 128 cycles wet (method B)			Outside surface color and staining: ≥ 3 (grey scale) after 100 cycles dry and 50 cycles wet (method A) ≥ 3 to 4 (grey scale) after 256 cycles and 128 cycles wet (method B)	Outside surface color and staining: ≥ 3 (grey scale) after 150 cycles dry and 50 cycles wet (method A) ≥ 3 to 4 (grey scale) after 512 cycles and 128 cycles wet (method B)	Outside surface color and staining: ≥ 3 (grey scale) after 100 cycles dry and 50 cycles wet (method A) ≥ 3 to 4 (grey scale) after 256 cycles and 128 cycles wet (method B)	Outside surface color and staining: ≥ 2 (grey scale) after 100 cycles dry and 20 cycles wet (method A) ≥ 2 to 3 (grey scale) after 256 cycles and 64 cycles wet (method B)	Outside surface color and staining: ≥ 3 (grey scale) after 100 cycles dry and 20 cycles wet (method A) ≥ 3 to 4 (grey scale) after 256 cycles and 64 cycles wet (method B)	
Lastability	EN ISO 17693	≥ 7,0 mm (for leather grain crack); ≥ 6,0 mm (for other materials first damage)								
Seam strength	ISO 17697	≥ 10 N/mm (method A)		≥ 8 N/mm (method A)		≥ 10 N/mm (method A)	≥ 4 N/mm (method A)	≥ 3 N/mm (method A)		
Bondability	EN 1392	≥ 4 N/mm		≥ 3 N/mm	≥ 3,5 N/mm	≥ 4 N/mm	≥ 3 N/mm	≥ 2,5 N/mm	≥ 3 N/mm	≥ 2,5 N/mm
Water vapour permeability and water vapour absorption	ISO 17699	WVP ≥ 0,8 mg/cm^2.h If WVP < 2,0 mg/cm^2.h, then WVA ≥ 8,0 mg/cm^2		WVP ≥ 0,8 mg/cm^2.h If 0,8 mg/cm^2.h ≤ WVP < 2,0 mg/cm^2.h, then WVA ≥ 8,0 mg/cm^2		WVP ≥ 0,8 mg/cm^2.h If 0,8 mg/cm^2.h ≤ WVP < 2,0 mg/cm^2.h, then WVA ≥ 5,0 mg/cm^2	WVP ≥ 0,8 mg/cm^2.h If 0,8 mg/cm^2.h ≤ WVP < 2,0 mg/cm^2.h, then WVA ≥ 8,0 mg/cm^2	(---)	WVP ≥ 0,8 mg/cm^2.h If 0,8 mg/cm^2.h ≤ WVP < 2,0 mg/cm^2.h, then WVA ≥ 8,0 mg/cm^2	WVP ≥ 0,8 mg/cm^2.h If 0,8 mg/cm^2.h ≤ WVP < 2,0 mg/cm^2.h, then WVA ≥ 6,0 mg/cm^2
Colour migration	ISO 17701	24 h, colour change and staining ≥ 4 (grey scale)	4 h, colour change and staining ≥ 4 (grey scale)	24 h, colour change and staining ≥ 4 (grey scale)						

