Kaunas University of Technology

Faculty of Mechanical Engineering and Design

SUBSTITUTION OF HAZARDOUS CHEMICALS IN FUR PROCESSING INDUSTRY

Master's Final Degree Project

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Sustainable Management and Production (621H17002)

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Substitution of hazardous chemicals in fur processing industry

Declaration of Academic Integrity

I confirm that the final project of mine, Vidhyalakshmi Chandrasekaran, on the topic „ Substitution of hazardous chemicals in fur processing industry " is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by law) have been paid to anyone for any contribution to this project.

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(name and surname filled in by hand) (signature)

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Abbreviations

Acronymn	Definition
BAT	Best Available Techniques
BOD	Biological Oxidation Demand
BREF	BAT Reference Documents
CLP	Classification, Labelling & Packaging
CML	Centre for Environmental Studies, Leiden, Netherlands
CMR	Carcinogenic, Mutagenic & Reproductive disruptive
COD	Chemical Oxygen Demand
DALY	Disability Adjusted Life Year
ECHA	European Chemical Agency
EIA	Environment Impact Assessment
EPS (2000)	Environment Priorty Strategies (2000)
EU	European Union
GHS	Global Harmonized System
HCHO	Formaldehyde
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
MIPS	Material Input per Service unit
NP/NPE	Nonylphenol/Nonyl phenol ethyoxylates
PBT	Persisitant, Bioaccumulative, Transgeneic
PFC	Perfluorochemicals
PIC	Prior informed consent
PLA	Polymers polyacide
POP	Persistant Organic Pollutants
PP	Poly Propylene
RA	Risk Assessment
RAPEX	Rapid Alert system for non-food consumer products
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RoHS	Restriction of Hazardous Substances
SDG	Sustainable Development Goals
SVHC	Substances of Very High Concern
UN	United Nations
vPvB	very Persistant very Bioaccumulation
VOC	Volatile Organic Compounds

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Summary

Fur industry is one of the most polluting industries across world. The industry use several chemicals right from un-hairing of raw skins/hides till finishing of leather products. Currently, many fur industries practice conventional chrome tanning methods. The chemicals used for the purpose of leather making, is often, considered to be harmful and toxic to human health and environment based on their properties. In most of the case, the substances that are used for the tanning purposes is listed under EU's priority substances list. Moreover, the industry also produce huge amount of effluents and wastes during each stages of the production. The improper treated wastes imposes severe environmental and human health risks in long term.

As recommended by European legislation, REACH regulation (EC 1907/2006), the substances of very high concern, to be replaced with non-toxic or less hazardous substances of same functionality. By reviewing the current situation of the industry, the SHVC was shortlisted and comparing the shortlisted substances with the identified company, Chromium compound was selected for further study. Chromium compounds, that is listed under REACH legislation has potential CMR properties, so, it is mandatory to look for alternative substances of same purpose.

The study focus on the finding an alternative substances to replace with Chromium compounds. The identified alternatives was assessed with various criteria such as hazard, legal requirements, CMR properties and so on, to match with functionality and purpose. The identified alternative was evaluated for environmental impact using Life Cycle Assessment. A comparative evaluation was carried out for both conventional chrome tanning and also identified alternative tanning agent.

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Santrauka

Kailių pramonė yra viena labiausiai teršiančių pramonės šakų visame pasaulyje. Pramonė naudoja didelį kiekį įvairių cheminių medžiagų. Šiuo metu daugelis kailių pramonės šakų vid dar taiko tradicinius kailių išdirbimo metodus nauojant chromo junginius. Cheminės medžiagos, naudojamos odos gamybai, laikomos kenksmingomis ir toksiškomis žmonių sveikatai ir aplinkai, atsižvelgiant į jų savybes. Daugeliu atvejų medžiagos, naudojamos rauginimo procesuose, yra išvardytos ES prioritetinių medžiagų sąraše. Be to, pramonė taip pat naudoja didelius vandens išteklių kiekius ir generuoja didžiulius nuotekų ir atliekų kiekius kiekviename gamybos etape. Netinkamai apdorojamos atliekos ilgainiui kelia didelį pavojų aplinkai ir žmonių sveikatai..

Kaip rekomenduojama Europos teisės aktuose, REACH reglamente (EB 1907/2006), labai didelį susirūpinimą keliančios medžiagos turi būti pakeistos mažiau pavojingomis medžiagomis.. Atlikus įmonės analizę, nustatyta didelį susirįpinimą keliančios medžiagos, kurios pasirinktos tolesnei analizei amos su Chromo oksidas buvo pasirinktas tolesniam tyrimui. Chromas, cheminė medžiaga, įtraukta REACH reglamente, pasižymi CMR savybėmis.

Darbe buvo siekiama surasti tinkamą alternatyvą pakeisti kailių rauginimo procese chromo junginius mažiau pavojingomis cheminėmis medžiagomis. Nustatytos alternatyvos buvo vertinamos pagal įvairius kriterijus, taip pat atitikimą teisiniams reikalavimams. Poveikis aplinkai buvo įvertintas naudojant būvio ciklo vertinimo metodiką.. Rauginimo proceso poveikis aplinkai buvo įvertintas ir palygintas kartu su rauginimo procesui naudojant alternatyvią cheminę medžiagą.

Introduction

Chemicals are widely used in all aspects of human living, right from household utilities to food products. The range of chemicals is huge that is used in the technological process from manufacturing until disposal according to their properties. Subsequently, these chemicals also have toxicological, eco-toxicological or hazardous nature. These could potentially harm human health and environment depends on the exposure time and physio-chemical properties. Generally, the chemicals that are categorized as most hazardous substances, called “substances of very high concern” (SVHC), have Carcinogenic Mutagenic Reproductive disruptive (CMR), Persistent Bioaccumulative Toxic (PBT) and very Persistent very Bioaccumulative (vPvB) properties by nature. These are substances which are handled in European Union (EU) directives and considered for substitution with less hazardous or non-hazardous substances (1).

For achieving the goal of reducing risk and a straightforward approach to manage hazardous chemicals is by substituting less hazardous chemicals or alternative chemicals of the same purpose. As by definition, "replacement of hazardous substances in products and processes by less hazardous or non-hazardous substances, or by achieving an equivalent functionality via technological or organizational measures, is called substitution" (2). Moreover, substitution of chemicals as an integral part of sustainable development. Because the process brings closer to the state of sustainability. According to SDGs, "Responsible Consumption and Production" (SDG 12) aims in promoting “doing more and better with less”, increasing productivity and reducing the impact on resource, degradation and pollution in the entire process of production and consumption with a holistic approach (3).

Based on the study of six alternative frameworks, incorporating Life Cycle Assessment is a priority while approaching to achieve chemical substitution (4). Life Cycle Assessment (LCA) is a tool to evaluate inputs, outputs and significant environmental impact of a product or process. Application of LCA plays a vital role while broadening chemical alternatives; LCA promises better understanding of the flow of toxins and also gives a strong framework for organizing knowledge about intrinsic hazards associated with a product or process system (5).

Project Object: The tanning process and the hazardous chemicals used in the process

Aim

To assess the substitution possibilities of hazardous chemicals in tanning process of the fur industry.

Project Objectives

- To review legal requirements of fur and leather industry in Europe
- To analyse the current situation of fur and leather industry in Europe
- To review the hazardous chemicals used in fur and leather industry
- To review problems and prospectus of chemical substitution
- To identify the need for substitution
- To perform overall environmental impact assessment with Life Cycle Assessment

1. Literature Analysis

1.1. Legislation of Chemicals

The chemical industry is a highly diversified sector, expanding every minute. It also plays a vital role in developing the economy and providing opportunities. At the same time, the chemicals that we use impose severe damage to our health and the environment. So, there is a need for a regulation concerning chemicals, management, and its safe use. In European Union, comprehensive chemical legislation such as REACH and CLP aims to ensure the protection of human health and environment. Specific groups of chemicals, such as pesticides, pharmaceuticals or cosmetics, are covered by their own legislation (6).

1.1.1. REACH

REACH (EC 1907/2006) is a European regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals which came into force in 2007. It is not a directive but a regulation adopted to enhance the protection of the the environment and human health from the risk caused by chemicals. The regulation helps to identify the intrinsic properties of chemicals while boosting innovation and competitiveness of the chemical industry in EU. The regulation has four processes, namely, registration, evaluation, authorization, and restrictions of chemicals. The main process is represented in Figure 1.1. The regulation imposes responsibility for the industry to manage the chemicals based on their risk and to provide safety information. In principle, it applies not only to industrial chemicals that are used for manufacturing but also for the chemicals that are used in everyday lives (7).

The European Commission has a vital role in implementing this legislation and in decision making. REACH is followed and implemented across EU regions covering different issues and responsibilities under this regulation. Unlike RoHS, REACH does not require merging into local laws.

The importers or manufacturers are required to collect information of the chemicals such as chemical properties, and safe handling which is to register in a database managed by European Chemical Agency (ECHA). The database helps to manage, evaluate substances of high concern or suspicious chemicals and provide hazard information on chemicals to consumers, public and to the professionals (6).

REACH has wide impacts on several sectors of industries viz., manufacturers, importers, downstream users, and also companies which were established outside European Union. In general, all these layers had to comply with the regulation, if they, plan to import, export or even to supply within EU. The companies outside Europe have requirements such as pre-registration to export their products to EU.

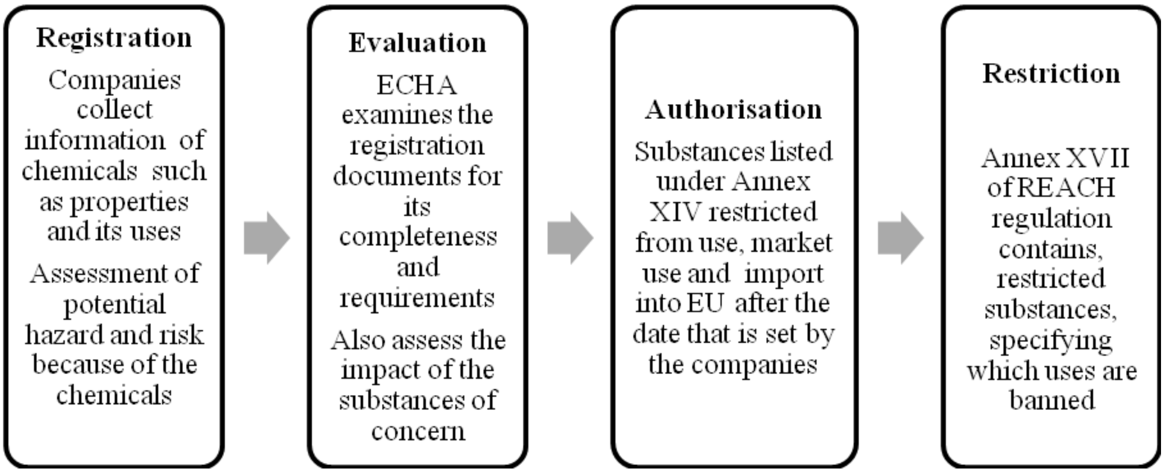

Figure 1.1. Main Stages of REACH implementation (8)

1.1.2. CLP

Consequently, to ensure the safe handling of chemicals, it is often required to formulate labels or safety data sheets. Companies, generally involved in the process, to create labels or data sheets according to the type of chemicals used in the products. But, it often leads to inconsistent and non-uniform to follow as it needs to follow multiple regulations regarding hazard classification and labelling.

The regulation of the Classification, Labelling, and Packaging of Substances and Mixtures (CLP) was adopted by European Parliament and Council in 2009. The regulation incorporates new criteria for classification, labelling, hazard symbols etc. CLP Regulation (EC 1272/2008) is implemented based on the United Nations' Globally Harmonized System (GHS). GHS contains the classification of chemicals by hazard types, harmonious hazard communication such as labels and safety data sheets. This provides a basis for the uniform formation of rules and regulations on chemicals at national, regional and worldwide as well, to facilitate the trade on chemical movement. The new system also helps to communicate physical hazards, toxicity from substance to human and environment during the transportation and use of these chemicals (9).

The CLP regulation replaces two important directives, namely, Dangerous Substances Directive (67/548/EEC(DSD)) and Dangerous Preparations Directive (1999/45/EC(DPD)). The regulation also extends with certain provisions of Regulation (EC 1907/2006) REACH, regarding the notification of classification, creation of labelling inventory and harmonized classification. The aim of the regulation is to protect workers, users, and environment with the help of labelling that denotes possible hazardous effects of dangerous chemicals. This database is also regulated by ECHA (10).

Figure 1.2. Hazard Pictogram - CLP (11)

The regulation has introduced new label - hazard pictogram, similar to the UN's GHS as in Figure 1.2. The label includes a symbol for warning and provides information about the particular substance that can damage our health or the environment. The regulation recently amended the structure of the image with a red diamond with a white background, from orange square symbols.

In REACH, CLP has pre-requisite to identify substances accurately, enable to obtain efficient and correct data for the substance registered under these regulations. Accurate identification of substance has some advantages apart from efficient data representation. Providing accurate data also prevent from unwanted animal testing, use of test data across different companies.

1.2. Legal Requirements for Fur and Leather Industry in Europe

Leather industry in Europe is diverse in both products and processes. There are different raw materials, chemicals, and other substances are used during the conversion process of leather into garments, furniture, footwear and so on. According to EU requirements, there is no dedicated legislation for the fur and leather industry. But it has to comply with various requirements based on other factors such as the effect on the environment, use of chemicals, raw materials like animal skin or hides, fur farming, or use of other dangerous substances.

The following regulations have implications with fur and leather industry in Europe.

Regulation (EC 1907/2006) on Registration, Evaluation, Authorization, and restriction of Chemical substances (REACH), as it uses a wide range of chemical substances and preparations (Refer Section 1.2).

Directive 2010/75/EU on industrial emissions which determines emission limit, based on Best Available Techniques (BAT). The regulation mainly deals with pollution, prevention, and control. It is an integrated approach that takes environmental performance into account. The BAT reference document (BREF) for tanning of hides and skins was adopted in the year 2013. The document ensures that the tanning industry across Europe follows environmental friendly procedures. The document is published by European Commission to Article 13(6) of the Directive. The BREF document for tanning industries exclusively covers where the treatment capacity exceeds 12 tonnes of products each day; independently operated wastewater treatment which was not covered in the Directive (91/271/EEC). In general, the document covers the core processes in the tanning of hides and skins and associated activities including any part of the process right from the raw skin to the product. It also deals with industry - a reduction of emission to water and land; efficient energy and water usage; minimization, recovery, and recycling of process residues (12).

Regulation (EC 1069/2009) and Commission Regulation (EU 142/2011) on animal by-products and derived products not intended for human consumption. Regulation (EC 1069/2009) and Commission Regulation (EU 142/2011) is replaced with old rules (Regulation EC 1774/2002) which consolidated into a single regulation. The regulation is mainly to address the animal by-products that cannot be consumed by a human. These animal by-products come from various source annually, these are categorized based on their risk and treated. If the by-products are not properly disposed of, it could pose a severe health risk to humans and animals. The rules regulate their movement, processing, and disposal. The measures are applied depending on the category of animal by-products (12).

Regulation (EC 649/2012) on export and import of dangerous chemicals or substances or mixture [Rotterdam Convention]. Certain substances or hazardous chemicals are subjected to prior informed consent (PIC) as per Rotterdam Convention. The chemicals are exported as per their classification, packaging, and labelling. It lays provision to facilitate the information of chemicals as well. Regulation (EC 689/2008) is replaced with Regulation EC 649/2012 (13).

Regulation (EC 850/2004) on persistent organic pollutants [Stockholm Convention]. The aim of the agreement is to eliminate the production and use of internationally recognized POPs. The regulation has provision for production, use of chemicals, management of stash and wastes; provides measures to reduce releases of POPs. Also, it ensures implementation of emission inventories of unintentionally produced POPs, monitoring and information exchange (14).

