Ministry of Environment and Food of Denmark
Environmental Protection Agency

Chromium VI and cobalt in leather goods

Control of chromium and risk evaluation of cobalt

Survey of chemical substances in consumer products No. 177

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Editors:
Barbara Kolarik[1]
Poul Bo Larsen[2]
Sara Björkqvist[1]
Anders Jensen[1]
[1]Danish Environmental Analysis (Dansk MiljøAnalyse)
[2]DHI

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Foreword

This project has been carried out as a co-operation between the chemical inspection unit of The Environmental Protection Agency of the Danish Ministry of the Environment. The focus of the investigation is the content of chromium (VI) and cobalt in leather goods.

The aims of the investigation are:
- to inspect consumer goods and determine whether the existing regulation on chromium (VI) in leather goods is respected
- to obtain further knowledge about the content of cobalt in leather goods and assess the risk of using leather goods containing cobalt.

The project has been carried out from March 2018 to December 2018 as a co-operation between Medico Chemical Lab/DMA (project management, surveying, chemical analyses and migration analyses) and DHI (health and risk assessments). Barbara Kolarik, MCL/DMA, has been in charge of overall management and Poul Bo Larsen has been responsible for DHI's part of the investigation.

Supervision of the project has been undertaken by a steering group with the following members:

- Grete Lottrup Lotus (Environmental Protection Agency)
- Louise Fredsbo Karlsson (Environmental Protection Agency)
- Hanne Thygesen (Environmental Protection Agency, The chemical inspection)
- Morten Thjellesen (Environmental Protection Agency, The chemical inspection)
- Barbara Kolarik (MCL/DMA)
- Poul Bo Larsen (DHI)

The project was funded by the Environmental Protection Agency.

Summary and conclusions

Background and purpose

Skin allergy is a major health problem. Approx. 10 % of the Danish population suffers from skin allergy to one or several chemicals. Among these, metal containing chemicals - incl. chromium and cobalt - constitute the most common allergens.

Leather goods are the most common origin of chromium allergy in Denmark. As of May 2015 leather goods in contact with human skin must not be marketed if they contain chromium (VI) in concentrations of - or higher than - 3 mg/kg (0.0003%) based on the dry weight of the leather (REACH, appendix 17, section 47, points 5 and 6). Recent investigations show that leather goods also can contain cobalt which may cause cobalt allergy. Cobalt is classified as a skin- and respiration-sensitizing agent according to existing, harmonized CLP Regulation[1]. Commercial cobalt containing goods are covered by the Act on product safety[2], which serves to assure only suitable goods on the market.

Thus, it was the aim of the project to obtain more information on the use of cobalt in leather goods and assess any risk of developing skin allergy by use of leather goods containing cobalt. Since the project focuses on leather goods in which both chromium and cobalt are used, a secondary purpose was to control how far products prepared from leather comply with the existing rules for content of chromium (VI) in accordance with the legislation.

Survey of the field

In order to survey the field a literature search was undertaken and combined with a data extract from Statistics Denmark (www.statistikbanken.dk) and from Eurostats Prodcom Database. Furthermore, contacts have been established to various industry associations, Danish importers and retailers of leather goods in Denmark in the intent to obtain information about their knowledge of the occurrence and use of cobalt in the production of leather goods.

Cobalt is used in the so-called premetallized dyes. A wide range of dyes are used in manufacturing of leather including regular dyes, reacting dyes, premetallized dyes, and acidic dyes. The last two sorts have better resistance against water and light. There are two types of premetallized dyes in which one or two dye molecules, respectively, are bound in a complex with a metal atom. Most often, chromium or cobalt are used as the metal. But copper, iron and nickel may be used as well.

Some investigations have shown a correlation between exposure to leather and development/induction of skin allergy in patients allergic to cobalt. Upholstery leather have been identified as the cause of skin allergy in two, Danish case-studies (Thyssen et al. 2013; Bregnbak et al. 2017), including a leather sofa with a cobalt content of 800 mg/kg, leather cushions containing 802 mg/kg, and another leather sofa with a cobalt content of 1250 mg/kg. Cobalt containing leather is used in goods other than furniture. In a Swedish report, cobalt was detected in 20 out of 21 samples of shoes in concentrations ranging between 0.5 and 16 mg/kg. Several other investigations have identified leather as a possible cause for cobalt skin allergy. However, these investigations lack analyses of cobalt in the products.

[1] CLP Regulation (EC) No 1272/2008, Annex VI

[2] Act on product safety no. 1262 of 16/12/2009

The overall conclusion of the market survey was that the industry associations, producers, and retailers of leather goods did not have any knowledge of the occurrence of cobalt in the products. Neither did they know whether the leather is dyed with premetallized dyes or whether cobalt was involved in other processes. Italy was the most commonly named country of origin for manufactured leather goods.

According to Statistics Denmark, Italy was also the leading importer of hides and skins from Denmark while simultaneously being the dominant exporter of manufactured leather to Denmark. However, information about the production and use of leather goods in Denmark is too scarce to allow for an evaluation of production and use of leather goods in Denmark and the exposure of the population to cobalt from this source. Footwear accounted for 70 % of the total volume of imported leather goods and may therefore be the category mostly used by the population. There are no statistics on the import and export of leather furniture. But from the case studies known it may be anticipated that leather furniture does have great significance for the overall exposure of the population to cobalt.

Results from analysis

The chemical inspection has performed XRF screening of a series leather goods and identified the products containing chromium. None of the products showed any cobalt according to XRF. A total of 74 products were selected for chromium (VI) and cobalt analysis, including 33 shoes for adults, 7 shoes for babies and children, 1 sole of shoe, 17 handbags/purses, 1 pair of pants, 1 pair of gloves, 6 belts, 6 watch straps/bracelets, 1 cushion and 1 keystring. The total number of analyses were 94 since several of the shoes were investigated for the occurrence of chromium in both the vamp and the inner sole. Since these categories of products did not include furniture - which may constitute an important source of exposure to cobalt - several major retailers of furniture were contacted and requested to submit samples of leather used in furniture sold on the Danish market. Three retailers submitted a total of 34 samples in several different colours.

The concentration of chromium (VI) was below the detection limit in 73 out of 94 leather samples being analysed. In 10 samples the concentration of chromium (VI) was higher than the limit value of 3 mg/kg dry matter, though was one result within the uncertainty of the analysis method and was thereby not regarded as a violation of the limit value. The highest measured values of 28 mg/kg, 16 mg/kg, and 11 mg/kg, respectively, were found in handbags. Chromium (VI) content exceeding the detection limit was found in 3 out of 8 shoes for babies and children. In one of these shoes the concentration was higher than 3 mg/kg.

The XRF screening returned negative findings for cobalt in all the samples collected. However, leather samples from furniture was not subjected to XRF screening. Quantitative chemical analysis revealed a cobalt concentration higher than the detection limit in 29 out of 128 leather samples, corresponding to 23 %. Cobalt containing products were found in all categories investigated, the highest values being found among handbags and purses together with watch straps and bracelets. The concentrations displayed a spread from < 1 mg/kg to 153 mg/kg. The highest concentration of 153 mg/kg was found in an upholstery sample of grey nubuck leather. In some specific parts of footwear relative high concentrations of cobalt were detected with a maximum value of 73 mg/kg.

Ten products have been selected for analysis of cobalt migration including all samples with cobalt values higher than 10 mg/kg and three samples with lower amounts of cobalt, intended for the use by children or when long-term contact with skin is anticipated. Cobalt migration was detected in 6 out of 10 leather samples investigated. Leaching of cobalt from the upholstery sample with the highest content was low, corresponding to 0.09 g/cm^2/week. The maximum concentration of cobalt found in the extract was 0.44 $\mu g/cm^2$/week from ladies's boots featuring

a content of 12 mg/kg dry matter. Neither was any correlation found between the amount of cobalt in the other leather samples investigated and the leaching of cobalt from said samples.

Risk assessment and conclusions

The migration parameter is expressed as µg cobalt released per cm^2 surface per week of extraction. It is considered a valid parameter for assessment of the worst-case exposure a consumer may suffer when using the goods.

The following values for leaching from the various leather goods were obtained:

Man's shoes, black (inner sole):	*0.27 µg Co/cm^2 / week*
Ladies's shoes, brown (vamp):	*0.44 µg Co/cm^2 / week*
Bracelet, black:	*0.33 µg Co/cm^2 / week*
Watch strap, red:	*0.07 µg Co/cm^2 / week*
Upholstery leather, grey:	*0.09 µg Co/cm^2 / week*
Upholstery leather, beige:	*0.13 µg Co/cm^2 / week*

Relating the migration parameters to the consumption patterns of the products led to the conclusion that brown ladies's boots and the black bracelet are representative for the most potential sources of cobalt exposure. Both types of products are being used many hours a day and moisture/sweat may promote migration of cobalt.