Property	Test Method	Sports	School	Casual	Men's town	Cold weather	Women's town	Fashion	Infants	Indoor
Water resistance	ISO 17702	Penetration time ≥ 60 min, absorption after 60 minutes ≤ 20 % (water resistant) Penetration time ≥ 180 min, absorption after 180 minutes ≤ 25 % (highly water resistant)				Penetration time ≥ 240 min, absorption ≤ 20 %	Penetration time ≥ 60 min, absorption after 60 minutes ≤ 20% (water resistant) Penetration time ≥ 180 min, absorption after 180 minutes ≤ 25% (highly water resistant)	(---)	Penetration time ≥ 60 min, absorption after 60 minutes ≤ 20 % (water resistant) Penetration time ≥ 180 min, absorption after 180 minutes ≤ 25 % (highly water resistant)	(---)
High temperature resistance	ISO 17703	≥ 80% of original tensile strength and elongation						(---)	≥ 80% of original tensile strength and elongation	
Abrasion resistance	ISO 17704	dry 25 600; wet 12 800; No worse than moderate abrasion degree		dry 12 800; wet 6 400; No worse than moderate abrasion degree		dry 25 600; wet 12 800; No worse than moderate abrasion degree	dry 12 800; wet 6 400; No worse than moderate abrasion degree	(---)	dry 12 800; wet 6 400; No worse than moderate abrasion degree	(---)
Thermal insulation	ISO 17705	(---)	(---)	(---)	(---)	≥ $24 \cdot 10^{-3} m^2 \cdot {}^{o}C/W$		(---)	(---)	(---)
Water soluble substance content	EN ISO 4098 EN ISO 4047	≤ 3 % Sulphated ashed water soluble (SAWS) ≤ 18 % total water soluble (TWS)								
Breaking Strength and elongation	ISO 17697	≥ 10 N/mm, elongation ≥ 15% (across) and ≥ 7 % (along)					≥ 8 N/mm, elongation ≥ 15% (across) and ≥ 7 % (along)	(---)		
Delamination resistance	ISO 17698	leather: dry ≥ 0,5 N/mm wet ≥ 0,3 N/mm other materials: dry ≥ 1,0 N/mm wet ≥ 0,7 N/mm		leather: dry ≥ 0,5 N/mm wet ≥ 0,3 N/mm other materials: dry ≥ 1,0 N/mm; No worse than moderate abrasion degree; wet ≥ 0,7 N/mm; No worse than moderate abrasion degree;	leather: dry ≥ 0,3 N/mm wet ≥ 0,2 N/mm other materials: dry ≥ 0,8 N/mm wet ≥ 0,6 N/mm	leather: dry ≥ 0,5 N/mm wet ≥ 0,3 N/mm other materials: dry ≥ 1,0 N/mm wet ≥ 0,7 N/mm	leather: dry ≥ 0,3 N/mm wet ≥ 0,2 N/mm other materials: dry ≥ 0,8 N/mm wet ≥ 0,6 N/mm	leather: dry ≥ 0,2 N/mm wet ≥ 0,1 N/mm other materials: dry ≥ 0,7 N/mm wet ≥ 0,5 N/mm	leather: dry ≥ 0,3 N/mm wet ≥ 0,2 N/mm other materials: dry ≥ 0,8 N/mm wet ≥ 0,6 N/mm	leather: dry ≥ 0,2 N/mm wet ≥ 0,1 N/mm other materials: dry ≥ 0,7 N/mm wet ≥ 0,5 N/mm

T21. Requirements for upper materials (ISO/TR 20879 – "footwear – performance requirements for components for footwear - uppers ").

Property	Test Method	Sports	School	Casual	Men's town	Cold weather	Women's town	Fashion	Infants	Indoor
Tear strength	ISO 17695	≥ 15 N (lining) ≥ 20 N (reinforcing lining)			≥ 10 N (lining) ≥ 20 N (reinforcing lining)	≥ 15 N (lining) ≥ 20 N (reinforcing lining)	≥ 10 N (lining) ≥ 20 N (reinforcing lining)			
Lining seam strength	ISO 17697 Method A	≥ 4,0 N/mm	≥ 3,5 N/mm	≥ 4,0 N/mm	≥ 3,5 N/mm	≥ 4,0 N/mm	≥ 3,0 N/mm	≥ 2,5 N/mm	≥ 2,0 N/mm	
Colour fastness	EN ISO 17700 Method A	≥ 3 (grey scale) after 50 cycles with perspiration solution								
Abrasion resistance	ISO 17704	dry 25 600; wet 12 800; Without hole through the thickness of the material component	dry 25 600; wet 3 200; Without hole through the thickness of the material component	dry 12 800; wet 3 200; Without hole through the thickness of the material component	dry 6 400; wet 1 600; Without hole through the thickness of the material component	dry 25 600; wet 12 800; Without hole through the thickness of the material component	dry 25 600; wet 3 200; Without hole through the thickness of the material component	dry 12 800; wet 3 200; Without hole through the thickness of the material component		dry 6 400; wet 1 600; Without hole through the thickness of the material component
Water vapour permeability and absorption	ISO 17699	WVP ≥ 2,0 mg/cm².h If WVP < 0,8 mg/cm².h, then WVA ≥ 8,0 mg/cm²								
Water soluble substances content	ISO 20869	≤ 1,5 % Sulphated ashed water soluble (SAWS) ≤ 16 % total water soluble (TWS)								
Perspiration resistance	ISO 22652	After 5 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance	After 3 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance	After 5 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance	After 3 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance	After 5 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance	After 3 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance			
Static friction	ISO 22653	≥ 0,7			≥ 0,6	≥ 0,7	≥ 0,5	≥ 0,4		
Flex resistance	ISO 17694	dry 15 000 cycles without visible damage								
Thermal insulation	ISO 17705	(---)	(---)	(---)	(---)	≥ $24 \cdot 10^{-3} m^2 \cdot {}^{\circ}C/W$	(---)	(---)	(---)	(---)