Regulation (EC 60/2000) on Water Framework Directive is a most substantial piece of environmental legislation. The aim of the legislation is to ensure the good status of water quality in both surface and groundwater. This is considered as an umbrella act which set quality standards for water bodies viz., surface water, fresh water, sea mollusks, bathing water and drinking water also emission limit standards for discharging waters such as hazardous substances directive and groundwater directive. Apart from quality standards it also addresses river basin management and other water quality aspects (6).

In case of the fur industry, there is no specific national legislation for animals welfare in many countries in European Union. Countries like Austria, Belgium, Denmark, Hungary, Croatia, Germany, Netherlands, Norway, and the UK have national legislation related to fur farming or animal welfare act whereas few other countries in European Union have no clear picture about fur farming. However, the concerns and prohibition of fur farming is increasing and widespread in Europe (15).

As a part of EU, Lithuanian leather industry had to implement regulations and environmental standards derived from EU legislation. For fur industry, the national legislation on Lithuanian Animal Welfare Regulation is put forward in 2012. Animals that are bred for fur is defined as domestic animals as per the regulation. It also defines requirements and methods for slaughter. There has been a campaign since 2014 against fur farming which raises awareness and also finds support for framing legislation for fur farming in Lithuania (16).

1.3. Production of Fur and Leather

1.3.1. Processing of Leather

Leather tanning is one of the oldest activities of a human. In ancient times, the skins of animals are obtained from hunting that was used for food, clothing, tents etc. whereas today, the animal skins are used as by-products from dairy and meat industries. The ancient Greeks were the first ones to develop the tanning process using some tree barks and water to preserve leather. Since then, the processing of leather has evolved with various methods and chemicals usage (17).

Tanning is a complicated process which changes its skin color. The skin has tannic acid which prevents them from decaying, keeping it supple and durable; used as an intermediate material to manufacture various goods. Generally, cattle, sheep, and pigs are reared for skins or hides which often used in leather manufacturing.

The process of leather consists of four main processes: beam house operation, tanyard processes, re-tanning and finishing (18). Each process is different and amount, type of waste produced are different. However, the production of leather is done by chrome tanning as a classical method. Prior to the process, the raw hides are trimmed. Soaking, unhairing, bating, liming and de-liming are considered as a pre-tanning process which generally takes place during beam house operation (19). Figure 1.3 represented the process flow of leather using both chrome tanning with inputs and outputs (12).

The preparation of leather starts with curing of hides and skins that are preserved to stop them deteriorating. The pre-tanning process is elaborated in as follows:

i. Soaking: The cured hides and skins are soaked in water for several hours or days. During this process, the water is reabsorbed and helps to clean them of salt and dirt.
ii. Unhairing: After soaking, the skins or hides are immersed into an alkali solution, this will help the structure of the skin to loosen and breaks down the roots and removes hair.
iii. Liming: The skins that are hair removed is immersed in alkali solution and sulfide to further remove the hair and also helps to alter the property of the skin which modifies into an open structure.
iv. Bating and Deliming: This process is done to flush out the impurities with the help of enzymes treatment. During the process, the skin becomes flaccid and the bating process makes the pelt smooth and silky (20).

Following the pre-tanning/ beam house operation, the pelt is further processed for degreasing and pickling before vegetable or chrome tanning process.

v. Degreasing and pickling: The pelt is degreased to remove and reduce the natural fatty acids which affect the absorption of chemicals in a later stage. Further, the skins are treated with acid to preserve for future is called as pickling.
vi. Tanning: the process of converting hides or skins of animals into leather is named as tanning. The skins or hides have the ability to change structure due to the protein present in the cell. The tanning of skins can be done with different methods. Chrome tanning is a widespread method. Chrome-tanned leather has a tendency to be gentler and flexible, has higher thermal strength, is extremely steady in the water. Chrome tanning is done with almost all lighter weight cattle hides such as sheep, goats, cows, and pigs. Chrome process is generally done with trivalent chromium salt. The process covers up in a salted state of pH 3 or lower.

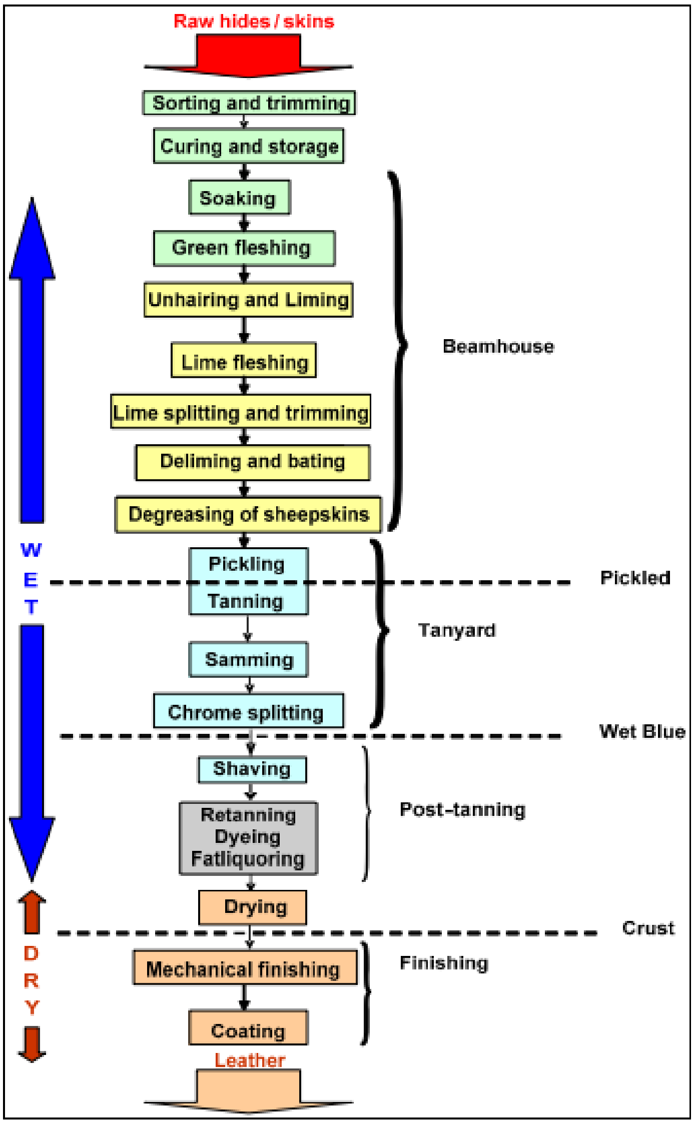

Figure 1.3. Process flow of Leather Manufacturing (12)

vii. Furthermore, the chrome leather undergoes re-tanning dyeing and fatliquoring process. During re-tanning, few chemicals are added to adjust the texture and thickness to achieve the quality of leather. Fatliquoring is the way toward bringing oil into the skin before the leather is dried to supplant the regular oils lost in beam house and tanyard forms. The tanned leather is wrung, set out, dried, and wrapped up and to make it suitable for further usage (18).

1.3.2. Processing of Fur

The processing of fur is not so different from the leather processing. Common animals which are tamed for fur fox, minks, chinchilla, opossum, rabbit, beaver, dogs, cats etc. Some of these furs are highly prized and there are many grades and colours. In the modern fur industry, leather made from animal fur especially as a first step, the leather side of the animal skin is tanned, so that the leather will stay supple and soft for years without deterioration. Typically, the pelt is scraped and cleaned by washing and impregnated with animal oil. Unlike the leather tanning, the fur is removed from hiding whereas the fur solution is used to enhance and maintain the natural beauty of fur. Industry grades the pelts according to the general condition of the pelt, fur length, patterning etc. and the pelts go through several treatments called fur dressing (21). Lastly, the leather undergoes the following process of degreasing, cleaning, buffing, brushing etc. The following Figure 1.4 represents process flow chart of fur clothing (22).

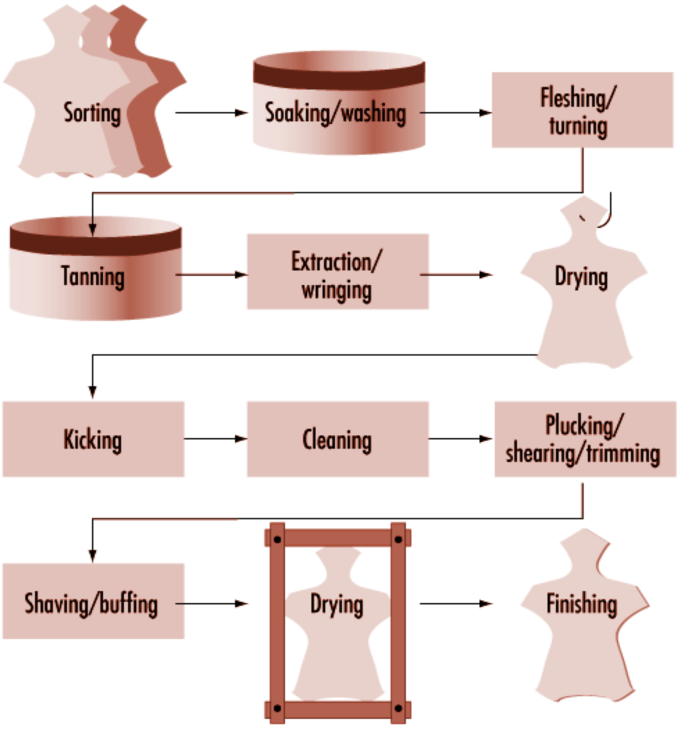

Figure 1.4. Process Flow Chart of Fur Production (22)

1.4. Fur and Leather Industry in Europe

Tanning industry uses skins and hides (a by-product from meat and dairy industry) that disposed or sent to landfill otherwise. Tanned leather is made into several products for consumer goods industry. In Europe, the leather industry comprises about 36,000 enterprises which employ around 435,000 people (23). The leather sector in European Union is generally family-based small and medium enterprises with a long tradition. This industry has a high economic value that contributes to the local and regional economy. The distribution of leather manufacturers in European Union in 2007 which represented Table 1 (24).

Table 1. Structure of Leather Manufacturers in Europe (24)

2007	Employment/ Employees	Companies/ Enterprises	Turnover (1000 Euro)
Belgium	124	1	21.742
Finland	147	12	19.000
France	1.721	62	296.000
Germany (prov.)	2.125	30	440.000
Greece (est.)	476	68	
Hungary	65	3	4.200
Italy	18.195	1.464	5.383.056
Netherlands (prov.)	380	15	85.00
Portugal			
Slovenia			
Spain	4.056	132	883.694
Sweden	430	4	76.500
UK	1.300	25	220.000
Lithuania (prov.)	200	4	15.000
Bulgaria		19	
TOTAL	29.219	1.839	7.444.192
Norway	102	2	19.000
Switzerland			
TOTAL	29.321	1.841	7.463.192

++ in volume: estimated by cotance

*including deers, elks, buffaloes, etc.

** including pig leather

The most important outcome for EU's tanners' production is used in various industries like clothing, footwear, furniture etc. Figure 1.5 represents the leather manufactured products in Europe.

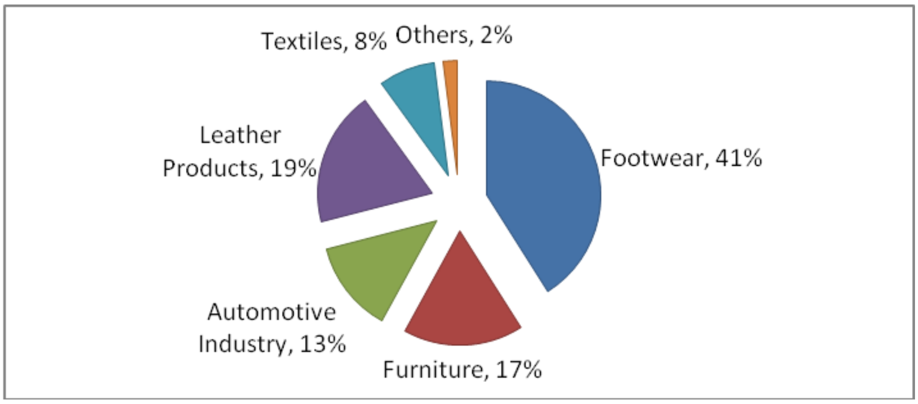

Figure 1.5. Major uses of Tanned Skins/Hides in EU (23)

EU leather industry is world's largest supplier of leather in the international market with 2/3 of all EU sales by sectors. In 2016, EU imported and exported around USD 721.8 million and USD 711.7 million worth of leather respectively, country-wise statistics are represented in Table 2 (25). Some of the leather sectors in EU is highly skilled and industrialized with economic, social, environmental and technological challenges due to growing demand and shift towards sustainability.

Table 2. Top 10 countries leather exports and imports in Europe in 2006 (25)

Country in EU	Exports (million USD)	Country in EU	Imports (million USD)
Italy	365.4	Italy	213.7
Spain	105.8	France	125.0
France	103.2	Spain	91.2
Germany	37.1	Portugal	72.8
Austria	14.2	Romania	51.7
Slovakia	11.0	Germany	43.5
Greece	8.9	Austria	24.5
Hungary	8.5	Hungary	24.4
Netherlands	6.9	Belgium	12.9
Finland	4.6	Poland	11.8

Tanners in Europe are highly dependent on access to raw materials. Europe has a restriction to access raw materials due to a decrease in production and slaughter rates. Importing of raw materials from non-EU countries is crucial as many maintain export bans or restriction on raw skins or hides. To ensure fair trade and accessibility of raw materials to European traders, European Commission has presented an integrated strategy to address the critical needs for growth (23). To extract fur, the fur farming is carried out traditionally in Europe, about 50 % of global fur production comes from European countries.

1.4.1. Lithuanian Fur and Leather Industry

Lithuania has textiles, clothing and leather industry that accounts about 1.6 % of GDP, employing about 2.9 percent of total employment. Lithuanian textile industry is growing fast with 3/4 production exported around the world. Particularly, Lithuanian leather is the rather small economic sector with approximately 172 enterprises in 2015 (26). The productivity of this sector is quite low in textile and leather industry at the beginning of 2000. According to the available data, in 2004, the number of leather companies present were considerably less with employing fewer than 50 people as number companies were closed down in 2000, as shown in Table 3 (27).

Table 3. Leather enterprises in Lithuania between 2000 and 2005 (27)

Year	2000	2001	2002	2003	2004	2005
Number of Companies	164	116	115	102	91	83

However, during 2008-2016, the growth was substantial with more than 150 enterprises. The following Figure 1.6 shows the number of leather manufacture and related products enterprises present in Lithuania between 2008 and 2016 (28).

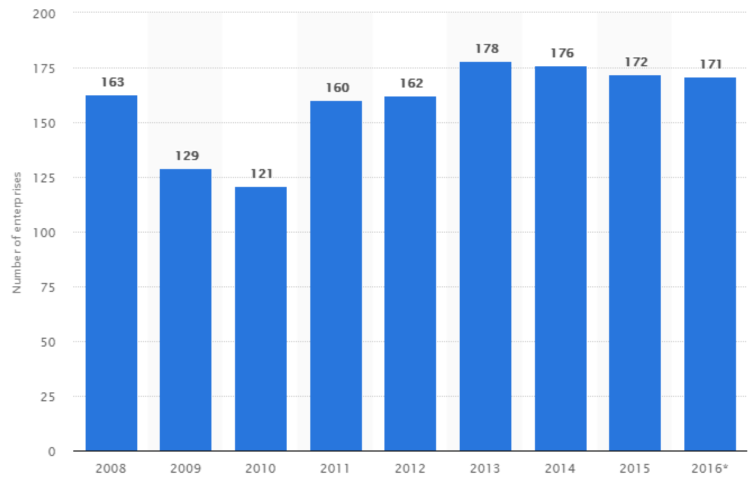

Figure 1.6. Leather Enterprises in Lithuania between 2008 and 2016 (28)

Lithuania mainly exports to EU countries (Denmark, United Kingdom, Sweden, Latvia) and raw materials such as hides and skins were imported from Germany, China, Italy and Poland (27). In 2016, the major export was done with Germany of 16% (total Lithuanian produced textiles, clothing, and leather). The following Figure 1.7 shows the export structure of the country in 2016. Similarly, Figure 1.8 shows the year-wise comparison of exports of fur and leather products (26).