Regarding the action of leather goods as the source of cobalt allergy only few cases have been reported in Denmark. In a single instance of allergy caused by the emissions from a leather cushions, the cobalt content in the leather was found to be 802 mg Co/kg. However, several examples of skin allergy caused by cobalt in leather shoes have been observed in the rest of Europe. The allergic reactions to cobalt appear as eczema, flushing, vesiculation and skin wounds, eventually.

Once cobalt allergy has been initiated, the patient may become extremely sensitive to subsequent cobalt re-exposure. Clinical trials with cobalt allergics have revealed that exposure for 48 hrs to solutions with cobalt concentrations as low as 0.441 - 1.95 µg kobalt per cm^2 skin can provoke skin reactions among the most sensitive.
The REACH regulations recommend to institute risk assessments of chemicals, for which no zero-effect level can be set, based on a Derived Minimal Effect Level (DMEL), rather than a Derived No Effect Level (DNEL) value.). Therefore, the DMEL-value for cobalt is determined to be 0.441 - 1.95 µg cobalt/cm^2.

The risk assessment is made by comparing these values to each other and calculating the risk characterization ration (RCR = exposure / DMEL) from there. If the RCR value is above 1, this immediately indicates that the migration is higher than the DMEL value and therefore may pose a potential risk.

The table below shows the risk assessment for cobalt migration from ladies's boots and bracelets:

	Migration	**DMEL**	**RCR**
Brown ladies's boots (vamp)	0,44 µg Co/cm^2	0.441 – 1,95 µg Co/ cm^2	***0,23 - 1,00***
Black bracelet	0,33 µg Co/cm^2	0.441 – 1,95 µg Co/ cm^2	***0.17 – 0,75***

The RCR intervals are below the value 1, except for the upper part of the RCR interval for women's boot, which touch the critical level of 1. This is however not considered to be of a high concern, bearing in mind that the migration values express migration over 7 days, while the DMEL value is an expression of 48 hours exposure. In an exposure scenario for a user of women's boots, the migration would not occur for 7 days, but only for a shorter period corresponding to a few hours where the boots are wet or damp with sweat. The migration is therefore expected to be considerably lower in this shorter time course. Similarly, the DMEL value is based on 48 hours, which is much above the expected exposure time. A DMEL value based on shorter period, for example 2 hours, is considered to be substantially lower than a DMEL value for 48 hours of exposure. Using more realistic values for migration and DMEL would therefore result in significantly lower RCR values than the calculated, even for a worst-case multi-hour consumer scenario. However, the existing knowledge does not make possible to conduct more precise calculations of the RCR values, due to lack of more relevant data for migration and DMEL value.

It is estimated from these results that there are no risks for initiation of cobalt allergy from the use of the brands of ladies's boots and bracelets investigated here. Furthermore, the risk for induction of symptoms when cobalt allergics are wearing these goods is considered to be low.

The same conclusion can be drawn regarding the other products for which cobalt migration has been determined. The potential for allergic action is estimated to be significantly less than the already minor threat from ladies's boots and black bracelets.

Only one sample of leather trousers and one pair of leather gloves were investigated. With data from only two products no conclusions can be drawn about the general occurrence of cobalt in leatherwear.

Neither can the results from the investigation be used in the assessment of cobalt in other types of leather goods like covers for mobil phones and products used in cars and bicycles.

However, it should be stressed that instances of skin allergy caused by cobalt in leather goods cannot be completely ruled out since cases have been reported - domestically as well as internationally - in which allergic symptoms have been observed as a consequence of emission of cobalt from leather furniture and leather shoes.

1. Introduction

1.1 Background

Skin allergy is a major health issue. The most recent study of the Danish population in 2006 showed that ca. 10 % suffer from skin allergy to one or several chemical substances. However, The Danish Center for Allergy considers the real prevalence in Denmark to be higher since a significantly higher fractional prevalence (27 %) was derived from data collected 2008-2011 in a similar study among the populations in five EU-countries (Diepgen et al. 2016). Metal containing chemicals constitute the most common skin allergens. In the European survey, metals were found to cause skin allergy in 16 % of the persons investigated (Diepgen et al. 2016).

For decades cobalt has been recognized as an allergen causing allergic skin reaction and/or allergy- or asthma symptoms upon inhalation[3]. According to the existing, harmonized classification within CLP[4] (Classification, Labeling and Packaging) cobalt is classified as a skin- and respiratory-sensitizing agent with the tags Skin sens.1; H 317 and Resp sens. 1; H334, respectively. Furthermore, cobalt is labeled as mutagenic (Muta 2; H341), carcinogenic (Carc 1B; H350, SCL 0.01 %), and as a reproductional toxin (Repr 1B; H360F) in a motion to a new CLP harmonization[5]. Cobalt containing goods on the market are covered by the Act on Product Safety[6], which serves to assure only suitable goods on the market.
Cobalt is a metal often found together with nickel and persons diagnosed with cobalt allergy are often sensitive to nickel as well. Among other occurrences, cobalt is often found in shiny metal used in jewelry, buttons, and watches etc. In the already mentioned European survey cobalt allergy was found for 0.9 - 2.3 % of the people included in said study (Diepgen et al. 2016). Among patients suffering from eczema in Denmark the frequency of cobalt allergy was found to be 3.2 % in average (3.8% for women and 2.3 % for men; data from 2016)[7]. However, several studies have shown that cobalt allergy and nickel allergy far from always occur concomitantly. Thus, an American study (unpublished data; Flower, 2016) reveals that as many as 40 % of patients with cobalt allergy were tested negatively for nickel. In recent years new sources have been identified as potential causes of cobalt allergy, including leather goods among others.

Chromium (VI) is another recognized allergen, which may cause skin allergy. As a metal chromium is a constituent of alloys like stainless steel. It also goes into raw materials for making cement and for tanning of leather. Leather goods are the most common source of chromium allergy in Denmark because chromium is released from leather used in shoes, gloves, and straps etc. The frequency of chromium (VI) allergy was found in the range 0.2 - 1.1 % in the previously mentioned study of European populations (Diepgen et al. 2016). Among Danish patients tested for skin allergy, a frequency of 2.0 - 3.8 % chromium (VI) allergy was found[1]. As of 1 May 2015, leather goods used in contact with skin must not be marketed if they contain chromium in amounts of 3 mg/kg dry matter (0,0003 %) or higher (REACH, annex 17, entry

[3]https://echa.europa.eu/substance-information/-/substanceinfo/100.028.325

[4] CLP Regulation (EC) No 1272/2008, Annex VI

[5] Proposal for Harmonised Classification and Labelling, Substance name: Cobalt, December 2016

[6] Act on product safety no. 1262 af 16/12/2009

[7]https://www.videncenterforallergi.dk

47, points 5 and 6). The rule is also applicable to other products containing leather constituents which may touch the skin. The rule does not apply to recycled materials which were in terminal use in The Union before 1 May 2015 (REACH, annex 17, entry 47, point 7).

1.2 Purpose

The project focuses on products of leather in which both chromium and cobalt are used. Thus, the project comes with a twofold purpose:

- to obtain more knowledge about the use of cobalt in leather goods and assess if there is a risk of induction of skin allergy from the use of leather goods containing cobalt.
- to determine whether the existing regulations for chromium (VI) in leather are obeyed.

Products made from synthetic leather are not covered by the project, neither are other products in which chromium or cobalt are used.

1.3 Project phases and the contents of this report

The project is divided into four phases. Surveying the field (phase 1) and risk assessment (phase 4) deal with cobalt only. Selection of products for analysis (phase 2), analysis, and discussion of the results (phase 3) address both chromium and cobalt.

Phase 1: Survey of the content of cobalt in leather goods
A survey of the accessible literature about cobalt in leather goods is provided in Chapters 2, 3, and 4.

Chapter 2 reviews the existing knowledge about use, functionality and occurrence of cobalt in leather goods. Questionnaires have been sent out to manufacturers and retailers in order to obtain information about the distribution and use of cobalt and the general knowledge in the business regarding these issues. Information about the volume of relevant products are obtained from statistic data bases and discussed in consideration of the relevant exposure of the population.

Chapter 3 provides a general, preliminary health assessment and evaluation of overall exposure extracted from available knowledge.

In Chapter 4 the relevant product categories for XFR-screening and chemical analysis are identified.

Phase 2: Selection of leather goods for control and analysis
On the basis of the information provided in Chapter 4 of phase 1, The chemical inspection unit of The Environmental Protection Agency carries out phase 2 in which relevant leather products are subjected XRF-screening and samples are selected for chemical analysis. The results of the screening are presented in Appendix 3 and discussed in Chapter 5.2.