T22. Requirements for lining materials (ISO/TR 20882 – "footwear – performance requirements for components for footwear – lining and insocks").

Property	Test Method	Sports	School	Casual	Men's town	Cold weather	Women's town	Fashion	Infants	Indoor
Colour fastness	EN ISO 17700 Method A	≥ 3 (grey scale) after 50 cycles with perspiration solution								
Abrasion resistance	ISO 17704	dry 25 600 wet 12 800			dry 25 600 wet 6 400	dry 25 600 wet 12 800	dry 25 600 wet 3 200	dry 12 800 wet 3 200 Without holes in the wearing surface		dry 6 400 wet 600 Without holes in the wearing surface
Water absorption and desorption	ISO 22649 method B	absorption ≥ 70 mg/cm^2 desorption ≥ 60 %			absorption ≥ 60 mg/cm^2 desorption ≥ 60 %	absorption ≥ 70 mg/cm^2 desorption ≥ 60 %	absorption ≥ 60 mg/cm^2 desorption ≥ 60 %			
Water soluble substances content	ISO 20869	≤ 1,5 % Sulphated ashed water soluble (SAWS) ≤ 16 % total water soluble (TWS)								
Perspiration resistance	ISO 22652	After 5 cycles the com-ponent shall not devel-op any cracks when bent and must keep 80% tear resistance	After 3 cycles the com-ponent shall not devel-op any cracks when bent and must keep 80% tear resistance	After 5 cycles the com-ponent shall not devel-op any cracks when bent and must keep 80% tear resistance	After 3 cycles the com-ponent shall not devel-op any cracks when bent and must keep 80% tear resistance	After 5 cycles the com-ponent shall not devel-op any cracks when bent and must keep 80% tear resistance	After 3 cycles the component shall not develop any cracks when bent and must keep 80% tear resistance			
Static friction	ISO 22653	≥ 0,7			≥ 0,6	≥ 0,7	≥ 0,5	≥ 0,4		
Flex resistance	ISO 17694	dry 15 000 cycles without visible damage								
Tear Strength	ISO 17696	≥ 15 N			≥ 10 N	≥ 15 N	≥ 10 N			
Thermal insulation	ISO 17705	(---)	(---)	(---)	(---)	$\geq 24 \cdot 10^{-3} m^2.°C/W$	(---)	(---)	(---)	(---)

T23. Requirements for insock materials (ISO/TR 20882 – "footwear – performance requirements for components for footwear – lining and insocks ").