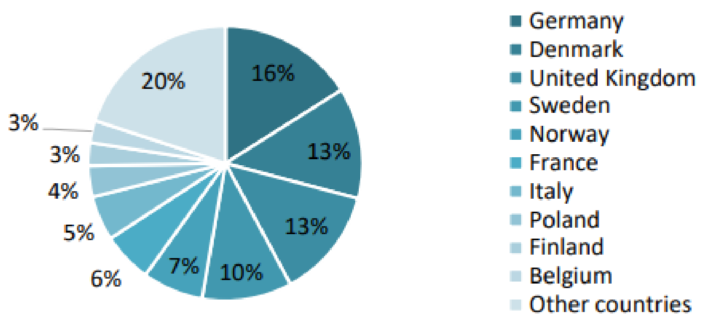

Figure 1.7. Lithuanian Exports by Country - 2016 (26)

Exports of Lithuanian produced textiles, clothing and leather by category, million EUR

Category	2011	2012	2013	2014	2015	2016
Wearing apparel, except fur apparel	331.7	319.4	349.9	361.7	344.4	341.7
Made-up textile articles, cordage, rope	131.6	139.0	155.6	184.3	196.4	213.4
Textile yarn and thread	67.1	64.3	70.4	77.4	79.9	89.1
Woven textiles	44.4	47.1	48.0	52.2	50.0	54.4
Knitted and crocheted apparel	39.9	34.1	37.7	42.6	43.3	40.6
Tanned and dressed leather	38.9	45.4	47.4	41.0	48.3	36.0
Footwear	5.4	4.2	6.1	5.8	7.2	9.4
Articles of fur	0.3	0.2	0.2	0.7	0.5	0.3
Grand Total	659.3	653.8	715.3	765.7	770.0	784.9

Figure 1.8. Year-wise comparison of exports of leather and fur products from Lithuania (26)

1.5. Chemicals used in fur and leather industry

Different chemicals are used in fur and leather industry for various processing of leather that classified as bulk and performance chemicals. The following chemicals are listed in Table 4 based on the usage in each stage.

Table 4. List of commonly used chemicals in leather industry (29)

Chemicals used in Beam-house and Tanyard process	**Chemicals used in dyeing process**	**Chemicals used in the finishing process**
Biocides	Surfactants	Acrylic resins
Surfactants	Degreasers	Butadiene resins
Degreasers	Sodium formate	Polyurethane resins
Swell regulating agents	Sodium bicarbonate	Fillers
Lime	Formic acid	Dullers
Sodium Sulphide	Chrome syntan	Crosslinkers
Sodium hydrosulphide	Chromium sulphate	Handle Modifiers
Low Sulphide unhairing agents	Syntan	Nitrocellulose lacquers
Caustic Soda/ Soda Ash	Resins	Acrylic lacquers
Fungicide	Polymers	Polyurethane lacquers
Ammonium Sulphate	Dyes	Viscosity modifiers
Ammonium Chloride	Dye Auxiliaries	Pigments
Sodium meta bisulphite	Fat liquors	Dyes
Formic Acid		Defoamers
Sulphuric Acid		
Salt		
Sodium formate		
Chromium sulphate		
Aldehyde tanning agents		
Magnesium oxide		

There are also chemicals that of high concern and prohibited substance in Europe as per the legislation. In the following section, the most relevant substances of leather are put together in Table 5 (30), (31). The restricted substances are substances which manufacture, place in the market, use is limited or banned in EU. The list of substances restricted and its conditions are put forward in REACH regulation Annex XVII. Restricted Substances List has been used by leather manufacturers to comply with the control and regulation standards irrespective of geographical locations.

Table 5. List of Restricted Substances relevant to Leather industry in EU (30), (31)

S. No.	Chemicals of Concern	Statement and Restriction	Regulation in EU
1.	Aromatic Amines and Azo dyes	detection limit of 30mg/ kg for each amine in leather. 22 aromatic amines forbidden. characterized as potential carcinogens	EU REACH Regulation (EC) No. 1907/2006 Annex XVII
2.	Biocides	Not dealt under REACH Major fungicide used : PCMC (para-chlor-meta-cresol), OIT (2-n-octylisothiazolin-3-one), OPP (ortho-phenylphenol), TCMTB (2-(thiocyanomethylthio) benzothiazole) allowable limits of active fungicide components: PCMC < 300 mg/kg, OIT < 100 mg/kg, OPP < 500 mg/kg and TCMTB < 500 mg/kg [The Blue Angel]	EU Directive 98/8 EC, Biocidal Products Directive (BPD)
3.	Boron-containing substances [Boric acid and disodium tetraborate]	Notified as candidate in SVHC list	EU REACH Regulation (EC) No. 1907/2006 Annex XVII and Candidate List
4.	Chlorinated paraffins (C10-C13)	Prohibited Listed in REACH SVHC candidate list	EU POPs Regulation (EC) No. 850/2004 Annex I
5.	Chlorinated Phenols	List : [Pentachlorophenol (PCP); tetrachlorophenol (TeCP); trichlorophenol (TriCP)] Detection Limits - 5mg/kg	EU REACH Regulation (EC) No. 1907/2006 Annex XVII
6.	Chromium (VI)	Not detected (detection limit 3mg/kg) Characterized as carcinogenic if inhaled and restricted in EU	EU REACH Regulation (EC) No. 1907/2006 Annex XVII and Candidate List
7.	Dimethyl fumarate	Prohibited Detection Limit :0.1mg/kg Footwear, articles and produced Importation also suspended for marketing or free seats and footwear containing Dimethyl fumarate in France	EU REACH Regulation (EC) No. 1907/2006 Annex XVII
8.	Formaldehyde	No EU regulation restricting use of formaldehyde in leather Eco-labels limits - 20mg/kg for children and 75mg/kg for adult shoes	Nil
9.	Heavy Metals	Leather containing less than 0.1 % of Cr(III), Al, Ti, Zr, Fe standard for ecolabels	EU REACH Regulation (EC) No. 1907/2006
10.	Nonylphenol ethoxylate and nonylphenol	Maximum Limit: 100 mg/kg New alternative surfactant is replaced in EU	EU REACH Regulation (EC) No. 1907/2006 Annex XVII and Candidate List
11.	Organotin compounds	Various list of substances Maximum Limit: 0.1% by weight of tin	EU REACH Regulation (EC) No.

			1907/2006 Annex XVII
12.	Perfluorochemicals	A list of chemicals under PFCs is restricted and prohibited	EU F-gas Regulation (EC) No. 842/2006 EU REACH Regulation (EC) No. 1907/2006 Annex XVII and Candidate List
13.	Phenol	Phenolic compounds used in polymers production and it is regulated by RSL, REACH	EU REACH Regulation (EC) No. 1907/2006 Restricted Substances List
14.	Phthalates Di (2-ethylhexyl) phthalate (DEHP); Di-n-butyl phthalate (DBP); Benzyl Butyl phthalate (BBP)	Detection limit: DEHP +DBP+BBP = 0.1% (by weight) Restricted in children articles, apparel, footwear	Denmark Statutory Order 855 of 05/09/2009 EU REACH Regulation (EC) No. 1907/2006 Annex XVII
15.	Polycyclic Aromatic Hydrocarbons (PAH)	A list of PAH is restricted under REACH Detection Limit: Articles in direct skin contact with 1mg/kg (each); Children article:0.5mg/kg	EU REACH Regulation (EC) No. 1907/2006 Annex XVII
16.	SVHC	All substances listed under SVHC are not allowed for importing in EU. Leather containing more than 0.1 % of any SVHC chemicals are not allowed	EU REACH Regulation (EC) No. 1907/2006
17.	VOC	Emission of organic compounds regulated as per regulation Organic Compounds of interest - formaldehyde, acetaldehyde, benzene, toluene, xylene, ethylbenzene, styrene.	VOC Solvents Emissions Directive 1999/13/EC

Based on the literature survey, the following chemicals were identified as Substances of Very High Concern (SHVC) and selected for further study. The substances that are shortlisted based on the Candidate list of REACH regulation which should be considered for substitution.

1.5.1. Chromium

Chromium is used for tanning and dyeing processes in fur and leather processing industry. Chromium is considered to be a major pollutant in most of the industries that have a great impact on the environment and human health. Chromium metal does not occur naturally but there are produced from chrome ore. It exists in different forms (i.e., Cr - Cr(III) - Cr (VI)) and has different properties. Trivalent Chromium [Cr(III)] occurs naturally in soil, rocks, animals, plants and volcanic emissions. Cr(III) oxide is widely used in the industrial process with high temperature to make metals, or alloys. Cr(VI) is generally produced industrially by heating Cr(III) in presence of atmospheric oxygen and presence of mineral bases (32).

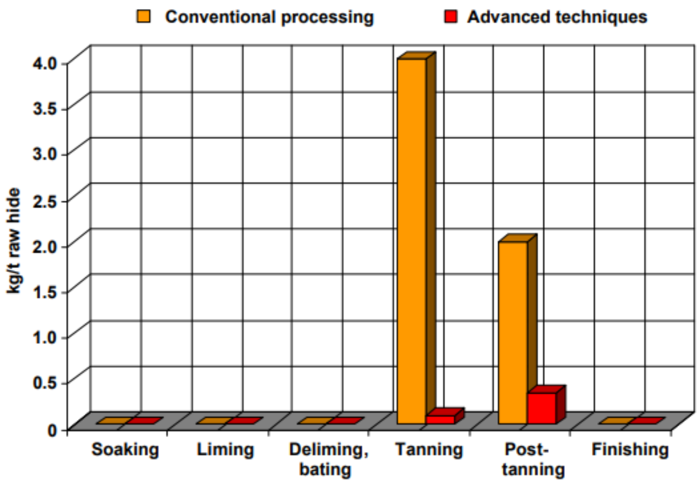

Figure 1.9. Comparison of Chromium load in the processing of leather (33)

Chromium sulphate (Cr(OH)SO4) is commonly used tanning agent with a high proportion (80-90%) of all leather produced (12). Figure 1.9 shows the chromium load in tanning and post-tanning process, consumption of chromium is high in tanning process rather considering other stages of manufacturing. Ammonium dichromate is used as tanning agent as well and it is chosen in this study.

Usage of chromium [Cr(VI)] several industrial application has imposed human health hazards according to the exposure levels while it is toxic and carcinogenic properties. Chromium that is used in metal and tanning industries is often found in soil and water as well as impose potential health risks for workers. Almost ten chromium substances are listed on ECHA's Candidate List of Substances of Very High Concern (SVHC) for Authorization list. Hexavalent Chromium is also regulated under RoHS, which applies for Electrical and Electronic Equipments.

1.5.2. Formaldehyde

Formaldehyde has been used as a tanning agent in fur and leather industry because of it is the ability to crosslink proteins like collagen. Formaldehyde also used in the manufacturing of certain polymeric-based synthetic tanning agents. It is a highly soluble chemical in water and usually supplied in an aqueous form named as formalin. Formaldehyde is readily found in nature at the same it can be synthesized as well.

To be specific, formaldehyde is used in the production of textile, leather and animal fur as it is known for its powerful bactericide quality. But, it is listed as potentially carcinogenic substance in nature. Formaldehyde alert is high when it comes to clothing to children, which was issued by RAPEX system (European System for alert for consumer protection) in 2009. A study conducted showed a content of 106 mg/kg to 630 mg/kg formaldehyde in children clothing. Studies also found that high levels of formaldehyde and ethoxylates are found in most fur trims, that cause allergies, cancer and hormonal imbalance (15). Formaldehyde is listed under REACH candidate list and it requires authorisation before it is used by manufacturers and importers.

1.5.3. Nonylphenol, ethoxylates

Nonylphenol (NP) and Nonylphenol Ethoxylates (NPE) are commonly used by members of the larger alkyl phenol and alkyl phenol ethoxylate family of non-ionic surfactants. NP's main usage is to manufacture of NPEs. NPEs are used in wide range of industrial applications, but persistent and highly toxic to aquatic organisms. Presence of NP has also been detected in breast milk, blood and urine samples and associated with reproductive and developmental effects in fishes as well.

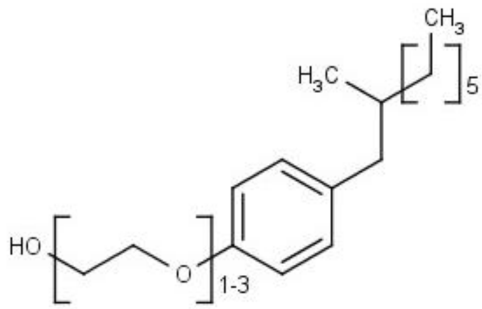

Figure 1.10. Structure of Nonylphenol ethoxylates

Under REACH, Nonylphenol ethoxylates are listed as substances restricted (Annex XVII) with maximum tolerable of 100 mg/kg during the manufacturing stage. The chemical is widely used in textiles, leather, and fur processing industry as surfactants. Few legal restrictions is placed for NP, NPE for marketing and use of preparations in concentration. In particular, NP or NPEs are considered as endocrine disruptors as they have a tendency to break the natural balance of hormones of the organisms affected (34).

Non-ionic surfactants, such alkoxylates, are commonly used in the beam house area for processing where skin or hide is cleaned with detergent and to help emulsify, remove fats (12). Alkyl phenol ethoxylates are used in the production of animal fur and also to degrease furs (34).

1.6. Substitution of Chemicals

As per EU regulation, it highly recommends and places responsibility for chemical management on industries. EU regulation prioritizes hazardous substances used in food packing, household, and other manufacturing chemicals. So, it has the possibility to decide to switch to alternative technique or to a different product design or substitution of a less hazardous chemical.

Primarily, substitution is a step closer to sustainable development. It is an ideal way to manage chemicals of very high concern, as it imposes a potential risk to the user and also the manufacturer in a long run as well. It also provides a platform for the company to improve efficiency, innovation, enhance safety and save costs. The principle of substitution is also incorporated in EU directive 98/24/EC that ensures the safety of workers with respect to the elimination of hazardous chemicals in the workplace. Thus, substitution could improve room for workers' safety (1). Substitution of chemicals is not a just simple replacement of one chemical. It should be prioritized based on the needs (35).

In general, substitution can be done in different ways based on the type of hazardous substance. As a first step, it is important to identify the Substances of High Concern that has been used in a process or manufacturing. The substances that are hazardous in nature dispute human health and environment with following characteristics are considered for substitution:

- Environmentally persistent, bio-accumulative and toxic chemicals
- Carcinogenic, mutagenic and toxic for reproduction
- substances that impose a serious threat to the environment or human, if they are not treated properly

Before substitution, it is important to ensure the hazardous nature of substances (36). There are main steps to perform substitution in a process which represented in following flowchart Figure 1.11 (36).

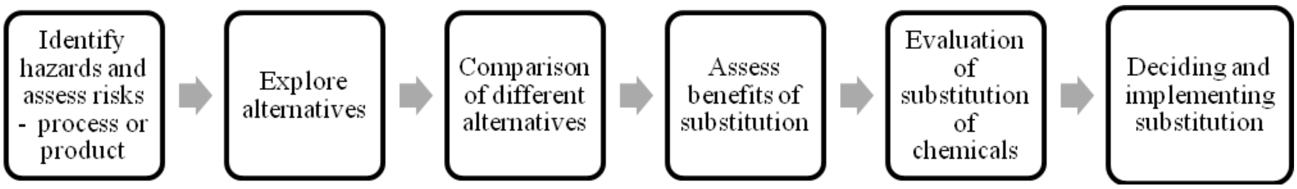

Figure 1.11. Main steps in substitution

Substitution could be implemented in several ways by using different and safer substances instead of the initial or omitting another, without or with a change in technology; or using technological, organizational measure instead of initial material. The main aim of substitution is to eliminate or reduce the use of hazardous chemicals or substance. Nevertheless, the chemical that of interest or alternatives may pose a hazard to human health or the environment or both. Triggering substitution would prevent identification of all potential risks to human or environment; hence it is vital to consider the evaluation of substitution. This also calls a need for analyzing other environmental impacts than just assessing chemical risks. For example, substitution could take place with an alternative substance might be accompanied with other changes like energy optimization or water consumption, which may be either beneficial for the environment or cause an additional pressure. The complexity of the substitution process is represented in the Figure 1.12.