Phase 3: Chemical analysis of chromium and cobalt
Phase 3 includes chemical analysis of the leather samples obtained in phase 2. The samples are analysed for cobalt, total-chromium and chromium (VI). Migration tests employing artificial sweat are performed on 10 products selected on the basis of cobalt content. The results from phase 3 are reported in Chapters 5 and 6.

Phase 4: Risk assessment of exposure to cobalt in leather goods
Data from the chemical analysis is summarised in Chapter 7 and provides the basis for the draw up of exposure scenarios. A "worst case" approach is applied in the risk assessment by assessing the effects of the leather product displaying the greatest migration.

2. Survey of cobalt in leather goods

The purpose of the survey is to collect information from the available literature about cobalt in leather goods and its impact in relation to the development of skin allergy. This chapter reviews application and content of cobalt in leather goods, the occurrence of these products on the market, the use by the population of said products, and the causative exposure of cobalt from leather goods. A survey of the health conditions, which previously have been linked to cobalt in leather goods, is provided in Chapter 3.

2.1 Procedure for the survey

The survey of the present knowledge of application and content of cobalt in leather goods has been carried out by searching the internet on the background of existing national and international literature. Further information has been obtained by way of contacts to producers and retailers of leather goods including relevant business organizations. Information regarding the volumes of imported leather goods to Denmark and the country of origin of the products has been obtained from Statistics Denmark.

2.1.1 Survey of existing literature

Information about the general application of cobalt and the functioning of cobalt in leather goods has initially been obtained from websites and available reports.
A search of the scientific literature has been performed in PubMed. A search for keywords ”cobalt AND leather” provided 28 hits. These articles have been reviewed and the reference lists therein screened for relevant publications. A supplementary search was performed on the internet using keywords "cobalt" in combination with "leather" and "premetallized dye", respectively, using Danish entries as well.

2.1.2 Information from market operators

As part of the market survey, contacts have been established to various industry associations, producers, importers, and retailers of leather goods in Denmark in the intent to obtain information about their knowledge about the occurrence and use of cobalt.

They were identified by means of The Yellow Pages, Europages and by searching the internet for specific producers and industrial organizations. Leads from the primary contacts were followed up as well. Subsequently, the individual operators were contacted either by phone or via mail according to preference. Thus, a total of 25 producers, importers, and retailers, together with 5 industrial organizations were contacted in the period from 28 March 2018 to 25 April 2018. The group included producers and dealers of belts, bags, gloves, purses, furniture, shoes, and horse saddles. Furthermore, a slaughterhouse with their own tannery and dealers of leather dyes were contacted.

The focus of the market survey has been to obtain information about the functioning, frequency and general occurrence of cobalt in various types of leather goods on the Danish market. Based on the information obtained from the literature, the use of premetallized dyes was identified as the pertinent part of the process where cobalt might be used (Chapter 2.2.1.1). The questionnaire for the producers and dealers of leather goods is shown in Appendix 1. Questions were asked about the origin of the leather, about on which level in the overall preparation process they receive the leather, if they dye the leather themselves, if premetallized

dyes are used, and if they have any knowledge about whether cobalt or other metals take part in the dyeing process.

There were four dealers of leather dyes among the market operators. In particular, they were asked whether their dyes contain cobalt and if they had any knowledge of the content of other metals in premetallized dyes.

The slaughterhouse with their own tannery was specifically asked about the following:

- which animals/hides are processed?
- what is the country of origin of the animals?
- is cobalt used in the tanning process?
- what is the destination of the hides for further processing?
- what types of products is the leather being used for?

2.1.3 Quantities and origins of leather products on the Danish market

Data concerning import and export of leather goods is obtained from Statistics Denmark.
The pertinent information is obtained from “Imports and exports CN (EU combined nomenclature) by imports and exports, commodities, unit and data source” under position ”External economy/Detailed external trade statistics”.
"Leather" is used as keyword in the search in order to identify the relevant product categories.
Data is obtained for the last three years, *i.e.* 2015, 2016, and 2017.
A total of 78 different product categories are identified. Statistics can be derived in 57 of these.
Subsequently, they are grouped in the following, broader categories:

- Footwear with a vamp of leather
- Safety shoes with a vamp of leather
- Bags, trunks, wallets, etc. with outer side of leather, artificial leather or patent leather
- Clothing and accessories to clothing of leather or artificial leather
- Gloves of leather or artificial leather
- Working gloves of leather or artificial leather
- Belts and shoulder straps of leather or artificial leather
- Other goods of leather or artificial leather

Notably, no data has been found for leather furniture or saddles. An existing category is called "42010000 Saddlery and harness for any animal, incl. traces, leads, knee pads, muzzles, saddle cloths, saddlebags, dog coats and the like, of any material (excl. harnesses for children and adults, riding whips and other goods of heading 6602)”. That is, both leather goods and goods made of other materials are included. Consequently, this category is not included in the survey.

No quantities are given for the category ”91139010 – Watch straps, watch bands and watch bracelets, and parts thereof, of leather or of composition leather” which indicates, that no statistical data is gathered. Accordingly, this category is not included either.

Regarding leather and hide as materials - not products - a total of 64 different categories are identified but statistics is only provided for 35. These categories are grouped in two superior categories: Raw hides/skins and pure leather. The classification is based on a motion to limit the occurrence of chromium (VI) compounds (ECHA, 2012).

2.2 Outcome of the survey

2.2.1 Application of cobalt

Cobalt is a common element. It is a hard, silvery metal with properties much like iron and nickel. The free metal is not found in nature but won from different ores. Occurrence of cobalt

is often found as a mix of different species of ores. For this reason, cobalt is often won as a by-product from the mining of copper and nickel. In chemical compounds cobalt most often occur in oxidation states +2 and +3 with oxidation state +2 being the most stable. Almost all cobalt compounds are coloured.
Cobalt has the symbol Co and atomic number 27. The only stable cobalt isotope has atomic mass 59. However, there are many unstable and/or radioactive Co-isotopes, most prominently cobalt-60 (^{60}Co) which is used commercially, for one thing in radiation treatment of cancer tumours.

Cobalt occurs in vitamin B12, which is an essential nutrient for humans and other mammals, who cannot produce the vitamin and therefore must obtain it through the diet.

Cobalt compounds are used for many means. Elemental cobalt is often used together with other metals in alloys, which may be more resistant to wear and corrosion. These alloys are used in military and industrial contexts. Cobalt alloys are also used as colorants in glass, ceramics, and paints. It also occurs in catalysts for the oil industry, as drying agents in paint, and as additive in agriculture and medicine. Cobalt has found a booming application in the preparation of modern batteries, *e.g.* as a supplement for the Ni/CdNi-metal hydride battery, and as the main component in the lithium ion cell ($LiCoO_2$). Cobalt is also used in X-ray generators. Eventually, ^{60}Co is used as a gamma source in the treatment of cancer, for industrial sterilization of medical equipment, and as an external source in radiography and radiation treatments (ATSDR, 2004).

People are often exposed to cobalt since cobalt is widely distributed and commonly used in daily life. Even though food is considered to be the prevailing source of cobalt exposure, the general population are also in contact with cobalt through the use of jewelry, various implants, and other metal products (Fowler, 2016; Hamann et al. 2013). Furthermore, cobalt occurs in blue tattoo pigments (Fowler, 2016) and in cosmetic products. In defiance of legal prohibition of cobalt and cobalt salts in cosmetics, elevated levels of cobalt have been found in eye shadow, face painting supplies, hair cream, and henna dyes (Bocca et al. 2014). Likewise, recent studies reveal that leather goods can contain cobalt and cause cobalt allergy (Fowler, 2016; Leyssens et al. 2017).

2.2.1.1 Application of cobalt in leather goods

Leather is animal hides and skins which have been processed in order to obtain flexibility, toughness, and water tightness. The process goes through several steps, including tanning, dyeing, fat liquoring, and drying[8]. Cobalt is used as mordant for the dyes in the tanning business which is crucial for the dyes to adhere to the leather. The mordant improves the resistance to water and light (Bregnbak et al. 2014). A broad array of dyes is used in the processing of leather including conventional dyes, reactive dyes, premetallized dyes, and acidic dyes.
The increasing demand among the costumers for resistance against water and light has caused a shift from regular dyes and acidic dyes to premetallized and reactive colorants[2]. The supreme properties of premetallized dyes have made them preferable for dyeing of wool, nylon, and silk as well (Zarkogianni et al. 2012). However, these materials are not covered by this project.

There are two types of premetallized dyes, designated 1:1 and 1:2, in which one or two dye molecules is/are bound to a central metal atom, respectively. An example of the structure of a 1:2-premetallized dye is shown in FIGURE 1 in which M designates the metal. Chromium and

[8]https://nzic.org.nz/app/uploads/2017/10/5C.pdf.

cobalt are most often used, but copper, iron and nickel find applications too. There is a tendency for the premetallized dyes to be somewhat brighter than the other types of dyes (Thyssen et al. 2013).