<table>
<tr><th>Property</th><th>Test Method</th><th>Sports</th><th>School</th><th>Casual</th><th>Men’s town</th><th>Cold weather</th><th>Women’s town</th><th>Fashion</th><th>Infants</th><th>Indoor</th></tr>
<tr><td>Water soluble sub-stances content</td><td>ISO 20869</td><td colspan="9">≤ 1,5 % Sulphated ashed water soluble (SAWS)
≤ 16 % total water soluble (TWS)</td></tr>
<tr><td>Delamination resistance</td><td>ISO 20866</td><td colspan="2">Fore part-.≥ 700kPa dry; ≥ 650 kPa wet
Seat part-.≥ 600kPa dry; ≥ 450 kPa wet</td><td>Fore part-.≥ 650kPa dry; ≥ 550 kPa wet Seat part-.≥ 600kPa dry; ≥ 450 kPa wet</td><td>Fore part-.≥ 500kPa dry; ≥ 300 kPa wet Seat part-.≥ 500kPa dry; ≥ 300 kPa wet</td><td>Fore part-.≥ 700kPa dry; ≥ 650 kPa wet Seat part-.≥ 600kPa dry; ≥ 450 kPa wet</td><td>Fore part-.≥ 500kPa dry; ≥ 300 kPa wet Seat part-.≥ 500kPa dry; ≥ 300 kPa wet</td><td>Fore part-.≥ 300kPa dry; ≥ 150 kPa wet Seat part-.≥ 300kPa dry; ≥ 150 kPa wet</td><td>Fore part-.≥ 300kPa dry; ≥ 50 kPa wet Seat part-.≥ 300kPa dry; ≥ 50 kPa wet</td><td>(---)</td></tr>
<tr><td>Abrasion resistance (testing not necessary if full sock is used)</td><td>ISO 20868</td><td colspan="3">No surface tearing before 400 cycles</td><td>No surface tearing before 300 cycles</td><td>No surface tearing before 400 cycles</td><td>No surface tearing before 300 cycles</td><td colspan="3">No surface tearing before 200 cycles</td></tr>
<tr><td>Resistance to stitch tear (only applicable for sewn insoles)</td><td>ISO 20876</td><td colspan="3">≥ 140 N</td><td>≥ 100 N</td><td>≥ 140 N</td><td>≥ 100 N</td><td colspan="2">≥ 80 N</td><td>≥ 60 N</td></tr>
<tr><td>Dimensional stability</td><td>ISO 22651</td><td colspan="9">increase in size ≤ 2,0%
shrinkage ≤ 2,0 %</td></tr>
<tr><td>Water absorption and desorption</td><td>ISO 22649 (method B)</td><td colspan="3">absorption ≥ 70 mg/cm²
desorption ≥ 60 %</td><td>absorption ≥ 60 mg/cm²
desorption ≥ 60 %</td><td>absorption ≥ 70 mg/cm²
desorption ≥ 60 %</td><td colspan="4">absorption ≥ 60 mg/cm²
desorption ≥ 60 %</td></tr>
<tr><td>Heel pin holding strength</td><td>ISO 20867</td><td>(---)</td><td colspan="4">≥ 700 N dry ; ≥ 600 N dry
(if it applies)</td><td colspan="2">Heel height, measured vertically at back:
Less than 50 mm: ≥ 700 N dry;
≥ 600 N wet;
50 mm to 74 mm: ≥ 900 N dry;
≥ 800 N wet;
75 mm to 99 mm: ≥ 1100 N dry ;
≥ 1000 N wet
100 mm and over: ≥ 1300 N dry ;
≥ 1200 N wet</td><td colspan="2">≥ 700 N dry ; ≥ 600 N dry
(if it applies)</td></tr>
</table>

T24. Requirements for leather insole materials (ISO/TR 20881 – “footwear – performance requirements for components for footwear - insoles “).