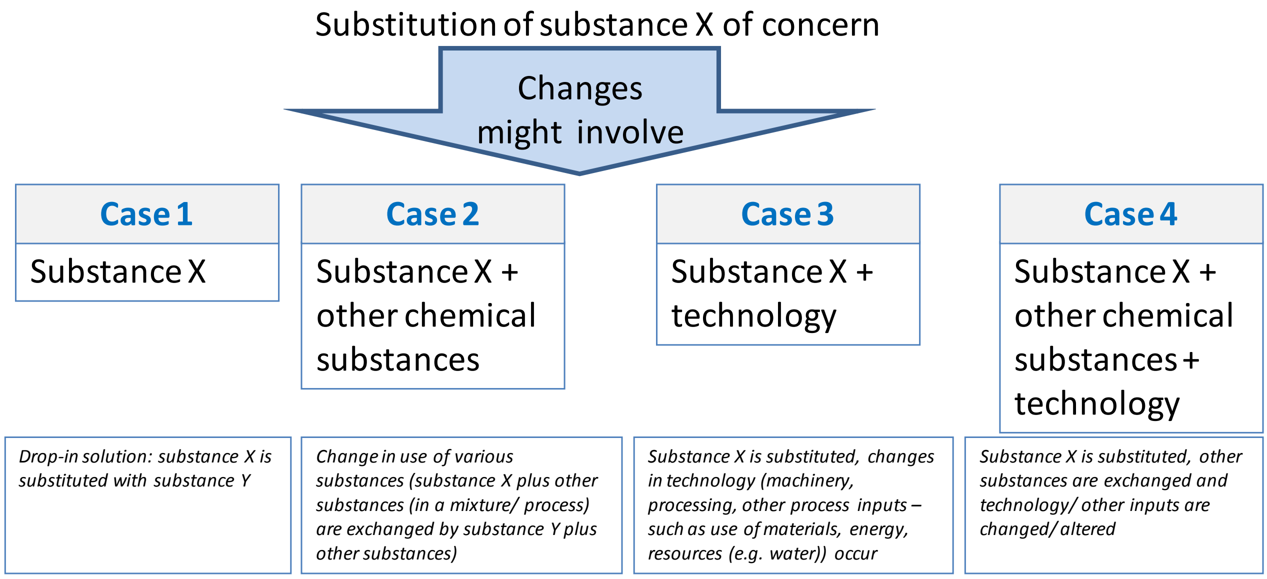

Figure 1.12. Complexity of Substitution (37)

As suggested in FIT for REACH project, it is vital to carry out an environmental assessment for the target chemical that has to be replaced and also for the substituted chemicals. This can be assessed using major tools like Environment Impact Assessment and Life Cycle Assessment (36). Risk Assessment could help in estimating the severity and likelihood hazard of a chemical to human health or environment. RA indicates how safe a chemical could be; rather the likelihood of environmental impact remains unanalyzed. However, to assess the exhaustive environmental impact of a target substance, alternative assessment such as EIA and LCA suit the need. To study the chemical risks is critical while evaluating the substitution of chemicals; it is vital to figure out a comprehensive tool to estimate environmental impacts during the entire process (37).

Although several kinds of tools and methodology could be used to study the alternative but to highlight different potential problems and impacts, it is important to formulate an environmental indicator. This indicator could help to measure and quantify the flow of a system or product throughout the assessment. In this case, LCA is considered as an integrated tool for comprehensive environmental assessment. It could help to evaluate environmental impacts due to emissions of the certain chemical concern + other related chemical substances + other changes in the process as a result of substitution (37).

1.7. Life Cycle Assessment

Manufacturing is a very complex process which includes several inputs and outputs. Raw materials are an important input in a production process whilst it comes from various sources and involves different materials that each of which has an impact on the environment. To identify the entire environmental impact of a product or services, life cycle analyses are used. It is an effective decision-making tool that recognizes all phases of a product's life from the time, the materials are extracted through manufacture, transportation, storage, use, recovery, reuse, and disposal. And these impacts can be quantified and compared to evaluate or to improve a process, design, products or services that perform the same function (32).

The procedures of life cycle assessment (LCA) are part of ISO 14000 environmental management standards with ISO 14040:2006 and 14044:2006. The use of LCA also encourages preventative and proactive management than end-of-pipe solutions. LCA involves four main processes as depicted in Figure 1.13, Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation.

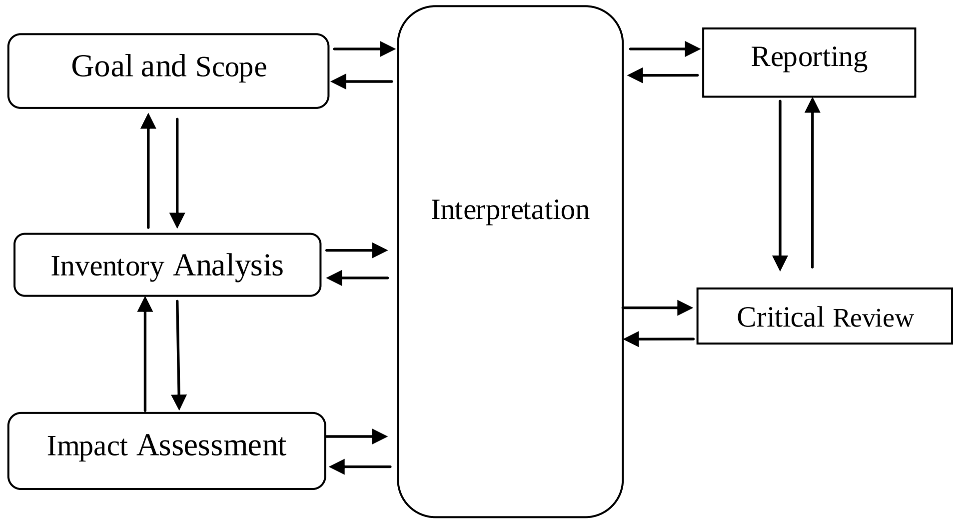

Figure 1.13. Main Stages of LCA according to ISO 14040

Goal and Scope definition ensures that LCA is performed consistently. This process helps to identify the purpose of conducting the LCA, and its study choice, i.e., assumptions, boundaries, limitations. The basic elements of issues are system boundaries, multiple output processes/allocation and avoided impacts.

Life Cycle Inventory includes outputs and inputs associated with a product or service, i.e., material extraction, chemicals, energy, wastes, emissions etc. that crossing the system boundaries. This step involves modelling of the product system, a collection of data, validation of data for inputs-outputs associated with a product or service. These can be calculated based on two approaches: process-based approach and input-output approach. This process can be evaluated on the basis with particular databases that are available online.

Life Cycle Impact Assessment (LCIA) models the impact pathways that are linked to different substances, as accurately as possible. With the inventory list of all input and output, it is difficult to interpret the result, in order to normalize the data, impact assessment is important. For each substance, there is a pathway of the environmental mechanism. Based on this, impact category of substances can be selected either at midpoint or endpoint level.

Midpoint impact category defines impacts into environmental issues such as climate change, eutrophication, acidification, human toxicity etc. This approach has an advantage that it include fewer undecided assumptions or less-established facts. **Endpoint impact category** also known as damage-oriented approach denotes environmental impacts i.e., natural resources, human health, environment. The main advantage of this approach is it gives instinctive metrics (Example. loss of life years instead of kg CO_2 equivalent).

The Life Cycle Impact Assessment can be performed either through qualitative or quantitative approach. Eco-indicator 99, ReCiPe 2009, The Red Flag Method, MIPS, EPS2000 etc. are some examples of qualitative and quantitative methods of LCIA.

Interpretation helps to identify the life cycle stages at which intervention is needed that could substantially reduce the environmental impacts of a product or system defined. This phase enables to analyze results, explain limitations or conclusions and provide recommendations based on the findings (38).

Major benefits arise through performing LCA. The main advantage of the LCA is, it is possible to analyze the entire process of a life cycle of a product or process and the environmental damage associated with it. Therefore, it helps designers or engineers in effective decision making, either to find alternative methods like the design, process change, etc. or to compare two different products or materials quantitatively. Moreover, performing LCA would benefit industries, Governments, and consumers as it serves as an effective marketing tool for industries if it is used appropriately. This also boosts the image and brand value for both suppliers and producers (32).

On the other hand, LCA has its own limitations. To complete an entire life cycle analysis for complicated products or process is much complicated, as it is difficult to formulate the bigger boundaries, sub-systems, pathways etc. While performing LCA, obtaining updated data could be a daunting task especially with industrial or practical scenarios, there might be a situation where companies are not willing to provide data to external analysts. During such instant, the data for comparison is obtained from online reliable resources. Yet, another problem would be the sources of data and where it came from and how relevant it is for the particular company or specific area.

Another drawback with LCA is with "Globally accepted standards". There are no globally accepted standards so the question arises about the credibility of the person who conducted LCA. However, to address the accepted standards, EU offers guidance and stringent rules on how to complete a successful LCA but the standards might differ across countries. If the standards and methodologies are used for developing countries like India or Africa, there will be global discrepancies of data as the process and design vary to a larger extent of the environmental impact. In most of the cases, the LCA is conducted within the company or organization. So, it is always impossible to compare two different parties LCA of same sector or areas and assess to make choice based on LCA (39).

There are few software tools available for conducting LCA. But, the main commercial software programme which is widely used for conducting LCA are GaBi and Simapro 7. This two software are used for industrial applications. Simapro could easily model and analyze complex cycles in a systematic and transparent way as per 14040 recommendations.

1.8. Research Studies on fur and leather industries

There is a number of chemicals that have been used for processing of tanning in both fur and leather industries. Classical tanning method like chrome tanning has a big contribution to pollution, contamination of water, soil etc. In general, finished fur and leather undergo a various number of treatments and processing especially with chemicals and salts such as ammonia, formaldehyde, chromium, peroxide etc. Apart from treating, the leathers and furs are further dyed and preservatives are added (40). Moreover, the production of fur and leather industry also consume lots of water for each process right from the animal rearing, slaughter and processing and until finishing of fur and leather. Each process has wastes, wastewater etc. is disposed of which cause land and water pollution. Additionally, during the manufacturing, extensive energy is used especially for fur production takes 20 times more energy than a faux-fur apparel (41); transportation of animals, animal carcasses, finished fur and leather in all stages.

1.8.1. Environmental pollution due to tanneries

Contamination due to Chromium prevalent while the effluent is discharged. More than 60% of Indian tanneries has (42) groundwater had high-level contamination which is not suitable for drinking. It also found that serious health issues such as hyperkeratosis, keratosis, melanosis, gangrene, skin irritation, abdominal pain, reduced appetite, diarrhoea, other GI tract, skin problems and sometimes even stomach cancer are caused (43). A similar study was carried out to find out of the possibility of interference of tannery wastewater with groundwater through damaged sewers and structures in Kasur district of Pakistan. The contamination is evident in the subsurface level of groundwater due to chromium concentration (44). Presence of other heavy metals due to tanneries are also imposed health risks and contaminate groundwater quality, in Kanchipuram District, Tamil Nadu, groundwater had chlorine and sodium presence far above the permissible limits (45).

Most of the tanneries use chromium tanning, during which large quantities of pollutants such as animal skin, hair, salt and lime, and acids are discharged. Waste from tanneries is subjected to treatment based on characteristics of the chemicals used during the process. Treatments such as chemical, physical, biological or combination of treatments are carried out to achieve discharge norms suggested per legislation.

1.8.2. Health Risks due to tanneries

Several researches also indicate about the harmful impacts to human health during manufacturing and also while usage of leather products. The finished leather products - in direct contact with skin has strong allergen and potentially harmful to human health. The products such as gloves, footwear etc., contain a high level of chromium(VI) (46). With background studies, accidents and disasters are prevalent in the industry due to continuous exposure to chemicals and handling of chemicals. Workers are potential victims exposed to occupational hazards in industrial premises while handling these chemicals of very high concern. A number of health risks also identified related to the leather industry in different case studies. In many developing countries, women and children are employed for manufacturing of leather goods, especially footwear. The continuous exposure to adhesives and handling of these products could potentially harm and impose respiratory problems, lung diseases and skin infections (47). This also associated with an enhanced risk for cancer, nose and nasal sinuses. Studies also reveal that several health hazards were identified to workers exposed to release of gas and tanning dust (48). Studies also confirm high morbidity rate among workers who are constantly exposed to chromium at the workplace (49).

Nevertheless, to address the issue of pollution, various treatments and technologies were developed and implemented to control implications over the past decade. Unlike end-of-pipe solutions, cleaner production attempts to eliminate pollution of different forms in most efficient and sustainable manner. Cleaner production advocates source reduction techniques and most commonly used six techniques are processed efficiency improvements, materials substitution, inventory control, preventive maintenance, good housekeeping practices, and recycling within the process (50). As per cleaner production technology, it is wise to reduce risk and prevent pollution at early stages. As in case of leather industries treated raw hides and skins with classical chrome tanning; at the same time, other alternatives are in existence which is not used often due to various reasons (51).

1.8.3. Alternative agents for leather processing

The study also finds an alternative to control low-waste and high chrome exhaust tanning, a polymeric syntan, to enable pickle-free chrome tanning. This method also enhances the uptake of Chromium to above 90%. The product also reduces chemical oxygen demand (COD), total dissolved solids (TDS) and chlorides and reduction in chemicals, water, time and power consumption (52). Recovery of chromium (III) is another option by regenerating process, thus allowing the reduction of chromium loss with wastewater. Panov *et al* also studied photochemical degradation of organic impurities (53).

Natural biopolymer can be developed to address the use of mineral tanning process in the leather industry. Kraft lignin degradation by biomimetic system was carried out to investigate the degradation. Hemin and hydrogen peroxide is used as a catalyst and an oxidizing agent to produce phenolic compounds. Based on the study, biomimetic degradation with kraft lignin could be used as synthetic organic tanning agents and serve as colouring agents as well. The kraft lignin is a by-product of industrial waste. The shrinking temperature was raised to $80^{\circ}C$ through hydrogen-bonding interaction between polymers and collagenic hide power (54).

Similarly, black liquor from pulp and paper industry waste was used to study its dual functionality in post tanning stage in the leather industry. In this study, liquid lignin was separated using acidification process and its characterization was studied. The results showed improved quality of leather with the high smoothness of surface and filling due to its presence of more hydroxyl groups. The liquid also used to test the post tanning and re-tanning, it influenced the process with high adsorption of dyeing and minimal leaching. Such that the liquid lignin has dual property polymer which can be used for sustainable leather processing (55).

A study carried out on Dissymmetry gemini sulfosuccinate surfactant (DGSS) has potential to used as fatliquoring agent in the leather industry. The properties of DGSS tested significantly reduce surface tension, has the ability to emulsify and poor foaming performance. DGSS applied as fatliquoring agent also improve the physical and mechanical properties of leather (56). A study was conducted on tanning of Glutaraldehyde as an alternative to chrome tanning system. The study was carried out for cattle skins with 10 kg and the laboratory study was done for skins with chromium and Gluteraldehyde, the physical and chemical characterization was done and found in some case, Gluteraldehyde tanned leather is better than chrome leather (57).