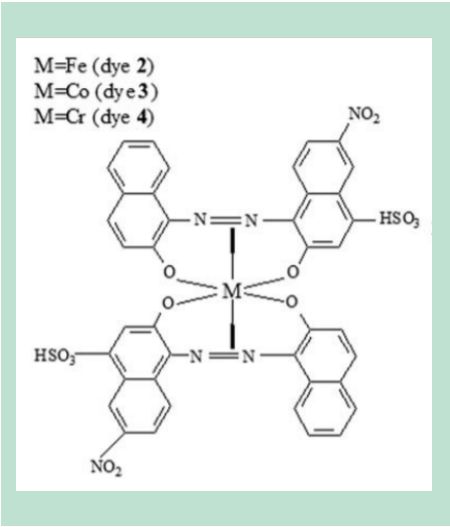

FIGURE 1. Structure of a 1:2-premetallized dye (Zarkogianni et al. 2012)

A series of environmental-labels put demands on the content of cobalt in leather goods. As shown in TABLE 1 both the Ecolabel flower and the German environmental labels put a limit value on the cobalt content of 4 mg/kg. However, the Ecolabel flower only allows an amount of 1 mg/kg in shoes for children under 3 years of age. The Nordic Swan Ecolabel prohibits the addition of cobalt altogether in colorants, dyes, and pigments and does not tolerate the application of metal complexes for dyeing of leather. Furthermore, the swan-label also put restrictions on the presence of impurities in dyes with affinity to fibers. For cobalt the present limit is 500 mg/kg in the pigment[9].

TABLE 1. Limit values for cobalt in leather as demanded by different labelling schemes

Country	Name	Product	Limit value, mg/kg
European Union	The Ecolabel (EU Flower)	Leather – furniture	4
		Shoes	4 (1*)
Scandinavia	The Nordic Swan Ecolabel (Svanemærket)		0**
Germany	The Blue Angel (Die Blaue Engel)	Leather – shoes	4
Germany	SG (Schadstoffgeprüft)	Leather	4

*for children under 3 years of age; ** Prohibition of active cobalt compounds in dyes; prohibition of more than 500 mg/kg impurities in cobalt pigments

2.2.2 Short summary of scientific literature

Even though cobalt has been a recognized allergen for decades, The American Contact Dermatitis Society proclaimed the element ”Contact Allergen of the Year 2016”. This may be explained by new information about the potential sources of exposure to cobalt which has emerged in recent years, leather being among them (Fowler, 2016).

[9]The limit value indicated addresses the purity of the pigment, not the occurrence of impurities in the leather. The concentrations in the final leather product will be much lower.

A case story (Thyssen et al., 2013) describes how a leather sofa has been identified as the source of the cobalt allergy developed by a 66 year old man. The sofa was produced in Northern Italy and had a yellow-brown colour. The analysis of the leather from the sofa revealed a cobalt concentration of 800 mg/kg and a chromium content of 36000 mg/kg. The nickel concentration was < 1 mg/kg. The cobalt content was confirmed by XRF analysis of the upholstery. On this background the authors of the present report contacted a prominent Danish furniture shop and acquired 14 random leather samples in different colours from their assortment. The XRF screening indicated the presence of cobalt in only one of the samples (brown colour). However, chromium was detected in all the samples. None of the 14 samples showed a positive reaction when subjected to a spot-test for cobalt leaching. The samples were not examined by ICP-MS.

In another study, 131 leather samples obtained from 14 different companies producing leather furniture for the US market were screened by use of two methods: The cobalt spot-test and XRF (Hamann et al. 2016). A total of 11 samples tested positive for cobalt either in the spot-test (5 samples) or in the XRF-screening (6 samples). These samples together with a random sample were subsequently analysed by ICP-MS. All six XRF-positive samples (>5% cobalt) contained more than 300 ppm cobalt. At the same time, these 6 samples tested negative in the cobalt spot-test. This discrepancy indicates that the cobalt spot test is unfitted for detection of cobalt in leather although it can be used for identification of cobalt in metal (Thysen et al. 2010). The randomly selected sample tested negative for cobalt in both XRF and spot-test turned out to contain 31 ppm cobalt according to ICP-MS. These findings imply that the real occurrence of cobalt in leather can be much higher than indicated by screening methods. The investigation demonstrates that XRF can serve as an adequate tool when screening for high concentrations of cobalt in leather whereas it is unfit for catching lower concentrations which may still induce skin allergy.

Leather furniture was shown to be the cause of skin allergy in two patients as reported in a case study by Bregnbak et al. (2017). One of the patients developed allergy from exposure to orange-coloured leather cushions with a cobalt content of 802 ppm (2415 ppm chromium and 1270 ppm nickel). For the other patient a brown leather sofa was identified as the source, featuring a cobalt content of 1250 ppm (21000 ppm chromium and 7 ppm nickel). The spot-tests were negative in both cases which emphasizes that this method is unfit for screening of cobalt in leather goods.

Cobalt containing leather is used in other products than furniture. A Swedish study (Naturfredningsforening, 2009) undertook the analyses of 21 pairs of shoes for a range of metals, semimetals and organic chemicals. The shoes were bought in different countries, 11 pairs in Sweden, and 2 pairs in South Africa, Uganda, India, The Philippines, and Belarus, respectively. Cobalt was detected in 20 out of the 21 samples in concentrations in the range 0.5 -16 mg/kg. The concentrations were somewhat lower in the shoes purchased in Sweden, ranging from below the detection limit to 2.6 mg/kg. The highest concentrations were found in the shoes purchased in South Africa (11 mg/kg), The Philippines (16 mg/kg), and India (11 mg/kg).

It has not been possible to identify other studies in which products and materials are subjected to cobalt analyses. However, the need for such investigations has been expressed in several connections (Bregnbak et al. 2014; 2017; Hamann et al. 2016; Thyssen et al. 2013). Several studies demonstrate the connection between exposure to leather and development of allergy for cobalt. A questionnaire study was launched among patients suffering from non-occupational cobalt allergy while not being sensitive to chromium. In this study leather was identified as the most common source for exposure to cobalt (Bregnbak et al. 2014; TABLE 4). Other studies have uncovered cobalt allergy among patients with eczema to be caused by shoes (Chowdhuri og Ghosh, 2007; Horev, 2016; Nardelli et al. 2005; Rani et al. 2003; Warshaw et al. 2007). Furthermore, cobalt allergy has been connected to occupational skin allergy among

workers in the textile- and leather industries (Rui et al. 2010; 2012). A statistical analysis of data from more than 185 000 patients (Uter et al. 2014) showed a correlation between cobalt allergy and "leather" and "shoes" as potential source of exposure and contact. Likewise, a correlation was found between the job description "leather worker" and cobalt allergy. Even if these investigations do not include analyses of cobalt in leather *per se*, they do point to leather as a potential cause for cobalt allergy. This theme is discussed further in Chapter 4.

2.2.3 Information obtained from market operators

More than half (52 %) of the 25 market operators being addressed volunteered to participate in the survey and the queries. However, a great many of the questions were left unanswered since the market operators could not provide the requested information. Thus, information on the volume of leather goods produced/marketed in Denmark is scarce and only few of the operators could provide these numbers. As a consequence, this market survey cannot serve to estimate the consumption of leather and/or evaluate the exposure to cobalt from leather goods in Denmark.

Cobalt in leather

The overall conclusion from the market survey was that business organizations, producers, and retailers do not have knowledge of the occurrence of cobalt in leather products. Neither do they know if leather has been dyed with premetallized colourants, nor if cobalt is used in other processes in the manufacture of leather products.

Dealers and producers do not make demands on the content of heavy metals in leather/leather goods. However, both the slaughterhouse/tannery and a handful of the producers claim that the REACH-regulation has been complied.
Following the contact made with couple of business organisations it is concluded, that none of these possessed information on the use of cobalt in dyeing or other processes in the manufacture of leather products.

Dyeing

On the basis of the feed-back from various producers and retailers it is concluded that the leather applied is received ready-for-use. That is, nobody dyes the leather themselves and they do not know whether cobalt or other metals occur in the dyes or if cobalt is used somewhere else during processing. However, the four distributors of dyes reported that cobalt containing dyes do not form part of their assortment. They did not possess any information regarding premetallized dyes.

Origin of the leather

The majority of the operators (producers of belts, gloves, and bags) in the survey informed that they predominantly import leather from Italy. A single producer referred to his tannery in Holland, which has been addressed by email. However, as of this writing no answer has been received. The producer of horse saddles stated that the leather was bought in Denmark and in England. One business organization reported that upholsterers most often apply leather from Switzerland, Austria, or Germany. Leather from these countries are used for quality furniture, while cheaper furniture usually is manufactured from leather produced in South America.