Property	Test Method	Sports	School	Casual	Men's town	Cold weather	Women's town	Fashion	Infants	Indoor
Flex resistance	EN ISO 17707	cut growth ≤ 4,0 mm and no spontaneous crack		cut growth ≤ 5,0 mm and no spontaneous crack	cut growth ≤ 6,0 mm and no spontaneous crack	cut growth ≤ 6,0 mm and no spontaneous crack, at -10 ºC	cut growth ≤ 8,0 mm and no spontaneous crack	cut growth ≤ 12 mm and no spontaneous crack	(---)	cut growth ≤ 12 mm and no spontaneous crack
Abrasion Resistance	ISO 20871	F0,9 g/cm^3 ≤ d ≤ 200 mm^3 0,9 g/cm^3 > d ≤ 150 mg		0,9 g/cm^3 ≤ d ≤ 250 mm3 0,9 g/cm^3 > d ≤ 170 mg	0,9 g/cm^3 ≤ d ≤ 350 mm3 0,9 g/cm^3 > d ≤ 200 mg	0,9 g/cm^3 ≤ d ≤ 200 mm3 0,9 g/cm^3 > d ≤ 150 mg	0,9 g/cm^3 ≤ d ≤ 400 mm3 0,9 g/cm^3 > d ≤ 250 mg	0,9 g/cm^3 ≤ d ≤ 450 mm3 0,9 g/cm^3 > d ≤ 300 mg	0,9 g/cm^3 ≤ d ≤ 400 mm3 0,9 g/cm^3 > d ≤ 250 mg	0,9 g/cm^3 ≤ d ≤ 450 mm3 0,9 g/cm^3 > d ≤ 300 mg
Delamination resistance or slip tear (only for multilayer outsoles)	ISO 20875	0,9 g/cm^3 ≤ d ≥ 3,0 N/mm 0,9 g/cm^3 > d ≥ 1,7 N/mm								
Slip resistance (ceramic floor and water and detergent)	EN 13287	≥ 0,30 (flat slip) ≥ 0,28 (heel slip)								
Dimensional Stability	ISO 20873	≤ 2,5 %								
Compression energy	ISO 20865	≥ 15 J							≥ 8 J	(---)
Bondability only for sewn footwear)	EN 1392	0,9 g/cm^3 ≤ d ≥ 4,0 N/mm 0,9 g/cm^3 > d ≥ 3,0 N/mm		0,9 g/cm^3 ≤ d ≥ 3,5 N/mm 0,9 g/cm^3 > d ≥ 3,0 N/mm			≥ 3,0 N/mm	≥ 2,5 N/mm	≥ 3,0 N/mm	≥ 2,5 N/mm
Water soluble sub-stances content	ISO 20869	Water soluble matter ≥ 18 % Sulphated ashed water soluble ≤ 3%								
Tear strength	ISO 20872	0,9 g/cm^3 ≤ d ≥ 8,0 N/mm 0,9 g/cm^3 > d ≥ 6,0 N/mm			0,9 g/cm^3 ≤ d ≥ 7,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	0,9 g/cm^3 ≤ d ≥ 8,0 N/mm 0,9 g/cm^3 > d ≥ 6,0 N/mm	0,9 g/cm^3 ≤ d ≥ 7,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	0,9 g/cm^3 ≤ d ≥ 5,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm		
Water resistance	EN/ISO 5404	0,9 g/cm^3 ≤ d ≥ 8,0 N/mm 0,9 g/cm^3 > d ≥ 6,0 N/mm	0,9 g/cm^3 ≤ d ≥ 7,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	0,9 g/cm^3 ≤ d ≥ 8,0 N/mm 0,9 g/cm^3 > d ≥ 6,0 N/mm		0,9 g/cm^3 ≤ d ≥ 7,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	0,9 g/cm^3 ≤ d ≥ 5,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	0,9 g/cm^3 ≤ d ≥ 8,0 N/mm 0,9 g/cm^3 > d ≥ 6,0 N/mm	0,9 g/cm^3 ≤ d ≥ 7,0 N/mm 0,9 g/cm^3 > d ≥ 4,0 N/mm	
Needle tear strength	ISO 20874	≥ 40 N/mm	≥ 35 N/mm		≥ 30 N/mm	≥ 35 N/mm	≥ 30 N/mm	≥ 20 N/mm		

T25. Requirements for leather outsole materials (ISO/TR 20880 – "footwear – performance requirements for components for footwear - outsoles ")

Substance		Test Method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather Board	PVC	EVA	Rubber	PU-TPU elasthano	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Acrylonitrile								5						5					5			
AZO – arylamines	When 4-aminoazobenzene is suspected	ISO 17234-1	1	1	1																	
AZO – arylamines		ISO 17234-2	1	1	1																	
AZO – arylamines		EN 14362-1										1	1	1		1	1				1	
AZO – arylamines		EN 14362-2									1										1	
AZO – arylamines	When 4-aminoazobenzene is suspected	EN 14362-3									1	1	1	1		1	1				1	
Cadmium	All plastics (mainly PVC)	EN 1122		1		1	1	1	1	1											1	
Choloorganic carriers		DIN 54232									3											
Chromium VI		ISO 17075	2	2	2																	
Colophony																			5			
Dimethyformamide (DMF)				4					4													
Dimethylfumarate (DMFU)		ISO/TS 16186	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Disperse dyes and dyestuffs		DIN 54231									2	2	2	2		2	2					
Flame retardant	Only for product claiming FR properties		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Formaldehyde		ISO 17226-1 and ISO 17226-2	2	2	2																	
Formaldehyde		EN 120 EN 717-3																2				2