However, the tanning agents have both disadvantages and advantages. The drawback of the present tanning agents includes their limited availability and low recovery or reusability from leather waste. Wastewater streams are also difficult to be treated with conventional treatment systems (58). Regardless, the logical and effective way to address the widespread toxic problem is to eliminate the hazardous substance at the source. This means it could be either done with the substitution of substances of high concern with less dangerous chemicals or with new technologies (59).

1.8.4. Chemical Substitution and Life Cycle Analysis

Several studies have been conducted on life cycle analysis to assess the environmental impact of a process by comparing two different production methods of biosynthetic oils. The study analyzed biosynthetic oils and mineral oil with the help of life cycle assessment. Environmental Design of Industrial Products 2003 and Impact 2002 methodologies was used to obtain results of life cycle analysis. The study revealed that biosynthetic oils,1.2-propanediol oleate cause the least impact on the environment based on endpoint categories. when compared with chemical production of biosynthetic oils (60).

Dong Jin-ning *et al.*, studied the energy consumption and environmental impact of soybean as biodiesel using LCA. Six stages of biodiesel production of soybeans such as planting, soy-straw power generation, oil refining, biodiesel production, transportation and combustion emission are studied. It is found that producing biodiesel from soybean is positive in reducing emission and friendly to the environment (61). Similarly, life cycle assessment was done for a straw generation by direct combustion. The energy consumption and environmental impact in each stage were calculated; rice straw generation by direct combustion was analyzed and found to be positive and reduce greenhouse gases (62). A similar study was done for environmental impacts of biodiesel production from microalgae. Two different scenarios of biodiesel and oil diesel was evaluated using LCA. A comparative LCA study evaluates whole energy process, environmental impacts of entire process chain from biomass production to consumption (63).

Bohlmann studied two polymers polylactide (PLA), a biodegradable polymer and polypropylene used in food packaging application with LCA. An inventory analysis and environmental impact assessment were carried out for two components. The result found some uncertainties regarding PLA biodegradation in a landfill could have an adequate impact on estimates of greenhouse gases. If assumed the carbon is fully sequestered in a landfill, PLA and PP emission of greenhouse gas is found to be equivalent (64).

An environmental assessment was carried out for the unhairing-liming process in tanning industry with the aim to evaluate the economic and environmental costs of the conventional and modified process. LCA is used for the study to analyze the net environmental benefits of the modified method. It was found that environmental and economic costs were reduced relative to the same conventional process (65). Similar, representative study was conducted in Latin America in the tanning industry. The environmental impact analysis was done and both technical and economic evaluation was carried out. LCA was used for quantification of impacts for chromium tanning process. With conventional chromium tanning, other improved tanning processes were compared while the improved methods should a significant reduction in emission and cost-cutting (66). An analogous study was carried out in cement industry located in Spain by implementing Best Available Techniques. The implementation was evaluated using life cycle assessment. The new production line was analyzed with existing one which showed a significant reduction in environmental impact like global warming, eutrophication, etc (67).

With access to LCI data and software, it possible to achieve LCA results for any process or production based on the need of the study. In general, for an individual chemical or product the prime most point to consider its environmental impacts or process designs. Quantitative metrics can be derived from LCA which enables greater transparency and decision making. Evaluation of environmental impacts of chemicals while substitution and after implementation provides a clear picture of the entire process cycle and impact on environment and human.

1.9. Conclusions

Based on the review of previous literature studies, fur and leather industries has some problematic chemicals that have been managed according to REACH regulation. Ammonium dichromate, Formaldehyde and nonylethoxylates were identified for further study which has been classified under REACH and CLP regulations for its level of toxicity to human and environment. The chemicals that are categorized under hazardous substances as per European Regulations, to be considered for substitution of less hazardous or non-hazardous substances. To achieve this goal, a detailed review on the substitution of chemicals was studied and a methodology was developed to look for an alternative or similar substances for the same purpose.

The identified alternatives will be assessed for hazard statement as per REACH regulation and an environmental assessment of chemicals, are to be substituted will be carried out. Life Cycle Assessment is used as a tool to evaluate the environmental assessment of the target substances. With the help of LCIA methodologies, it is possible to optimize environmental impacts using category indicator. By reviewing several research studies, ReCiPe 2008 to be considered for performing LCI study. ReCiPe endpoint is used for the assessing damage level of human health, ecosystem and resources. The data gathered in this methodology is on the European level. However, it also uses the impact mechanism that has global reach, wherever possible. ReCiPe also provides a suitable and in-depth approach to all three endpoint indicators compared to IMPACT 2002+ (68). Another important advantage is ReCiPe does not consider significant impacts from future processes during impact assessment stage. However, it assumes such impacts have been analyzed during inventory stage itself. This methodology will provide sufficient data to study the alternatives to be considered for substitution. With the outcome of the result, it is possible to consider the alternative substances for substitution in the tanning process of fur and leather industries.

2. Methodology

2.1. General

Based on the framework to the selection of chemical alternatives (69), the following flowchart (Figure 2.1) is developed to study the chemical substitution in the fur industry. The classical process is summarized, to identify the chemical of concern and it is alternative, the methodology is used for the entire study.

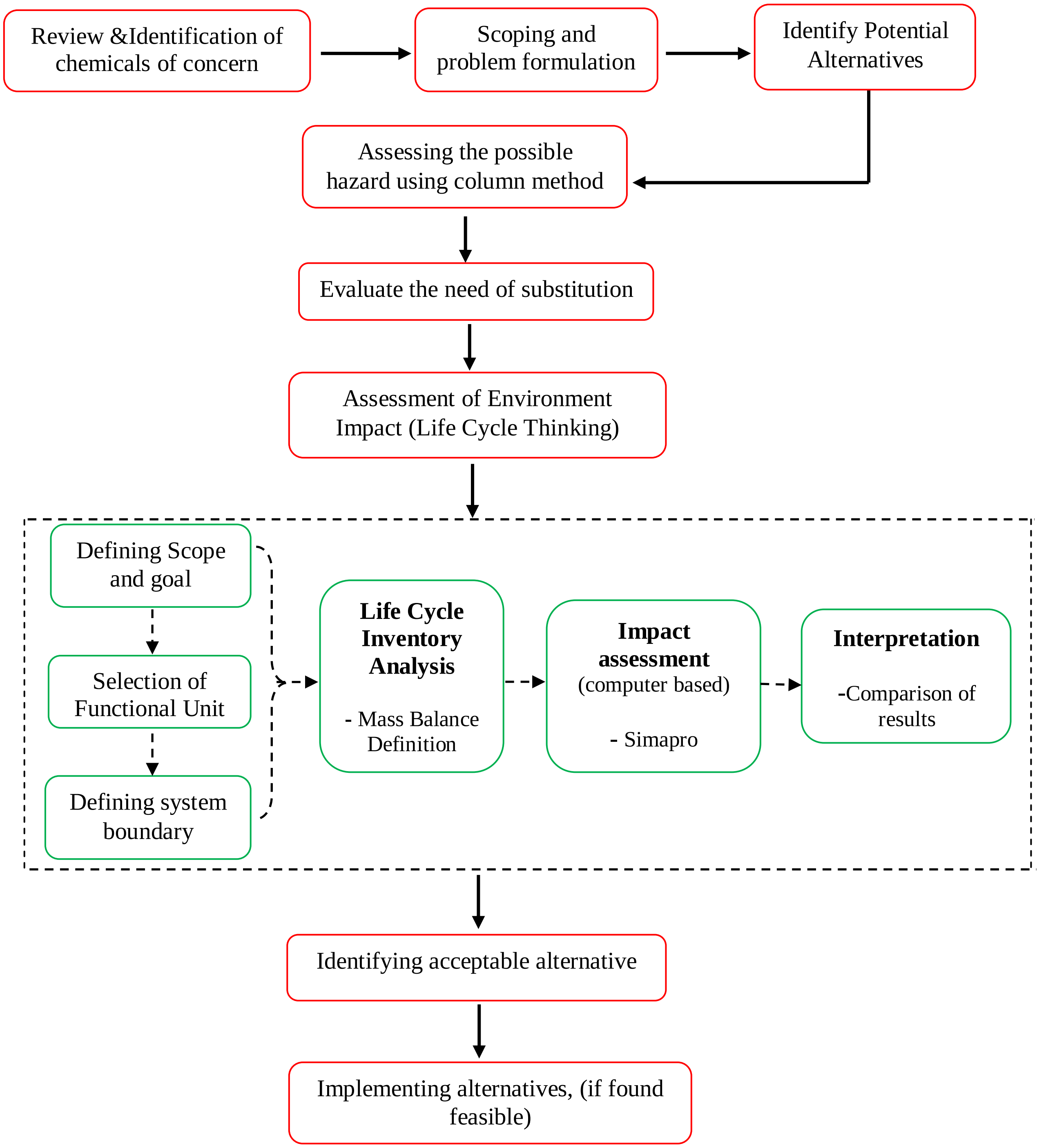

Figure 2.1. Flowchart for identification of alternative chemicals

2.2. Review and Identification of chemicals of concern

To identify the chemical of concern in the fur industry, it is important to review the substances that are listed under hazardous chemicals. The nature of substances and it is toxicity is mentioned in the EU regulations on chemicals as per their properties and characteristics of the chemicals used in a process or workplace. With the help of ECHA database, the chemicals of very concern were identified in the first place. As suggested in REACH, the SVHC should be considered for substitution or for other alternatives with no toxic or less toxic.

Table 6. Template used for identification of chemicals of concern

Substance Name	EC Number	CAS Number	Hazard Classification	Hazard Statement	CLP

2.3. Scoping and problem formulation

The identified substances of concern will be compared with REACH/CLP regulations and also in the ECHA databases. The main aim of this step to define a scope, by identifying a company that produces fur and leather goods. By analyzing the input-output balance and also the chemicals accounting, it is possible to identify the hazardous substances present in the process. Comparing the identified chemicals with the chemicals accounted from the company, the substances of high concern will be considered for the substitution. In this project, tanning process is the prime objective, such that the chemicals used in the process pertaining to tanning process will be studied.
Based on Table 7, the chemicals of very concern will be identified, summarized (36) and considered for the substitution or elimination. The hazard statement listed under FIT FOR REACH for the enterprises to comply with legislation.

Table 7. Substances with hazard statement considered for substitution

Substitution is very important	Substitution should be considered
H300, 310, 311, 314, 330, 340, 350, 360, 361, 362, 370, 372, 400, 410, EUH032	H301, 302, 304, 312, 314, 315, 317, 318, 319, 331, 332, 334, 341, 351, 371, 373, 411, EUH029, EUH031

2.4. Identify potential alternatives

Having analyzed the data from the company and also previous studies, it is possible to identify the potential alternatives for the chemicals of very high concern. SUBSPORT (70), a portal exclusively for alternative substances and technologies for chemicals of hazardous nature. The platform is used as an information exchange platform to support companies or anyone interested in fulfilling substitution as per EU regulations, in which the possible alternatives can be found based on the already existing studies. The following steps can be considered while identifying the alternatives:

- Hazard/Risk Assessment
- Functionality of alternatives
- Availability of alternatives
- Integration into process
- Life cycle considerations such as energy, emission, waste etc.

Hazard assessment will be carried out for both existing chemicals and identified alternatives. The column method will be used for evaluating the severity of hazard (70) (71). Four factors will be considered for assessment namely, acute toxicity, chronic toxicity, environmental hazard, and physical hazard of the chemicals. The hazards will be rated from negligible to very high based on the level of severity. In this method, R-phrase and H-phrase will be used to measure the risk and also GHS codes.

The severity is numbered as per category as well from 1 to 5 i.e., 1-negligible, 2- low, 3-medium, 4-high, 5-very high.

Table 8. Hazard assessment for identified chemicals of concern and potential alternatives

	Acute Toxicity	Chronic Toxicity	Environmental Hazard	Physical Hazard
Very High				
High				
Medium				
Low				
Negligible				

The colour variation also implies the level of severity from zero to very high. The following legend explains the colour shading of the severity or impact level.

Very High	High	Medium	Low	Negligible
Very High	High	Medium	Low	Negligible
Very High	High	Medium	Low	Negligible
Very High	High	Medium	Low	Negligible

The identified alternatives are assessed and accounted with following points as given in Table 8 and Table 9.

Table 9. The template used for identifying alternatives

Possible Alternative	Data Source	CAS No.	Health Hazards	Environment Hazards	Functionality of alternative

2.5. Assessing the chemical/health hazards

Assessing alternatives is about making sure whether a best available alternative is chosen as per the criteria that were defined. Firstly, the shortlisted alternatives will be checked in authorized databases, as in our case, ECHA and SINLIST are used for studying the nature of the alternatives. A list of criteria was developed to evaluate the toxicity of the identified alternatives, and it is substitution capacity as per EU directives. The template used for assessing alternatives as shown in Table 10.

Table 10. The template used for assessing alternatives

EXISTING SUBSTANCES OF VERY HIGH CONCERN										POSSIBLE ALTERNATIVES														
		Use and impact		**Environment and Human Concern**								**Substitution**		**Environmental and human concern**										
				unwanted properties								Substituted amounts, kg/year		Unwanted properties										
SHVC Chemicals	CAS number	Usage per year (kg)	Media affected	PBT/vPvB	CMR	Others	REACH Annex XIV	SVHC (Candidate List)	REACH Annex XVII	**Possible Alternative**	CAS number	At the beginning	5 years beyond	PBT/vPvB	CMR	others indicate	REACH Annex XIV	SVHC (candidate list)	REACH Annex XVII	WFD Priority/priority hazardous substances	SIN list substance	SUBSPORT Recommended	Other	Available of information of on hazards

Other methodologies could be used to proceed the assessment of alternatives, various new methodologies have been discussed. Most of the cases, REACH regulation is used to assess chemicals before it is used in a process. Material Safety Datasheets and other scientific publications are used to identify the alternatives. In this project, databases such as ECHA, SINLIST, and CHEMSEC are used for identification and assessment of alternatives.

2.6. Evaluate the need for substitution

The following methodologies are used to identify the need for change:

- Input-Output Analysis
- Accounting of Chemicals
- Legal factors
- Economic Assessment

In general, a need for substitution is initiated by analyzing the technological process of an identified company. For the project, a company that process fur production was identified and the input-output balance was analyzed. The production of the fur will be summarized in next section.

2.7. Life Cycle Assessment

In order to study the Life Cycle Assessment, Simapro 8 will be used throughout this project. With the help of the software, the environmental impact assessment can be studied for the identified chemicals of concern and the identified alternative. Prior to the assessment, it is important to set the goal and scope of the study and its functional unit for the entire study.

Figure 2.2. SimaPro software

With the help of LCI, it is possible to evaluate the entire life cycle of a product. The purpose is to provide an quantitative information on effects of human health, environment, and resources. The main environmental aspect depends on the input and output of a process. The life cycle analysis is performed by setting the functional unit and system boundary. The life cycle assessment is usually conducted with following categories to study the impact analysis.

- Climate Change
- Ozone Layer Depletion
- Acidification
- Eutrophication
- Human Toxicity
- Eco-toxicity
- Depletion of energy carriers
- Depletion of material carriers
- Land use impacts
- Water use impacts

3. Results and Discussions

3.1. Review and Identification of chemicals of concern

Appendix 4.

Table 11Table 11 lists down the identified substances of concern in the fur industry, based on the review and literature study carried out. The chemicals are classified based on their nature of hazard classification and extent of usage in the fur industry. As per EU regulation, REACH and ECHA database, the chemicals are identified as toxic to human and environment. Ammonium dichromate and Formaldehyde is enlisted under Authorisation List of REACH; NPE is enlisted under restricted substances (Annex XVII). The substance information from ECHA is attached in the Appendix 4.