The slaughterhouse with their own tannery could inform, that pre-tanning treatment is done in Denmark on cattle hides from Northern Germany, Denmark, and Sweden. The hides are subsequently sent to Italy to be finished and dyed according to intended colour and softness.
It is not known, whether it is the very same hides which are received by the producers and dealers in Denmark. Chromium - but not cobalt - is used in the pre-tanning processes in Denmark. The leather is used in clothing, in the interior of cars, etc.

Overall the survey did not provide an estimate of the use of cobalt in leather goods on the Danish market. Italy was the dominating country-of-origin regarding consumer goods made from leather. Although the knowledge among the market operators was limited regarding cobalt and its occurrence in leather products, the concentration of cobalt in leather can be quite high according to the few investigations published to date (Thyssen et al. 2013; Bregnbak et al. 2017). Furthermore, cobalt is frequently found in leather shoes (20 out of 21 investigated; Naturfredningsforening, 2009). The lack of knowledge and attention among the market operators held up together with the limited number of investigations illustrate the need for a comprehensive investigation of the variety of products which have been identified as critical for development of skin allergy in the population.

2.2.4 Quantity and origin of leather goods on the Danish market

Data were obtained from Statistics Denmark and Eurostat in order to obtain a better overview of consumption of leather and leather goods in relationship to country-of-origin. The data are summarized in TABLE 2 and in TABLE 3.

The statistics of yearly turnover is presented in TABLE 2. The table is derived from Eurostats Prodcom Database, which only contains data expressed in monetary units. Data from Denmark exist only for few categories. Consequently, TABLE 2 also displays the total numbers for all EU-28 countries. Supplementary data regarding import and export in Denmark have been obtained from Statistics Denmark and are displayed in units of kilogram for the years 2015 – 2017. These two databases do not use the same nomenclature. Information about the product categories used in the tables is provided in Appendix 2.

Globally ca. 6.0 million. metric tons raw hides are being processed yearly resulting in ca. 522,600 metric tons heavy leather and ca. 1,185 million square metres light leather (ECHA, 2012). For comparison Europe yearly produces ca. 71,700 metric tons heavy leather and roughly 230 million. square metres light leather. That is, the European production of light leather constitutes ca. 19 % of the global production (ECHA, 2012). All numbers are obtained as an average from the years 2001-2003.

The total value of the production in 2016 was 25,751 million € in EU and 112 million € in Denmark. However, it must be emphasized that data about production of leather and leather goods in Denmark is limited. Production of footwear made up almost half the total value of leather goods produced in EU. The main categories for the leather production in Denmark are "raw hides and skins" and "processed leather". In sum they constitute 99 % of the total value of the production. This conclusion can also be derived from the data in TABLE 3, which shows, that Denmark’s export of raw hides and skins has increased significantly in recent years. The export markedly exceeds the import.
The biggest share of raw hides and skins is exported to Italy (data from 2017). The situation is different for the other product categories for which the import volume is 2 - 7 times bigger than the export volume TABLE 3. Footwear is the biggest category among imported leather goods and the shoes come predominantly from Portugal, Germany, and China. Other contractors include Italy, Sweden, India, and Pakistan. Raw hides and skins are predominantly imported from Italy. This is in accordance with the information obtained in the market survey, in which producers and retailers reported that they predominantly receive leather from Italy. It also agrees with earlier reports according to which Italy represents ca. 60-65 % of leather production in EU (ECHA 2012).

With reference to the earlier investigation of the occurrence of chromium III and (VI) in leather goods on the Danish market (MST, 2002), it must be reemphasized that shoe- and clothing producers in most cases buy the leather from abroad. This implies, that the country of origin of the product not necessarily is the same as that of the leather.

TABLE 2. Production of leather goods in Denmark and in Europe

	Production1 2016, (mio. €)	
Product category	**EU-28**	**Denmark**
Raw hides and skins	1,276	67
Manufactured leather	7,018	432
Handbags, suitcases, purses, etc.	4,209	0.02
Accessories incl., gloves, belts, watch straps, etc.,	737	0.53
Footwear	12,511	0.44

[1]Yearly turnover; [2] Data available for a single sub-category only; [3]Data for three out of six subcategories; [4]Data for three out of 11 subcategories.

TABLE 3. Import and export of leather goods to and from Denmark

Product category	**Import /1000 kilo**			**Export /1000 kilo**			**Top countries, import from in 2017**
	2015	**2016**	**2017**	**2015**	**2016**	**2017**	
Raw hides and skins	34	10	13	3	258	2,914	Italy, Spain, Pakistan
Manufactured leather	953	951	1,368	794	632	572	Italy, Brazil, Germany
Footwear with vamp of leather	14,895	17,076	14,522	6,904	5,739	5,768	Portugal, Germany, China
Safety shoes with vamp of leather	1,495	1,817	1,880	329	278	404	Italy, Germany, China
Handbags, suitcases, wallets, etc., with outer side of leather, artificial leather, or patent leather	1,291	1.259	1,505	659	718	767	India, China, Italy
Clothing and accessories to clothing of leather or artificial leather	742	791	686	412	412	422	India, China, Pakistan
Gloves of leather or artificial leather	190	181	185	77	51	70	China, Pakistan, Sweden
Industrial gloves of leather or artificial leather	779	775	818	274	253	252	Pakistan, India, China
Belts and shoulder straps of leather or artificial leather	369	452	333	240	240	195	China, Italy, Morocco
Other goods of leather or artificial leather	560	407	671	167	213	238	India, Sweden, China

Quantity of leather goods on the Danish market and use of these products by the population
Data for production of leather in Denmark indicate that raw hides and skins together with manufactured leather constitute the two main categories, which combined make up for 99 % of the total value of production. However, a major part of hides and skins is exported to other countries, primarily Italy, which also served as the main exporter of manufactured leather to Denmark.

Information about production and use of leather goods in Denmark is limited which obstructs evaluation of the volume of the market and the extent to which the population is exposed to the products. If the quantities of imported goods are considered separately, the three dominating categories are leather footwear, leather safety shoes, and bags/suitcases.

Footwear makes up for 70 % of the total volume of leather imports and may therefore be expected to be the category most widely used by the population. This estimate is supported by an earlier assessment of sales of leather shoes in Denmark which showed that each household spent 405 DKK on leather shoes in 2008 corresponding to ca. 0.7 pairs of leather shoes per household (MST, 2011). Quantities of the different products categories are given in kilos in TABLE 3. However, it should be noticed that the number of products depend on the design and size of the product.

Exposure of population to cobalt from leather goods

The results from the survey do not permit identification of specific products in which premetallized dyes were used or for which an elevated content of cobalt otherwise could be predicted. Therefore, it is difficult to evaluate exposure of the population to cobalt from existing data. As indicated above, footwear must come in as a highly important and potential source with reference to the massive and wide application by the population and long exposure times. Leather furniture is another category which likewise may be important as a source of cobalt exposure for the population. TABLE 2 and TABLE 3 do not include leather furniture, since the NACE codes for furniture does not differentiate for leather products. Thus, the quantities of produced and imported goods are unknown. However, the literature provides several cases of skin allergy being induced by elevated amounts of cobalt in leather furniture. Other cobalt containing products may be considered as potential sources for exposure. When evaluating these products attention should be turned to normal habits for use and whether prolonged and close contact with the skin is expected. These aspects are discussed in Chapter 4.

3. Introductory health- and exposure assessment

The content of chromium (VI) in leather is already subject to regulative limits and a risk assessment has been performed by the European Chemicals Agency (ECHA). Thus, it is only relevant for the present project to carry out an evaluation of the potential hazards from using cobalt containing leather.

3.1 Harmful health effects of cobalt

Exposure to cobalt compounds can have a range of harmful effects on human health. Water soluble cobalt chemicals are subject to the following classifications according to EU:

Carc. 1B, H350i	*(May cause cancer by inhalation)*
Muta. 2, H341	*(Suspected of causing genetic defects)*
Repr. 1B, H360F	*(May damage fertility)*
Acute Tox. 4, H302	*(Harmful when swallowed)*
Skin Sens. 1, H317	*(May cause an allergic skin reaction)*
Resp. Sens. 1, H334	*(May cause allergy or asthma symptoms of breathing difficulties if inhaled)*

As indicated, the cobalt ion is considered to have carcinogenic and mutagenic properties, to be a toxin for reproductive capabilities, and to cause allergic reactions in skin and bronchi. However, cobalt compounds have been found to be carcinogenic only by inhalation and cobalt is not considered carcinogenic by dermal exposure or oral intake.