Substance		Test Method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather Board	PVC	EVA	Rubber	PU-TPU elasthano	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Ortho-phenylphenol		ISO 13365	5	5	5		5				5	5	5	5	5	5	5	5				5
Ozone depleting substances											3	3	3	3		3	3					
PAH – polycyclic aromatic hydrocarbons			4	4	4	4	4	4	4	4												
PCP -TeCP – TriCP - polychlorophenols		ISO 17070	2	2	2																	
PCP -TeCP – TriCP - polychlorophenols		CEN/TR 14823																2				
PCP -TeCP – TriCP - polychlorophenols		XP G 08-015														2	2					
Pesticides			5	5	5											3	3					5
PFOS/PFOA (Perfluorooctane sulfonate/perfluorooctanoic acid)	Only for products claiming FR properties and water resistance	CEN/TS 15968	1	1	1						1	1	1	1		1	1					
pH		ISO 4045	4	4	4																	
pH		ISO 3071									4	4	4	4		4	4					
Phenol			4	4	4			4								4	4		4			4
Phthalates		ISO/TS 16181				3	3	3	3	3												
	Footwear for children less than 36 months old	ISO/TS 16181		2		2	2	2	2	2	2	2	2	2		2	2				2	
PCB - Polychlorinated biphenyls			5	5	5						3	3	3	3		3	3					

Substance	Test Method	Leather			Synthetic material									Natural material				Miscellaneous			
		Leather	Coated leather	Leather Board	PVC	EVA	Rubber	PU-TPU elasthano	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Polychloroprene or neoprene							5											5			
PPD Paraphenylene diamine		5	5	5						5	5		5		5	5				5	5
PTBF Paratertiary butyl phenol formaldehyde																		5			
Short-chained chloroparaffins (C10 C13)		3	3	3			3			3	3	3	3		3	3					
TCMTB (2-(thiocyanatomethylthio)-1,3-benzothiazole)	ISO 13365	5	5	5																	
Thiuram and thiocarbamate							5														
Vinyl chloride monomer	ISO 6401		4		4																

T26. Critical chemicals potentially present in footwear and footwear components (ISO/TR 16178– "footwear – critical substances potentially present in footwear and footwear components ").

Substance		Test Method	Leather			Synthetic material									Natural material			Miscellaneous			
			Leather	Coated leather	Leather Board	PVC	EVA	Rubber	PU-TPU elasthano	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Formaldehyde		ISO 14184-1									2	2	2	2		2	2					
Heavy metals	Extractible (Sb-As-Pb-Cd-Cr-Co-Cu-Ni-Hg-Zn)	ISO 17072-1	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4		4	4	4
	Extractible Footwear for children less than 36 months (Sb-As-Pb-Cd-Cr-Co-Cu-Ni-Hg-Zn-Ba-Se)	ISO 17072-1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2		2	2	
	Total content (Sb-As-Pb-Cd-Cr-Co-Cu-Ni-Hg-Zn)	ISO 17072-2	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4		4	4	4
	Total content (As-Cd-Pb)	EN 14602:2004	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3		3	3
Mercapto benzothiazole								5														
Extractable latex proteins		EN 455-3													4							
N-ethylphenylamine								5							4							
Nickel	Skin contact	EN 1811 CR 12471 (with or without EN 12472)																		1		
Nitrosamines	Footwear for children less than 36 months old	EN 12868						2														
Nitrosamines		EN 12868						3														
OP, NP, OPEO, NPEO Alkylphenols and alkylphenolethoxylates)			4	4	4						3	3	3	3		3	3					
Organic compounds (TBT, TPT)		ISO/TS 16179	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1
Organic compounds (MBT, DBT, DOT)		ISO/TS 16179	4	4	4	4	4	4	4	4	3	3	3	3	4	3	3	4	4		4	4

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