Table 11. Identified chemicals of concern

Substance Name	EC Number	CAS Number	Hazard Classification	Hazard Statement	CLP
Ammonium dichromate	232-143-1	7789-09-5	Oxidizer	H272	
			Skin Sens. 1	H317	GHS07
			Acute Tox. 3	H301	GHS08
			Acute Tox. 4	H312	GHS09
			Repr. 1B	H360FD	GHS05
			Resp. Sens. 1	H334	GHS03
			Skin corr. 1B	H314	
			STOT RE 1	H372	
			Aquatic Acute 1	H400	
			Aquatic Chronic 1	H410	
			Carc. 1B	H350	
			Muta. 1B	H410	
Formaldehyde	25214-70-4	500-036-1	Carc. 1B	H350	GHS07
			STOT SE 1	H370	GHS08
			Aquatic Chronic 1	H410	GHS09
			Muta. 2	H341	
			STOT RE 2	H373	
			Skin Sens. 1	H317	
			Aquatic Acute 1	H400	
			Acute Tox. 3	H301	
Nonylphenol, (branched and linear), ethoxylated	9016-45-9	500-024-6	Aquatic Chronic 2	H411	GHS05
			Eye Irrit. 2	H319	GHS07
			Skin Irrit. 2	H315	GHS08
			Acute Tox. 4	H302	GHS09
			Eye Dam. 1	H318	
			Aquatic Chronic 3	H412	
			STOT SE 3	H335	
			Repr. 2	H361	
			STOT RE 2	H373	
			Aquatic Acute 1	H400	
			Acute Tox. 4	H312	
			Aquatic Chronic 4	H413	
			Aquatic Chronic 1	H410	
			Acute Tox. 1	H304	

3.2. Scoping and problem formulation

A fur processing company in Lithuania was identified to carry out the further study. The study was carried out in a sheepskin processing unit, hence their process and technology are defined as follows.

The process consists of wet and dry operation. The raw material is initially sorted by purpose and fed into the wet operation. During the sorting, the wastes generated are sent to waste management company. The sheepskin is washed and rinsed with the help of centrifuge the moisture is removed. The layer of hides and the subcutaneous layer is removed separately, while the wastewater stream is sent separately. From this, the sheepskins are ready for tanning process where the tanning solution is added which is used repeatedly in the process. After the pickling and tanning process, the solution is generally discarded into the waste stream. The tanned skin is spread out and directed to drying. After drying, the treated skin is softened and cleaned using sawdust spreading in drums. Further, the treated skin is stretched, washed, coated, trimmed and applied with solvents for sheen and lubrication.

After pre-treatment process, the leathers are sorted and painted in batches. The oily skin is degreased with organic solvents. Further, the treated skins are sent for drying after the buffing process. The solid wastes and wastewater produced during the process is separately collected and sent for common treatment. The sawdust which is used for buffing and softening is sent to collection centre. As a finishing stage, the softened and stretched skin is measured and trimmed, marked and packed for selling. The company has two main waste stream during the process: concentrated wastewater contaminated with chromium compounds and total wastewater (72).

The company also extracts fur from sheepskins and various other small animals. The company produced about 68,000 pieces of semi-finished and finished sheepskin products. Products are exported to Italy, Finland, Denmark and other EU countries; only 8 % of products are sold in Lithuania.

For this part of the study, the data was derived from the previous research study carried out at the same company due to the non-availability of recent data. The company produces fur and leather products with conventional chrome tanning. The company produces semi-finished and finished leather of 453 t per year and also eliminates wastewater on average of 33000 m^3 per annum and chromium compounds about 3650 m^3 per annum.

3.3. Identified Alternatives

Based on the literature study and review of research, the following alternatives were found suitable for the identified target chemicals of substitution. As mentioned earlier, SUBSPORT portal was used to identified and verify the found possible alternatives. The portal has a detailed evaluation of substances that is of very high concern as prescribed by ECHA and EU regulation. To evaluate the hazard and other effects, this database was used as a vital source. Hazard assessment was performed based on column method as suggested in SUBSPORT for alternatives.

Ammonium dichromate, formaldehyde and NPE are identified as chemicals of concern; Glutaraldehyde, Formaldehyde-urea-melamine, ethoxylated alcohol are identified as possible alternatives respectively

The following Table 12 represent the hazard assessment of identified chemicals of concern. To assess the hazard, column method is used. The following four category acute toxicity, chronic toxicity, environmental hazard and physical hazard for range of severity from negligible and very high.

Table 12. Hazard assessment for identified chemicals of concern

	Acute Toxicity	Chronic Toxicity	Environmental Hazard	Physical Hazard
Very High				
High	Formaldehyde; Ammonium Dichromate; NPE	Ammonium Dichromate	Ammonium dichromate	
Medium		Formaldehyde	NPE	Formaldehyde; Ammonium dichromate
Low		NPE	Formaldehyde	NPE
Negligible				

Table 13 represent the evaluated alternatives for fur industry. The alternatives are evaluated based on few criteria as suggested.

Table 13. Hazard assessment for identified alternatives

	Acute Toxicity	Chronic Toxicity	Environmental Hazard	Physical Hazard
Very High				
High	Glutaraldehyde			Glutaraldehyde
Medium	Ethoxylated Alcohol		Glutaraldehyde	
Low	Formaldehyde-Urea-Melamine		Formaldehyde-Urea-Melamine; Ethoxylated Alcohol	Formaldehyde-Urea-Melamine; Ethoxylated Alcohol
Negligible				

With the help of this hazard assessment, it is can be observed that Ammonium dichromate and formaldehyde have high chronic toxicity. Chronic toxicity implies carcinogenic and mutagenic properties. All three chemicals have high level of acute toxicity. As in case of identified alternatives, there is low or negligible level of severity for chronic toxicity; but Glutaraldehyde has high to medium impact on acute toxicity, environment and physical hazard.

Table 14. Identified Alternatives and Risk Analysis

Possible Alternative	Data Source	CAS No.	Health Hazards	Environment Hazards	Functionality Use
Glutaraldehyde	ECHA	111-30-8	H301 H334 H314 H317 H330 H331 H318 H335 H313	H400 H411	Disinfectant, fixing agent, industrial biocide
Ethoxylated alcohol (linear)	ECHA	68213-23-0	H318 H302 H319 H315	H400 H411 H412	Used as surfactants, cleaning agent, degreaser, adhesives
Formaldehyde-Urea Concentrate, Formaldehyde-Melamine Concentrate (polymer)	ECHA	Mixture	H314	H413 H411 H12	Bactericide, fungicide, intermediate in production of industrial chemicals and plastics

As it is seen, different alternatives are existing with the same functionality and with less complication with hazard and legal issues. But, the substitution of these substances could have both disadvantages and advantages as per the process involved and the method used. Additionally, implementation of substitution can be studied and the impact on the environment also be studied.

3.4. Assessment of Alternative chemicals

The shortlisted alternatives were assessed based on the list of criteria developed. The main aim of this detailed evaluation is to compare the level of severity of both existing chemicals and possible alternative. As the scope of the study is to substitute chemicals of concern, it is important to analyze and compare the possible alternatives with existing one so as to identify it is functionality and legal implications. The data was obtained from ECHA, SINLIST, and other EU official websites. The alternatives were assessed on the scope of substitution, hazard, and other legal requirements.

The following Table 15 indicates the assessment of identified possible alternatives. The table help to assess and compare the existing SHVC chemicals and possible alternatives. The proposed alternatives were assessed in detail based on REACH regulation, Water Directive, SINLIST and SUBSPORT such that it is possible to evaluate the associated risk to human health and environment as per the regulation.

The issue of substitution is directly linked to regulations and legal requirements. During the assessment of identification of potential alternatives, SUBSPORT database does not qualify Glutaraldehyde as suitable substitute or alternative based on the criteria that has been formulated by SUBSPORT. Yet, Glutaraldehyde is chosen for further study based on other literature studies. As per the previous studies, Glutaraldehyde is a best suit for tanning process, though, it is categorized as chronic toxic to environment. Similarly, Formaldehyde-Urea-Melamine resins, as a mixture, it is used for various purposes, as it is potentially less toxic and not estimated for carcinogenic properties as well. In case of Nonylphenol Ethoxylates, widely used as surfactants in the fur industry; can be replaced by various other substances of same group, in which, Ethoxylated alcohol is chosen for further study. The chosen alternatives also referred based on BAT of hides, skins and leather.

To conclude with, Glutaraldehyde is proposed as an alternative for ammonium dichromate and considered for evaluation of environmental impact study in the further chapter.

Table 15. Assessment of Identified Alternatives

EXISTING SUBSTANCES OF VERY HIGH CONCERN										POSSIBLE ALTERNATIVES														
SHVC Chemicals	CAS number	Use and impact		Environment and Human Concern						Possible Alternative	CAS number	Substitution		Environmental and human concern										Available of information on hazards
		Usage per year (kg)	Media affected	unwated properties			REACH Annex XIV	SVHC (candidate List)	REACH Annex XVII			Substituted amounts, kg/year		Unwanted properties			REACH Annex XIV	SVHC (candidate list)	REACH Annex XVII	WFD Priority/priority hazardous substances	SIN list substance	SUBSPORT Recommended	Other	
				PBT/vPvB	CMR	Others						At the beginning	5 years beyond	PBT/vPvB	CMR	others indicate								
$Cr_2H_8N_2O_7$	7789-09-5	8387	Water, Soil, Human Health	NA	Yes (H360FD, H350, H351, H340)	H314, H312, H334, H372, H318, H330	Yes	Yes	NA	$C_5H_8O_2$	111-30-8	8387	8387	data lacking	data lacking	H400, H411, H330, H314, H301, H317, H334, H33, EUH071	No	No	No	No	Not listed	Not recommended due it's sensitizing properties	(Biocidal) Active substance candidate for substitution	Sufficient
NPE	500-024-6	3635	Water	Yes (H361, H373)	NA	H413, H410, H400, H412, H319, H315, H302, H318, H312, H373	NA	NA	Yes	AE (Linear)	68213-23-0	3635	3635	No	data lacking	H400, H318, H302, H412	No	No	No	No	Not listed	Recommended as alternative for textile and leather	NA	Insufficient
HCHO	500-036-1	19,26	Air, Human Health	NA	Yes (H350, H351, H341)	H311, H301, H307, H314, H331, H318, H330, H307, H335, H441	Yes	Yes	NA	HCHO-Urea- Melamine	Mixture	19,26	19,26	No	data lacking	H413, H411, H412, H411	No	No	No	No	Not listed	Recommended as alternative for preservative	NA	Insufficient

Note: $Cr_2H_8N_2O_7$-Ammonium Dichromate; NPE- Nonylphenol Ethoxylates, HCHO-Formaldehyde; $C_5H_8O_2$-Glutaraldehyde; AE- Alcohol Ethoxylated(linear); HCHO-Urea-Melamine-Formaldehyde-urea-melamine mixture

3.5. Evaluation of need for substitution

Input-Output balance and accounting of chemicals used is particularly noted during the project evaluation. Based on the evaluation, it is possible to measure out the chemical that is required to substitute. The evaluation will also help in to match the already identified problematic chemicals based on the previous literature studies.

3.5.1. Input-Output Analysis

Input and Output balance is an important aspect of life cycle analysis. This helps to quantify the physical system with its material entering and leaving the system such that possible to measure the existing process input and outputs. Moreover, it is possible to define the functional unit and system boundary to carry out an impact assessment. While creating the input and output balance sheet, it is important to distribute the flows of chemicals products into the product and flow of emission as well. The equality of input and output will not be achieved always. Figure 3.1. Input and Output Flowchart is represented below.

3.5.2. Accounting of Chemicals

To study the process and input-output flow, it is important to account for the chemicals used in the processing of fur. The following table indicates the list of chemicals used in the identified company. This inventory will help to derive substances of very concern in the process of this identified company.

Table 16. Accounting of Chemicals

Substance Name	CAS Number	Amount consumed in tonnes	CMR	Hazard Details	Data Source
Sodium Chloride	7647-14-5	10,000 - 100,000	No	Skin Corr. 1B, Eye Dam.1, STOT SE 1	ECHA
Formic Acid	64-18-6	100,000 - 1 000,000	No	Skin Corr. 1A, Skin Irrit. 2, Eye Irrit. 2, Skin Corr. 1B	ECHA
Sulphuric Acid	7664-93-9	100,000 - 1 000,000	No	Skin corr. 1A,Eye Irrit. 2, Skin Irrit. 2,	ECHA
Chromium Sulphate	10101-53-8 13520-66-6	100,000 - 1 000,000	Yes	Skin Sens. 1, Eye irrit. 2, Acute Tox. 4, Repr. 1B, Resp. Sens. 1, Aquatic Chronic 4, STOT SE 3, Aquatic Acute 1, Skin Irrit. 2	ECHA

Bicarbonate soda	144-55-8	1 000,000 - 10,000,000	No	Eye irrit 2, Skin irrit. 2, Eye Dam. 1, Acute Toxic. 4, STOT SE 3	ECHA
Sodium formate	141-53-7	100,000 - 1 000,000	No	Eye Irrit 2, Skin Irrit. 2, STOT SE 2	ECHA
Neatsfoot oil (tanning oil)	8002-64-0	Not Available	No	Skin corr. 1A, Eye Irrit. 2, Skin Irrit. 2,	MSDS

By comparing the shortlisted SVHC from literature and the company's accounting of chemicals, Chromium Sulphate is considered for further evaluation, as it is the priority substance, as the scope of the study limits with tanning process. LCA will be carried based on the identified chemicals in this stage.

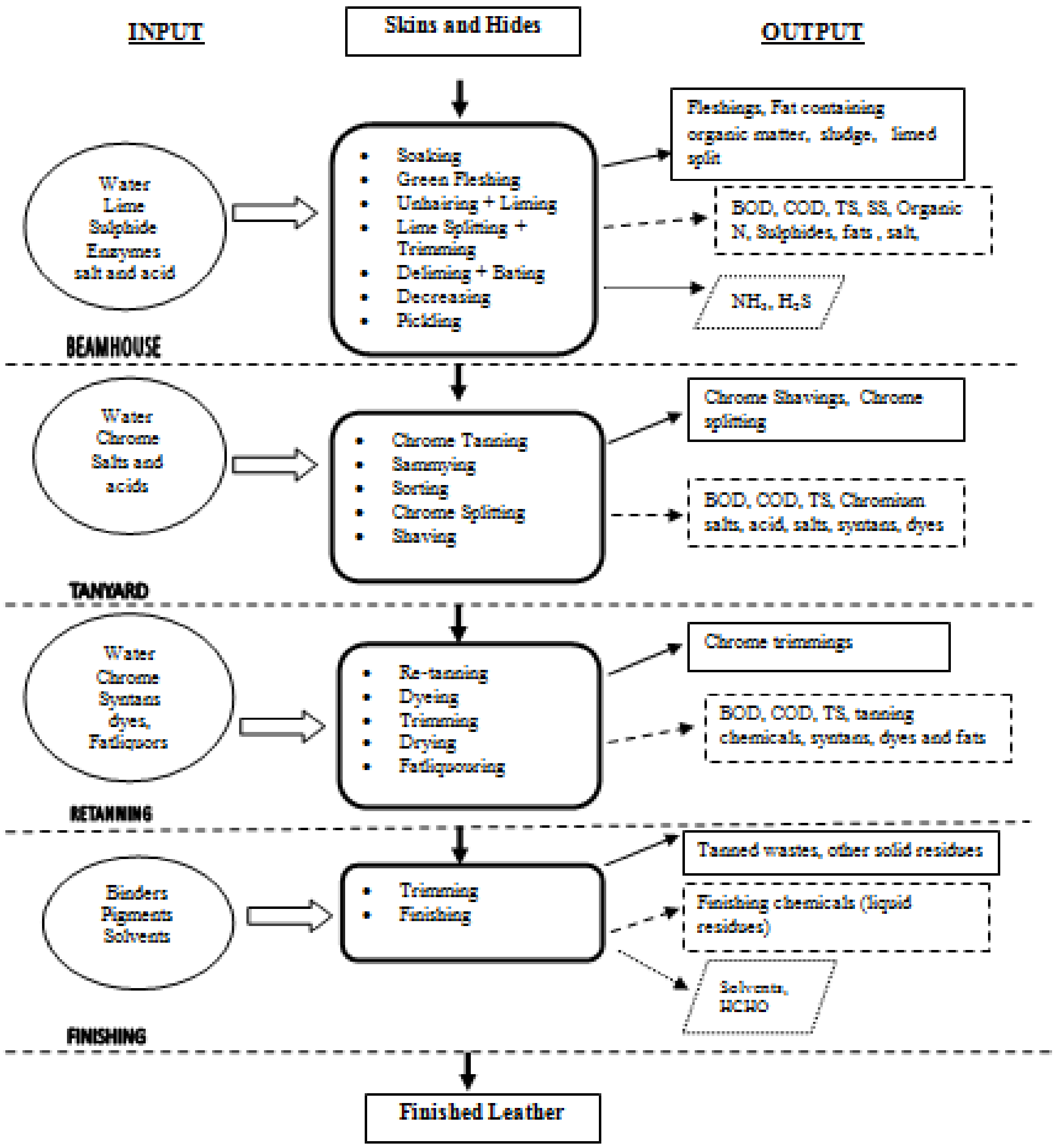

Figure 3.1. Input and Output Flowchart

3.6. Life Cycle Assessment

LCA complies with several components such as goal and scope, inventory analysis, impact assessment and interpretation. Purpose of performing an LCA should be defined in the beginning.