Allergy

Cobalt (II)-compounds (like nickel (II)- og chromium (VI)-compounds) may cause allergy in the skin upon direct contact. Therefore, this kind of allergy is often termed *contact allergy*. Skin allergy may be induced when chemical substances penetrate the skin and interact with the immune system. There are no symptoms when a person is exposed to the allergen the first time. This is called the "induction phase" during which the immune system prepares for a reaction, the next time the person is exposed. Thus, when this "provocation" occurs, the allergic reaction manifests as eczema, flushing, vesiculation, and eventually sores in the skin, which starts on the point of contact with the object leaching cobalt.

Minute quantities of an allergen like cobalt can induce skin allergy and even smaller doses may be needed to trigger a reaction upon re-exposure. Thus, cobalt has been revealed as a powerful allergen in animal studies. Cobalt allergy often occurs together with allergy to chromium (VI) and nickel. Among patients with eczema 6 % of the women and 2 % of the men were allergic to cobalt (National Allergy Research Centre, Denmark, 2018).

Beyond skin allergy, cobalt can induce respirational allergies when particles are inhaled. Cobalt compounds (like cobalt containing salts, dyes and pigments) are solids with negligible vapor pressure. That is, the common person will generally not be exposed to cobalt particles, unless some product containing cobalt is either ground or sprayed on the location. It seems unlikely that inhalation of cobalt containing particles can occur from manufactured leather goods. It is consequently considered irrelevant to assess the risk of respirational allergies from this source.

Further effects
Other toxic reactions like acute poisoning and damage on the ability to reproduce require much higher doses than the critical exposure needed for induction of skin allergy and triggering of eczema upon re-exposure. Greater amounts of cobalt must penetrate the skin, be distributed in the body and reach critical concentration in the target organ before toxic effects can occur.

Furthermore, the carcinogenic effect of cobalt compounds is not considered relevant in connection with leather goods since any mangling effect is conditioned by respiratory intake of particles.

Exposure to cobalt compounds and action levels
Cobalt is an element in the essential B12 vitamin. The average daily intake of cobalt by the population is 5 - 40 µg (WHO 2006). There is no information on any consequences for the health from elevated intake of cobalt. Neither the European Food Safety Authority, EFSA nor The World Health Organization, WHO has assigned a minimal threshold for the oral intake by humans. In the REACH-registration of the chemical *cobalt dichloride*, the registrar has estimated the tolerable level for the daily, oral intake to be 120 µg/kg body weight. This corresponds to 9000 µg cobalt a day for an adult.

As stated, even small concentrations of cobalt can cause allergic symptoms like eczema in the exposed skin area.
For instance, Fisher et al. (2015) reports that 10 % of a group of cobalt allergics will react to an exposure of 0.066 – 1.95 µg cobalt/cm^2 skin. This amount corresponds to the action of a cobalt solution with the concentration 31 - 259 mg cobalt/L.
While it is possible to determine thresholds for causing allergic reactions upon re-exposure (elicitation), it is difficult to estimate what level of exposure is needed to induce the sensitivity in the first place. Cobalt allergy often occurs simultaneously with allergy to chromium and nickel.

As outlined in the survey below, it is documented in the literature that exposure to cobalt containing leather goods can cause allergy, while. there are no reports on other health hazards like potential carcinogenic effects, induction of respiratory allergic reactions, or toxicological damage to reproduction capabilities from the use of leather goods. This makes sense since no more than a few µg cobalt on the skin can cause allergy while systemic daily oral intake of ca. 9000 µg cobalt is considered safe for humans.

3.2 Health hazards from cobalt in leather goods

A screening of the existing literature was performed on the purpose to obtain an updated survey of the health hazards from cobalt in leather. The basis has been provided by the know-how accumulated by the National Allergy Research Centre, Denmark, where researchers have carried out the internationally most comprehensive investigations of occurrence of cobalt in leather goods. Further searches have been performed on the internet using keywords, *e.g.* ”cobalt”, ”leather”, ”clothing”, ”shoes”, ”furniture”, ”toxic”, ”allergy”, ”sensitisation”, ”threshold”, ”elicitation”.

This search combined with a screening of the reference lists in prominent publications narrowed into the selection of 20+ articles. Among these, some were determined to be of particular relevance for assessment of cobalt allergy risks from leather goods.
These are listed in the table below together with the primary conclusions.

TABLE 4 Literature survey regarding health aspects of cobalt in leather

Purpose of investigation/ *Reference*	Method and Results
Dermal uptake of cobalt and reactions in the skin	
In vitro percutaneous absorption of cobalt Filon et al. (2004)	*In vitro* test for determination of dermal penetration of cobalt into human skin by means of Franz' diffusion cell test. The test demonstrated, that finely grinded cobalt powder (particle diameter ≤ 2 µm) mixed with artificial sweat can pass through human skin, presumably as free, oxidized metal ions. The speed of penetration was calculated as 0.0123 µg cobalt per cm^2 skin per hour.
Elicitation threshold of cobalt chloride: analysis of patch test dose–response studies *Fischer et al. (2015)*	A review of the results from six investigations of allergic reactions from cobalt sensitive allergics to dermal exposure of cobalt solutions. ED10 (*i.e.* the critical dermal dose for triggering an allergic reaction among the 10 % most sensitive) was found to be 0.066 – 1.95 µg cobalt per cm^2 (corresponding to exposure to a concentration of 31 – 259 mg cobalt/L).
Danish data regarding cobalt allergy and leather	
Allergic contact dermatitis caused by cobalt in leather – clinical cases *Bregnbak et al. (2017).*	Two cases of cobalt allergy are reported: A 12-year-old boy had developed skin eczema and allergy to cobalt as a consequence of exposure to leather cushions on kitchen chairs containing 802 mg/kg cobalt, 2415 mg/kg chromium, and 1270 mg/kg nickel. The boy was not allergic to nickel and chromium. A 70-year-old man had developed skin eczema and allergy to cobalt as a consequence of exposure to a leather sofa containing 12500 mg/kg cobalt, 21 000 mg/kg chromium and 7 mg/kg nickel. The man was not allergic to nickel and chromium.
Association between cobalt allergy and dermatitis caused by leather articles – a questionnaire study *Bregnbak et al. (2014)*	In order to clarify the source to the dermal reactions, a questionnaire was sent out to 1) 183 patients with dermatitis who was allergic to cobalt but not to chromium, and 2) 621 patients with dermatitis who was allergic to neither cobalt nor chromium. Leather was identified as the most common source for dermatitis among cobalt allergics (25.4%). Over all the cobalt allergics reported the most severe inconveniences and skin reactions relative to the other patients with dermatitis.
Allergic contact dermatitis caused by cobalt in leather – clinical case *Thyssen et al. (2013)*	A 66-year-old man had developed skin eczema and allergy to cobalt following exposure to a leather sofa containing 0.8 % cobalt and 7.8 % chromium in the leather (the content is given as % of the dry weight of the leather after subtraction of the carbon content).
Cobalt allergy and shoes	
The relation between foot dermatitis and the causative allergens in shoes *Nardelli et al. (2005)*	Analysis of data from 1168 patients with foot dermatitis at a Belgian allergy centre was carried out in order to identify the most important chemicals for the occurrence of foot dermatitis. Out of the 1168 subjects, 132 patients showed allergic reaction to a patch test with cobalt chloride concomitant to chromium. Only a patch test with potassium chromate showed a greater fraction (253 patients) of allergic reactions. Women were over-represented among the cobalt sensitive patients. Reactions were observed more frequently on the top side than on the underside of the foot. The authors identified cobalt containing pigments and dyes in the shoes as the source of the contact dermatitis.
Assessment of the frequency and causes of allergy from shoes causes *Warshaw et al. (2007)*	Analysis of data from 10061 North American dermatitis patients who were subjected to patch tests. Among these, a total of 109 patients were found to be allergic to chemical agents in shoes. Cobalt was found to be the third most common allergen, accounting for ca. 13% of the positive cases of contact dermatitis.
Cobalt allergy in the leather industry	

Frequency of sensitization to cobalt (and other metals) in relation to occupation. dermatitis. **Rui et al. (2010 og 2012)**	These two studies cover data from patch tests on 15,217 patients in Northern Italy. It was shown that 11.2 - 13 % among the women and 8.4 – 9.7 % among the men displayed allergic reactions to cobalt. 8.6 % among the women and 4.5 % among the men were allergic to cobalt in combination with allergy to nickel and/or chromium. 2.6 % among the women and 3.1 % among the men showed allergy to cobalt exclusively. The odds ratio for having cobalt allergy only and cobalt allergy in combination with nickel and chromium was significantly higher among employees in the leather industry, with OR 1.85 and 2.19 respectively. Women contributed predominantly to this enhanced frequency in the leather industry.

It is apparent from the data in the table that cobalt can penetrate human skin as cobalt ions (Filon et al., 2004) and induce cobalt allergy. Provocative tests on cobalt allergics have demonstrated that exposure by 0.066 – 1.95 µg cobalt per cm^2 (corresponding to the action of a cobalt solution with a concentration of 31 – 259 mg kobolt/L) can trigger allergic skin reactions among the most sensitive cobalt allergics (Fischer et al., 2015). These results can be applied to evaluate the migration data obtained for various leather products, since migration is reported in units of µg cobalt per cm^2. It has been discovered that a cobalt amount as small as 800 mg/kg in leather can induce cobalt energy, since this concentration in a leather cushion did indeed cause a child to become allergic to cobalt.

A series of Danish and international publications documents the risk of developing allergies from exposure to cobalt containing leather goods, *e.g.* furniture and shoes (Bregnbak et al. 2014 and 2017; Thyssen et al. 2013; Nardelli et al. 2005; Warshaw et al. 2007). An increased occurrence of cobalt allergy was observed among employees in the leather industry (Rui et al. 2010 and 2012). This result supports the supposition that leather is a prominent source of exposure to cobalt.

3.3 Exposure scenarios for use of leather goods

Since the present project aims at determining the leaching of cobalt from leather goods into artificial sweat, the exposure scenario applied to the risk assessment is fairly simple.

The level (in units µg cobalt/ cm^2 skin) of causative re-exposure necessary to trigger an allergic response in allergics is obtained from the literature. This level is determined as 0.066 – 1.95 µg cobalt per cm^2 among 10 % of the most sensitive cobalt allergics.

Likewise, the results from migration test are expressed as the amount of cobalt being leached per cm^2 leather. This migration value can be compared with the critical level of exposure as described above. If these values are close, we may consider it a worst-case scenario which implies a health risk. Consequently, a more detailed evaluation of the exposure scenario is required since various circumstances regarding the product and its use may influence the action (*e.g.*, duration of skin contact per day, any textile covering the leather, eventual soaking of the leather when used, etc.).

4. Selection of products for analysis

Two aspects were considered when selecting samples for quantitative analysis. A primary aim was to obtain further information about the amount of cobalt in common leather goods and the health hazards associated with this. Secondly, chromium content should be determined in order to decide whether existing limits for chromium (VI) are respected. Thus, this chapter provides guidelines for selection of products for cobalt analysis on the background of the literature survey. The resulting selection also reflects the wish to investigate the chromium (VI) contents.

4.1 Recommendations regarding cobalt analyses

The results from the literature survey does not allow for *a priory* classification of products as either cobalt-containing or cobalt-free.
However, the preliminary insight from the literature implies that the amount of cobalt in some products, *e.g.* furniture, may be high. The literature also shows that smaller - but still critical - concentrations of cobalt occur in shoes. The literature did not provide any information on cobalt in other types of leather goods. Inquiries among market operators did not provide any further information. It must be concluded that only a rudimentary knowledge and attention prevails regarding the occurrence of cobalt in leather goods and the application of premetallized dyes.

From the literature survey it must also be concluded that the spot-test is insufficient as a screening tool for determination of cobalt in leather goods. XRF is a useful means of analysis for screening of products with high cobalt concentrations. However, false negative results were observed at low - but still critical - concentrations. This is an important realization since XRF is used for identification of the products to be subjected to subsequent chemical analysis. The following criteria have been applied in the selection of products for chemical analysis:

- Since the main focus of the project is on skin allergy, the screening should concentrate on products which are used often (daily or many times during a day) in close contact with the skin. Based on the considerations described regarding the limitations on chromium in leather goods (ECHA, 2012), the following categories may be included:
    - Shoes
    - Clothes, including trousers, skirts, jackets, coats, gloves, hats, leather underwear, etc.
    - Working clothes
    - Handbags, purses
    - Watch straps and jewelry
    - Furniture, including sofas, chairs, armchairs, leather bolsters, etc.
    - Car interior products, *e.g.* wheel covers, upholstery
    - Bicycle saddles of leather
    - Dog leashes, riding equipment with close contact to the rider (*e.g.*, bridle, riding breeches, whip with a leather handle, etc.)
    - Covers for mobile phones and iPads

Sandals and shoes worn with bare feet, watch straps, trousers, gloves, furniture, and bolsters come in close contact with the skin from which the sweat may assist in release of cobalt from the leather. Furthermore, clothings like shoes, jackets, trousers and gloves may be soaked in the rain whereby the leaching of cobalt may be greatly enhanced.

- Products used by children

Skin allergy is for life. Therefore, particular attention should be directed to:

- clothing and shoes for children
- furniture for children
- leather toys, handbags, purses, rucksacks, etc. for children

- In the selection process it is important to choose a range of representative products from different producers and different price levels.

- Products which gave negative results in the XRF screening.

  As mentioned, XRF screening can only be considered a good screening tool among leather products with high content of cobalt. Since cobalt contact eczema in some cases can be induced at concentration as low as 30 mg/L (Fisher et al. 2015) it is recommended that a number of products with negative XRF response are included in the selection for further chemical analysis. It is important that all product categories and price ranges are represented here as well.

4.2 Products selected for chromium (VI) and cobalt analysis

The products for analysis of chromium (VI) and cobalt were selected by the chemical inspection of the Danish Environmental Protection Agency in consideration of the guidelines provided above taken together with the results from the XRF screening. The chemical inspection has performed XRF screening of a series of leather products and identified the products which contained chromium. None of the products gave positive response for cobalt in the XRF screening.

A total of 74 products were selected for chromium (VI) and cobalt chemical analysis, including 33 pairs of shoes for adults, 7 shoes for babies/children, 1 shoe sole, 17 handbags/purses, 1 pair of trousers, 1 pair of gloves, 6 belts, 6 watch straps/bracelets, 1 cushion, and 1 keystring. The total number of analyses was 94 since several of the shoes were analysed for chromium in both the vamp and the inner sole.

Since these categories of products did not include furniture - which may constitute an important source of exposure to cobalt - several major retailers of furniture were contacted and requested to submit samples of leather used in furniture sold on the Danish market. Three retailers submitted a total of 34 samples in several different colours. The furniture samples were only analysed for cobalt and do not form part of the chemical inspection supervision of chromium (VI) contents.

5. Quantitative analysis

This chapter describes the methods and results from quantitative analysis for chromium (VI) and cobalt in the 74 products (94 leather samples) and results from the analysis for cobalt in the supplementary 34 leather samples from furniture. Since the amount total-chromium is a quantity obtained as part of the analysis for cobalt, this number was also obtained for the original 94 leather samples.

5.1 Analytical method

All determinations were performed in duplicate. The amount of volatile material was determined in each sample as a necessary condition for calculation of cobalt, total-chromium, and chromium (VI) as mg/kg dry matter.

5.1.1 Dry matter

On receipt of the samples, each item was examined. The essential part(s) for analysis was/were selected and cut up in pieces of 3-5 mm cf. ISO4044:2017. The leather sample was weighed out at room temperature and heated to 102 °C for 8 hrs. After cooling the dry weight was determined and the amount of volatile material obtained by subtraction cf. ISO4684. The weight of the weighing pan was subtracted in both measurements.

5.1.2 Cobalt

A subset of the leather for cobalt analysis was weighed out and subjected to a digestion solution consisting of diluted *aqua regia* (nitric acid and hydrochloric acid). A rhodium compound serving as internal standard was added. The extraction was accomplished in a microwave oven. The extract was diluted before analysis by ICP-MS/MS. The concentration of cobalt was obtained from a calibration curve prepared from a certified standard. The method is a modified version of DS/EN 259:2003. The detection limit for the method is 1.0 mg/kg dry matter and the uncertainty is ± 20 %. At concentrations close to the detection limit the uncertainty is ± 50 %.

5.1.3 Total-chromium

A subset of the leather was weighed out for analysis of total-chromium and subjected to a digestion solution consisting of diluted *aqua regia* (nitric acid and hydrochloric acid). A rhodium compound serving as internal standard was added. The extraction was accomplished in a microwave oven. The extract was diluted before analysis by ICP-MS/MS. The concentration was obtained from a calibration curve prepared from a certified standard. The method is a modified version of DS/EN 259:2003. The detection limit for the method is 5.0 mg/kg dry matter and the uncertainty is ± 20 %. At concentrations close to the detection limit the uncertainty is ± 50 %.

5.1.4 Chromium (VI)

A subset of the leather was weighed out for analysis of chromium (VI). A solution of dipotassium hydrogen phosphate was prepared and pH adjusted to 8. The solution was flushed with nitrogen in order to remove oxygen. The leather sample was added to the phosphate buffer solution and extracted on a shaking table with a cap on. After 3 hrs the leather was removed by filtration and pH was measured. Any interfering colorants which may be visible at this stage was removed by passing the solution through an SPE column with florisil. A mixture of phosphoric acid and 1,5-diphenylcarbazide was added. The mixture was allowed to react for 15 min before it was analysed by means of UV/VIS spectrophotometry at 540 nm. The concentration of chromium (VI) was obtained from a calibration curve prepared from a standard chromium (VI) solution in the dry weight determination procedure. The method is based on ISO 17075-1:2017. The detection limit for this procedure is 1.0 mg/kg dry matter

and the uncertainty is ± 25 %. At concentrations close to the detection limit the uncertainty is ± 50 %.