Assumptions

To perform Life Cycle Assessment, two variants were selected. Tanning process was selected as a boundary for analyzing damage assessment. The data obtained from the company was used for performing the chrome tanning process. Due to non-availability of data for alternative substances, the previous relevant research data was used for further analysis of Gluteraldehyde tanning process (57). The data source has been computed accordingly to the nature of the evaluation.

3.6.1. Goal and Scope

The LCA for the leather tanning process was performed on basis of gate-to-gate. The main objective of the study is to compare the environmental impact of existing chemical and an identified alternative used in the process especially in pickling and tanyard phase.

3.6.2. Functional Unit

This unit provides a reference to the input and output of the process. The tannery which is under the study has a capacity of 454 t/year (64,800 items) of sheepskin and the functional unit set as a reference for the study is 1000 kg per year using chrome-tanning process.

3.6.3. System Boundary

It is to define the product system and the other environment related to product system. The schematic diagram, Figure 3.2 represents the entire process of tanning industry and marked system boundary. Under this study and the boundary defined is analyzed for impact assessment, i.e., two main subsystems is considered all input and output of the process are evaluated. Pickling, tanning and re-tanning contribution high level of Chromium input and wastage. With the evaluation, it is possible to look for the environmental impact of alternatives and the target chemical for substitution.

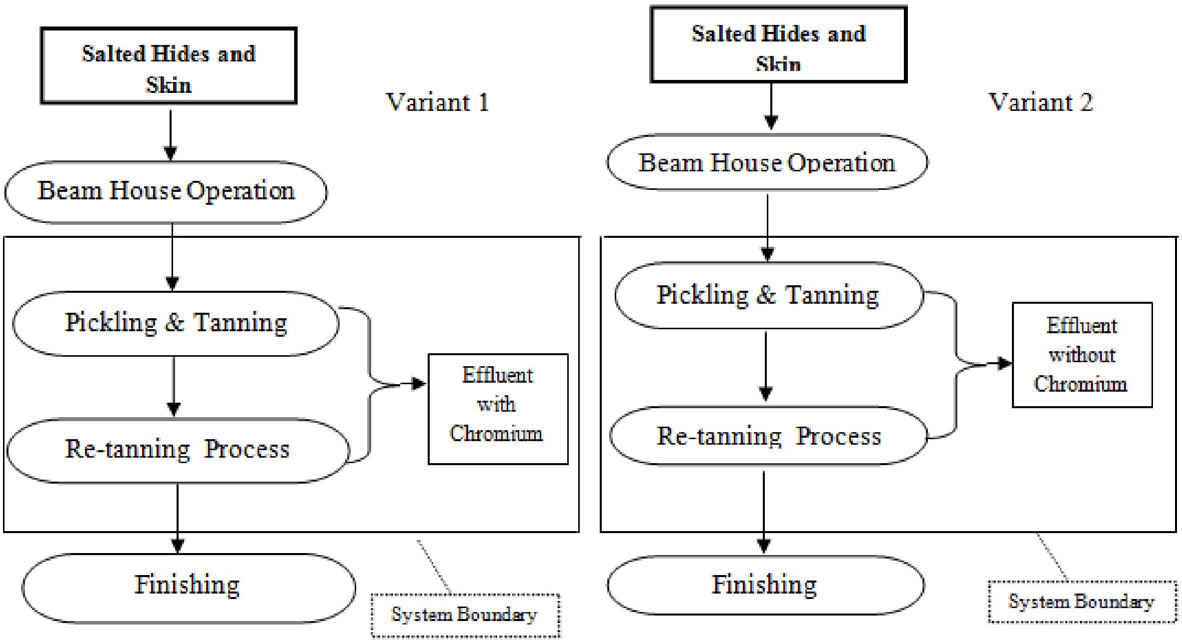

Figure 3.2.System boundary for the tanning process
[Variant 1 - Tanning with Chromium; Variant 2 - Tanning without Chromium (Glutaraldehyde)]

3.6.4. Inventory Analysis

Analysis of input and output was carried out for tanyard process. The characterization of physical and chemical of wastewater emissions is presented. The following corresponds to input and output characterization of tanyard and re-tanning process for chrome tanning and Gluteraldehyde tanning, for 1000 kg of sheepskins as input in pickling and tanning processes.

The process is named as 'before substitution' and 'after substitution' for the convenient understanding during the LCA study. Before substitution corresponds to chrome tanning process which is kept as baseline point; after substitution corresponds to Glutaraldehyde tanning process which is an alternative.

Figure 3.3, Figure 3.4 represents the inventory of both chrome tanning and Glutaraldehyde tanning process.

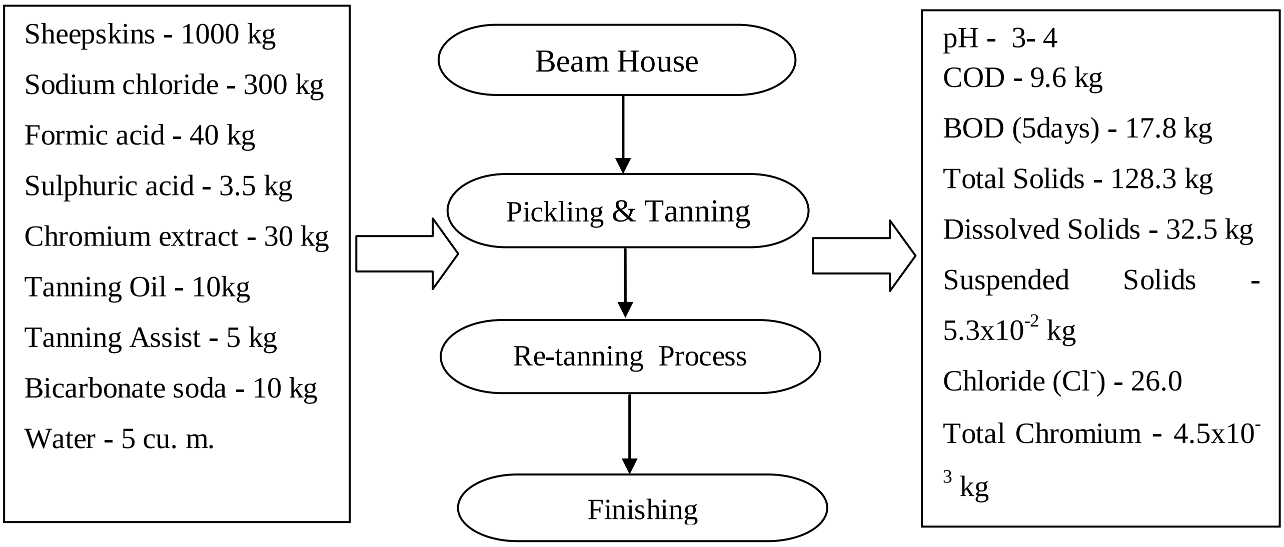

Figure 3.3. Input-Output inventory for Chrome tanning process (Baseline)

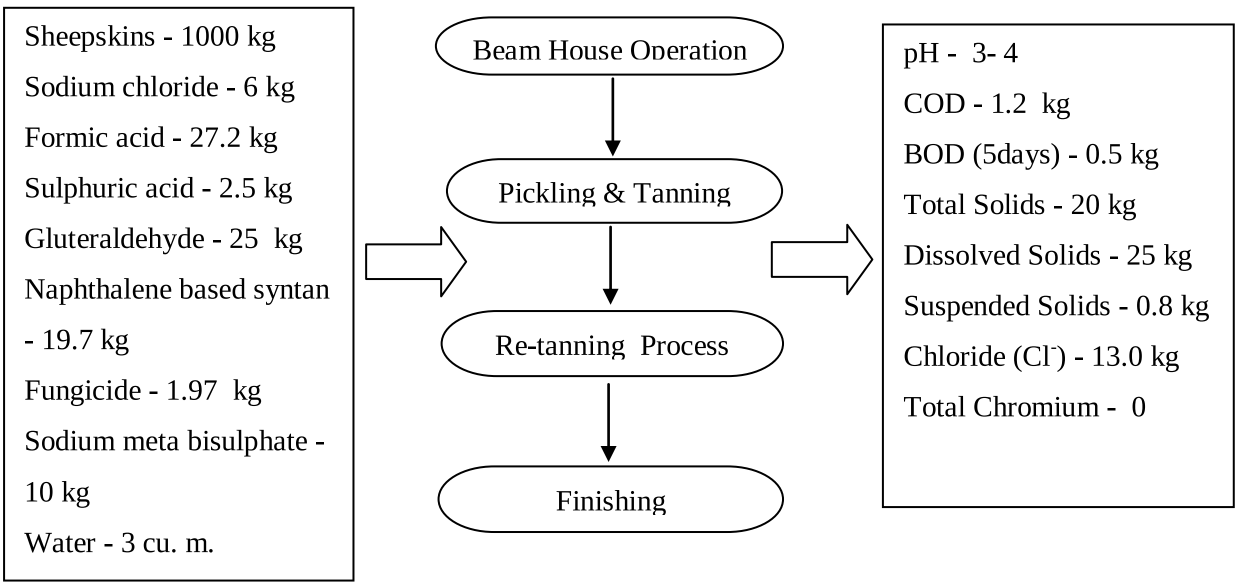

Figure 3.4. Input-Output inventory for Glutaraldehyde tanning process (Alternative)

3.6.5. Overall Impact assessment for alternative

The evaluation is carried out using SimaPro software 8. The software consists of a database of state-of-the-art methodologies and tools, to assess the entire process. The software assessed the effects of energy usage and also production. It also evaluated the impact of waste generation, emissions according to the process and their inputs. So, there it is important to know, which one has the greatest impact. Figure 3.5 shows the network diagram of the identified alternative Glutaraldehyde in replacing with Chromium. The flow diagram was calculated using the ReCiPe method.

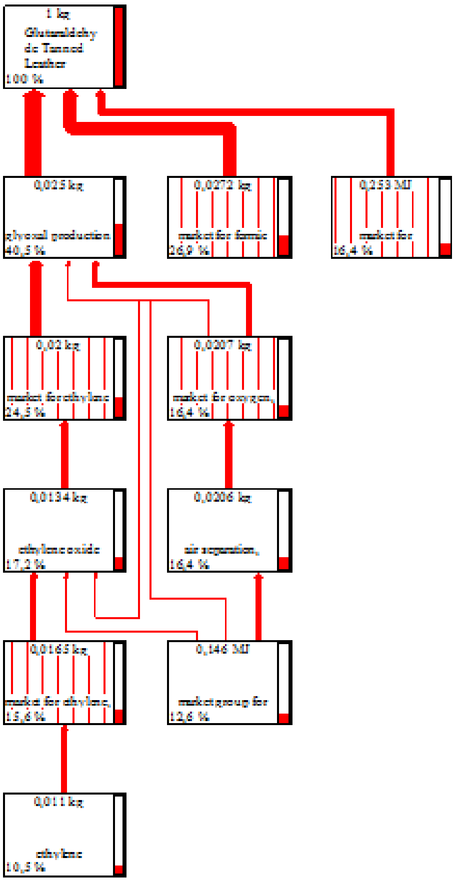

Figure 3.5. Network diagram of an identified alternative

The impacts are measured in terms of carbon equivalents, input of sheepskin have high impact on the entire process. In the network diagram, production of Glutaraldehyde, formic acid, and electricity has the great impact on cost and environment. Nevertheless, while evaluating midpoint indicator (using ReCiPe method), ozone depletion and fossil fuels have the greatest impact due to salted leather and production of Glutaraldehyde, as it is also grouped under ethylene.

The life cycle assessment is performed by comparing the conventional chrome tanning (before substitution) and with Glutaraldehyde tanning (after substitution) as output after the pickling/tanning process. The alternatives are assessing using Recipe methodology. The results of the comparison are presented for both characterization (midpoint indicators) and also damage assessment (endpoint indicators).

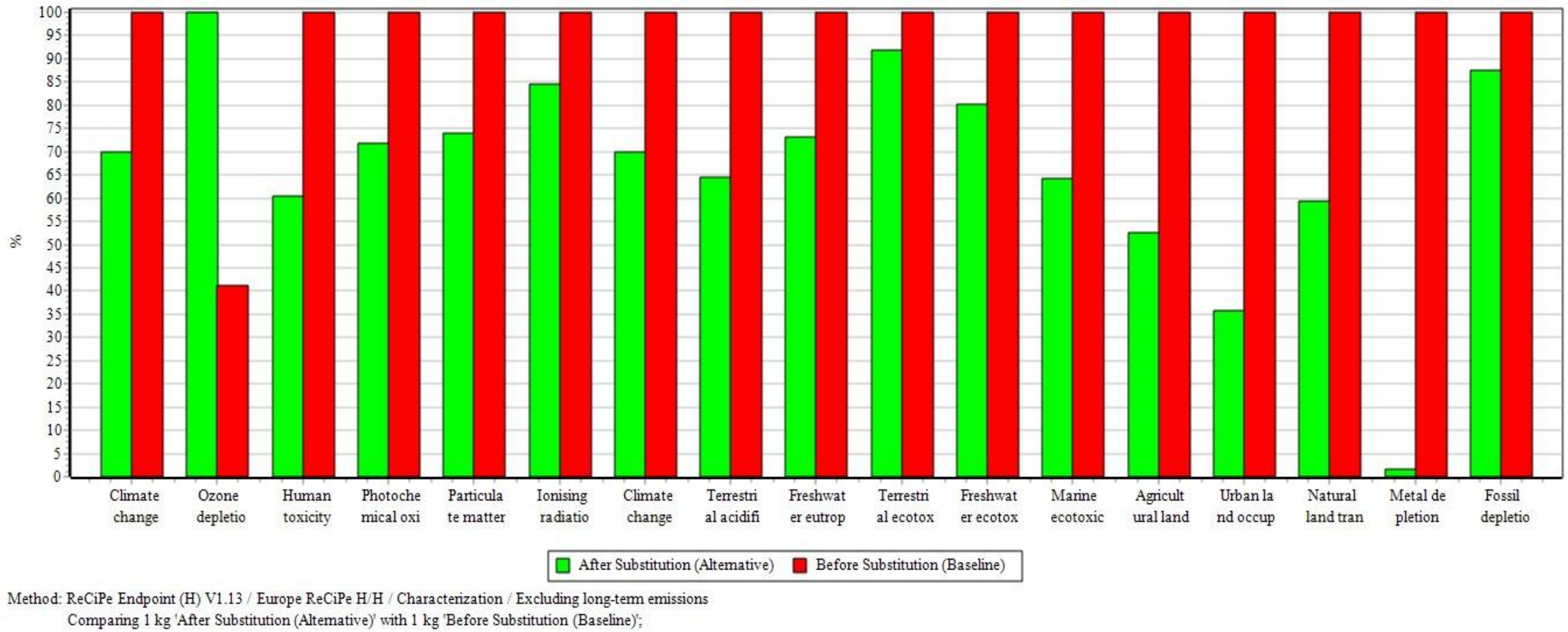

Figure 3.6. Characterization: Comparison of Chrome (Baseline) and Gluteraldehyde (Alternative) tanning
[Method: ReCiPe Endpoint (H) V1.13/Europe ReCiPe H/H]

Characterisation: ReCiPe methodology is used to evaluate the entire assessment over other methodologies. ReCiPe is an impact assessment tool that harmonized both endpoint and midpoint categories and it is also an improved method of Eco-Indicator 99 and CML 2000. ReCiPe has 18 midpoint indicators and three endpoint indicators. ReCiPe also expresses the environmental load in the single score and has suitable in-depth analysis. The comparison of chrome tanning and Gluteraldehyde tanning for midpoint characterization is provided in Figure 3.6.

Impact category such as climate change, ozone depletion, human toxicity, photochemical oxidation, particulate matter and ionizing radiation are calculated in DALY unit. The helps to measure the gap between the situation to the standard life expectancy in good health and the actual health situation. According to the evaluation, implementation of alternative tanning agent (Glutaraldehyde) also has a significant contribution to ozone depletion and ionizing radiation potential with an average of 85 %. The depletion of ozone could be because of the manufacturing of Glutaraldehyde as it uses enormous amount ethylene. Formalin and Glutaraldehyde contributes to VOC emissions to air.

Similarly, other parameters excluding metal depletion and fossil fuels are calculated in species/year. In general, the overall impact using proposed alternatives indicates 1/4th of impact compared to tanning in the conventional method. Usage of Glutaraldehyde as tanning agent also cause a significant impact on aquatic and terrestrial ecotoxicity with an average of 75 % and this could be well evidenced in substance information sheet from ECHA indicating aquatic chronic (H400 and H411). On the other hand, metal depletion has dropped almost to 5% comparing the conventional tanning method, which in turn, likely to reduce cost invested in human health and resource depletion.

Damage Assessment: The evaluation of damage assessment shows that there is considerable impact on both ecosystems and human health. Usually, the damage is evaluated using the Endpoint indicator, that is expressed and analyzed in three damage categories:

- Human Health
- Ecosystem
- Natural Resources

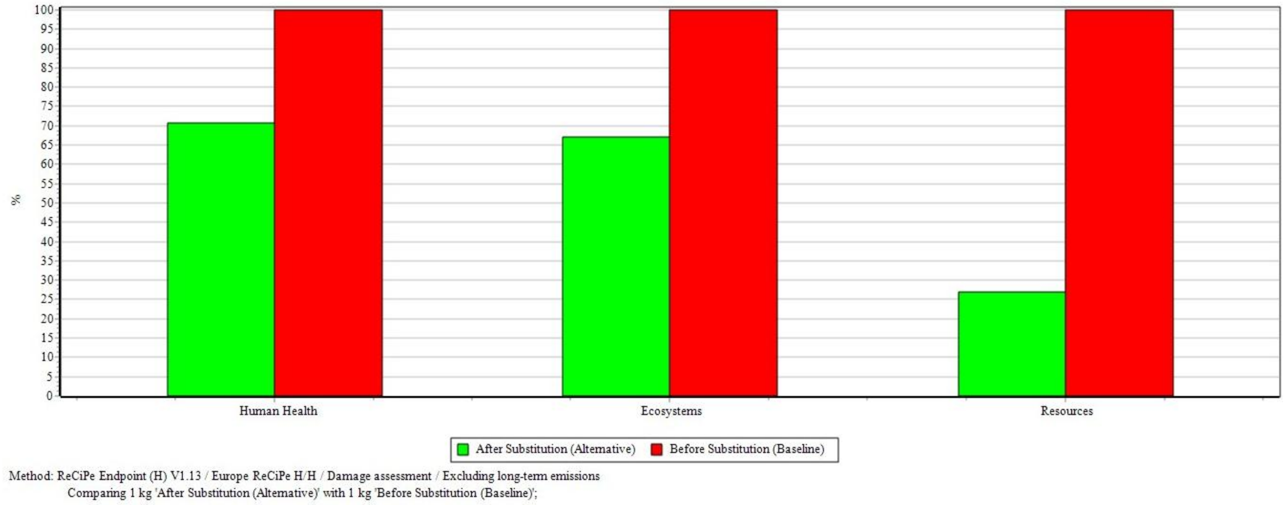

Figure 3.7. Damage Assessment: Comparison of Chrome (Baseline) and Gluteraldehyde (Alternative) tanning
[Method: ReCiPe Endpoint (H) V1.13/Europe ReCiPe H/H]

The evaluation of the proposed alternative is represented in Figure 3.7. The results are generally expressed in mPt. The main advantage of using damage evaluation is to evaluate overall impact of these three indicators. Human health is a prime factor in terms of social conditions as well. It is evident from the chart, the human health damage is much higher for conventional method than proposed alternative with weighted average 7 mPt. The damage to the human health with the conventional method is 11.7 mPt, i.e., the damage to human health is 1/3rd lesser than the conventional tanning method. This implies, overall weighted average score for conventional and proposed alternative tanning method is 85 mPt and 31 mPt respectively. This derives, overall damage assessment for after substitution reduce to 30 %.

The main benefits of proposed alternatives to the company:

- The proposed alternative does not exhibit CMR properties.
- Extraction of metals, and especially discharge of chromium and presence of Cr(III) will be controlled in finished products and also during emissions.
- The alternative also reduces the environmental costs due to outputs emission and extraction of minerals.

Overall, the impact on the environment is much lower than the conventional chrome tanning, though, the usage of alternative have potential hazard involved, it is also leads a way to possibility of substitution with less hazardous substance. Moreover, usage of alternatives would improve the image of the company and also the quality of products remains the unchanged.

4. Conclusions

1) The analysis of the fur industry has shown that the industry remains as most polluting industries that use potentially toxic chemicals which impose a huge risk to human health and environment.
2) The existence of stricter legal requirements for the use of hazardous chemicals encourages the companies to look for alternatives to non-hazardous substances or less toxic substances. However, the change involves numerous problems: often alternatives are, inappropriate technologically and expensive economically. The change is difficult when it is a small enterprise as there is lack of resource and technical expertise.
3) After analyzing the chemicals used in the Lithuanian fur industry, it has been concluded that companies still use the substances included in the list of priority substances such as sodium dichromate, formaldehyde, chromium sulfate, etc. even after the sunset date prescribed under REACH regulation.
4) After reviewing the list of hazardous substances that has been listed under restricted substances of REACH legislation, three widely used substances (Ammonium dichromate, formaldehyde, NPE) in fur industry which was considered and analyzed as per REACH legislation.
5) After analyzing the list of identified substances based on the literature study, the alternatives for the same is also studied with the help of safety data sheets, official databases and researches. Three alternatives, Glutaraldehyde, ethoxylated alcohol, formaldehyde-urea-melamine concentrate was chosen for assessment of alternatives. The proposed alternative was assessed for various criteria on hazards, functionality, legal requirements, CMR properties, substitution limit, cost and so on.
6) Evaluating of hazard for both existing and proposed alternatives, revealed that Ammonium dichromate and formaldehyde have high chronic toxicity (severity score 4) and all three SVHC chemicals have high level of acute toxicity (severity score 4); as in case of identified alternatives, there is low or negligible level of severity for chronic toxicity (severity score 1 or 2); but Glutaraldehyde has high to medium impact on acute toxicity to environment and physical hazard (severity score 4 and 3, respectively).
7) Analyzing the chemicals used in the company for the process of tanning, chromium sulphate found to be toxic and substances of concern. The Ammonium dichromate was considered for substitution with Glutaraldehyde as an alternative. Assessment of alternatives helped to find that Glutaraldehyde has same functionality as chromium. The proposed alternative was assessed for environmental impact using LCA.
8) In ReCiPe Midpoint method, it has been observed that the alternative is most harmful and

potential contributor to ozone depletion, aquatic and terrestrial ecotoxicity with an average of 75 % and this could be well evidenced in substance information sheet from ECHA indicating aquatic chronic (H400 and H411). However, the almost 40% less, when it is compared to human toxicity indicator. At the same time, depletion of metal is almost reduced to 5% of impact produced due to conventional tanning agent.

9) The evaluation of endpoint indicator was estimated for three damage categories: human health, ecosystems, resources. The damage to the human health with the conventional method is 11.7 mPt, i.e., the damage to human health is 1/3rd lesser than the conventional tanning method. By shifting into proposed alternative, the conventional system reduces the impact of human health by 30%.

10) Expected benefits for the company: The proposed alternative do not have CMR properties, it helps to reduce or eliminate the outputs of chromium waste. Improve health and environment aspects and enhance company's image.

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Appendices

Appendix 1

Explanation of Hazard Statements (H - Code)

H400	Very toxic to aquatic life
H410	Very toxic to aquatic life with long lasting effects
H411	Toxic to aquatic life with long lasting effects
H412	Harmful to aquatic life with long lasting effects
H413	May cause long lasting harmful effects to aquatic life
H300	Fatal if swallowed
H301	Toxic if swallowed
H302	Harmful if swallowed
H304, H305	Maybe fatal if swallowed and enters airways
H310	Fatal in contact with skin
H311	Toxic in contact with skin
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H330	Fatal if inhaled
H331	Toxic if inhaled
H332	Harmful if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H340	May cause genetic defects
H341	Suspected of causing genetic defects
H350	May cause cancer
H351	Suspected of causing cancer
H360	May damage fertility or the unborn child
H361	Suspected of damaging fertility or the unborn child
H362	May cause harm to breastfed children
H360F	May damage fertility
H360D	May damage the unborn child
H360FD	May damage fertility. May damage the unborn child
H360Fd	May damage fertility. Suspected of damaging the unborn child
H360Df	May damage the unborn child. Suspected of damaging fertility
H361f	Suspected of damaging fertility
H361d	Suspected of damaging the unborn child
H361fd	Suspected of damaging fertility. Suspecting of damaging the unborn child

Explanation of Hazard Statements (EUH - Code)

EUH001	Explosive when dry
EUH006	Explosive with or without contact with air
EUH014	Reacts violently with water
EUH018	In use may form flammable/explosive vapour-air mixture
EUH019	May form explosive peroxides
EUH029	Contact with water liberates toxic gas
EUH031	Contact with acids liberates toxic gas
EUH032	Contact with acids liberates very toxic gas
EUH044	Risk of explosion if heated under confinement
EUH059	Hazardous to the ozone layer
EUH066	Repeated exposure may cause skin dryness or cracking
EUH070	Toxic by eye contact
EUH071	Corrosive to respiratory tract
EUH202	Cyanoacrylate. Danger. Bonds skin and eyes in seconds. Keep out of the reach of children
EUH203	Contains Chromium(VI). May produce an allergic reaction
EUH204	Contains isocyanates. May produce an allergic reaction
EUH205	Contains epoxy constituents. May produce allergic reaction
EUH206	Warning! Do not use together with other products. May release dangerous gases (Chlorine)
EUH207	Warning! Contains cadmium. Dangerous fumes are formed during use.
EUH208	Contains <name of sensitizing substances>. May produce an allergic reaction
EUH210	Safety data sheet available on request
EUH401	To avoid risks to human health and the environment, comply with the instructions for use.

Global Harmonized System (GHS) pictograms for Hazard classification

GHS01 Explosive 	GHS02 Flammable 	GHS03 Oxidising 
GHS04 Gas Under Pressure 	GHS05 Corrosive 	GHS06 Acute Toxic 
GHS07 Harmful / Irritant / Skin sensitiser 	GHS08 Carcinogen / Germ cell mutagen / Reproductive toxin 	GHS09 Hazardous to the aquatic environment 

Substance Information Sheet - Identified substances of concern (1)

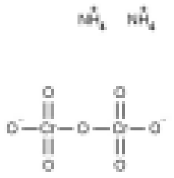
Ammonium dichromate

Substance identity

EC / List no.: 232-143-1

CAS no.: 7789-09-5

Mol. formula: Cr2H8N2O7



Hazard classification & labelling

Danger! According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance is fatal if inhaled, is toxic if swallowed, causes severe skin burns and eye damage, may cause genetic defects, may cause cancer, may damage fertility and may damage the unborn child, causes damage to organs through prolonged or repeated exposure, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects, may intensify fire (oxidiser), is harmful in contact with skin, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing difficulties if inhaled.

Additionally, the classification provided by companies to ECHA in **REACH registrations** identifies that this substance may damage fertility or the unborn child.

Properties of concern

C M R Ss Sr

Regulatory activities

- Substance of very high concern (SVHC) and included in the candidate list for authorisation.
- Substance of very high concern requiring authorisation before it is used (Annex XIV of REACH).

About this substance

This substance is manufactured and/or imported in the European Economic Area for industrial use resulting in the manufacture of another substance (use of intermediates).

This substance is used by professional workers (widespread uses) and at industrial sites.

Consumer Uses

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Article service life

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment. ECHA has no public registered data indicating whether or into which articles the substance might have been processed.

Widespread uses by professional workers

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Formulation or re-packing

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Uses at industrial sites

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Manufacture

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Substance Information Sheet - Identified substances of concern (2)

Formaldehyde, oligomeric reaction products with aniline

Substance identity

EC / List no.: 500-036-1

CAS no.: 25214-70-4

Mol. formula:

Complex multi-constituent substance, or UVCB:

Unknown or
Variable composition,
Complex reaction products or
Biological materials

Hazard classification & labelling

Danger! According to the classification provided by companies to ECHA in **REACH registrations** this substance causes damage to organs, may cause cancer, is very toxic to aquatic life with long lasting effects, is very toxic to aquatic life, is toxic if swallowed, is suspected of causing genetic defects and may cause an allergic skin reaction.

Properties of concern

C Ss

Regulatory activities

- Substance of very high concern (SVHC) and included in the candidate list for authorisation.
- Substance of very high concern requiring authorisation before it is used (Annex XIV of REACH).

About this substance

This substance is manufactured and/or imported in the European Economic Area in 100 - 1 000 tonnes per year.

This substance is used at industrial sites and in manufacturing.

Consumer Uses

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Article service life

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment. ECHA has no public registered data indicating whether or into which articles the substance might have been processed.

Widespread uses by professional workers

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Formulation or re-packing

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Uses at industrial sites

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Manufacture

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Substance Information Sheet - Identified substances of concern (3)

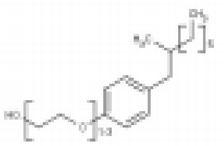
Nonylphenol, ethoxylated

Substance identity

EC / List no.: 500-024-6

CAS no.: 9016-45-9

Mol. formula: (C2H4O)1-3C15H24O



Hazard classification & labelling

Warning! According to the classification provided by companies to ECHA in **REACH registrations** this substance is toxic to aquatic life with long lasting effects, causes serious eye irritation and causes skin irritation.

Properties of concern

PBT

Regulatory activities

- Some uses of this substance are restricted under Annex XVII of REACH.

About this substance

This substance is manufactured and/or imported in the European Economic Area in 1 - 10 tonnes per year.

This substance is used at industrial sites.

Consumer Uses

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Article service life

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment. ECHA has no public registered data indicating whether or into which articles the substance might have been processed.

Widespread uses by professional workers

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Formulation or re-packing

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Uses at industrial sites

ECHA has no public registered data indicating whether or in which chemical products the substance might be used. ECHA has no public registered data on the types of manufacture using this substance. ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

Manufacture

ECHA has no public registered data on the routes by which this substance is most likely to be released to the environment.

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