5.2 Results from quantitative analysis

5.2.1 Chromium (VI) and total-chromium

The results from quantitative analysis of total-chromium and chromium (VI) for all 94 leather samples are presented in Appendix 3. The concentration of chromium (VI) was less than the detection limit in many of the samples. The results from the samples for which the concentration in both duplicates were above the detection limit are presented in TABLE 5. The numbers were obtained as an average of the two determinations.

In 10 out of 21 leather samples the concentration of chromium (VI) was higher than the limiting value of 3 mg/kg dry matter. Three samples, one above (nr 82) and two below the limiting value (nr. 106 and 115) are lying within the uncertainty of the analysis method and are therefore not regarded as violations. The three highest measured values were found in handbags (samples 59, 64 and 123). A chromium content above the detection limit was found in 3 out of 8 shoes for babies/children. The concentration was higher than 3 mg/kg in one of them.

All instances of chromium found in the XRF-screening procedure were confirmed by the quantitative analysis of total-chromium. However, the XRF-negative samples were not subjected to quantitative analysis, so there is no basis for evaluating XRF as a screening tool for total-chromium in leather goods. Furthermore, the quantitative correlation between the XRF-results and total-chromium was rather weak (FIGURE 2, R^2=0,3), likewise between the XRF-results and chromium (VI) (data not shown; R^2=0,2).

TABLE 5 Content of total-chromium and chromium (VI) in different leather products. Values higher than 3 mg/kg are highlighted in **bold**.

		Concentration, mg/kg dry matter[1]		
Sample # - cf. Appendix 3	**Product**	**Total-chromium XRF**	**Total-chromium Chem. analysis**	**Chromium VI**
Footwear				
61	Wooden shoe, vamp, black	5283	15500	1.5
65	Man's shoe, vamp, black	9047	24000	**4.7**
79	Baby's shoe, pink	4002	20000	1.8
82	Nubuck slippers – inner sole	2970	8750	2.2
82	Nubuck slippers – vamp	16487	30500	**3.4**
83	Baby's shoe, black	9065	31500	2.0
89	Baby's shoe, blue	8644	18000	**4.0**
90	Nubuck man's shoe, blue inner sole	7604	21500	**5.4**
92	Man's shoe, black, inner sole	n.d.	17000	1.6
96	Man's shoe, grey, vamp	9163	11500	2.0
106	Home sandal – inner sole	8610	31500	2.9
115	Ladies' boot, vamp, brown	6292	20500	2.5
116	Shoes, brown, vamp	8105	12500	2.0
121	Flip-flops, red, vamp	7143	16000	5.2
Handbags and purses				

59	Handbag, blue	11175	25000	**16**
63	Handbag, black	7041	20500	1.3
64	Handbag, brown	12465	25000	**28**
123	Handbag, brown	12979	22000	**11**
Belts and straps				
69	Belt, brown	497	22500	**4.0**
128	Watch strap	6564	9050	**4.8**
132	Keystring	6330	20500	1.6

n.d. – not determined. [1]XRF is reported in mg/kg, *i.e.* without prior drying

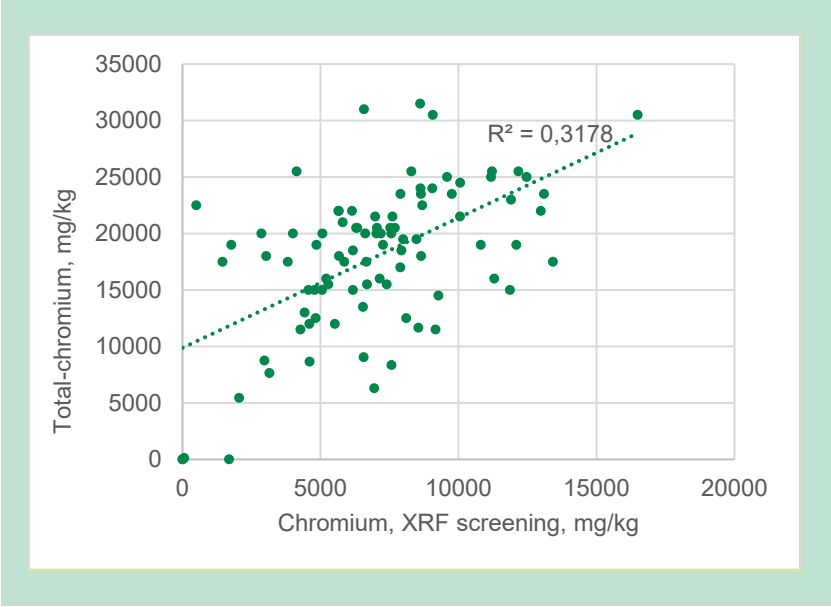

FIGURE 2 Correlation between total-chromium determined by quantitative analysis (y-axis) and XRF-screening (x-axis).

5.2.2 Cobalt

The XRF screening did not return any readings above the detection limit for cobalt (Appendix 3). However, quantitative analysis of cobalt was applied to the products selected for chromium (VI) analysis together with the 34 leather samples obtained from furniture production. The latter were not screened by XRF. The values obtained - that is, readings above the detection limit - are displayed in TABLE 6. There was no correlation between the contents of cobalt and chromium determined in the leather products (data not shown).

Readings above the detection limit revealed the occurrence of cobalt in 29 among the 128 leather samples, corresponding to 23 %. The numbers are provided in TABLE 6. All were obtained as an average of duplicate measurements. The greatest fractional occurrence of cobalt was detected among "handbags and purses" where 35 % contained a detectable amount of cobalt. In the category "belts and straps" 31% of the products contained cobalt.
However, the concentrations were fairly low. The highest concentration of 153 mg/kg was found in a furniture sample of grey nubuck leather. Relatively high concentrations were also found in a few parts from footwear, showing a maximum value of 73 mg/kg.

TABLE 6 Content of cobalt in leather goods

Sample # - cf. Appendix 3	Product	Concentration, mg/kg dry weight[1]	
		Cobalt XRF	Cobalt Chemical analysis
Footwear			
68	Slippers, gold, vamp	<LOD	1.1
75	Shoe, nubuck, sole	<LOD	42
76	Baby's shoe, dark blue	<LOD	1.8
86	Baby's shoe, brown, vamp	<LOD	2.1
87	Children's sandal, inner sole	<LOD	2.3
92	Man's shoe, black, inner sole	<LOD	73
93	Ladies' shoe, brown, vamp	<LOD	1.6
95	Ladies' shoe, blue, inner sole	<LOD	3.0
110	Ladies' shoe, purple, vamp	<LOD	1.3
115	Ladies' boot, brown, vamp	<LOD	12
116	Shoe, brown, vamp	<LOD	1.4
117	Boot, brown, vamp	<LOD	6.9
121	Flip-flops, red, inner sole	<LOD	6.2
122	Flip-flops, gold, vamp	<LOD	4.5
Handbags and purses			
74	Belt-bag, black	<LOD	11
99	Purse, blue	<LOD	3.4
100	Purse, black	<LOD	2.5
123	Handbag, brown	<LOD	1.4
129	Purse, brown	<LOD	2.7
130	Purse, brown	<LOD	2.2
Belts and straps			
120	Watch strap, black	<LOD	8.8
125	Bracelet, black	<LOD	13
128	Watch strap, red	<LOD	6.4
132	Keystring	<LOD	2.7
Furniture			
11.A	Upholstery leather – Nubuck grey	n.d.	153
18.A	Upholstery leather – Royal, beige	n.d.	54
3	Upholstery leather – grey/silver	n.d.	2.3
4	Upholstery leather –brandy	n.d.	1.3
9	Upholstery leather –cognac	n.d.	2.4

n.d. – not determined; <LOD – below the detection limit. [1]XRF is reported in mg/kg, *i.e.* without prior drying

5.3 Conclusions from analysis

The concentration of chromium (VI) was above the regulative limit of 3 mg/kg in 11 % of the leather samples investigated. The three highest values, 28 mg/kg, 16 mg/kg and 11 mg/kg, were found in handbags. However, the concentration of total-chromium was high in most samples. There was no correlation between the amounts of total-chromium and chromium (VI) in the leather samples.

All the findings from the XRF screening were confirmed qualitatively by chemical analysis. But in quantitative terms, only a weak correlation was observed between XRF-readings and the concentrations obtained from the chemical analyses of total-chromium. XRF-screening for cobalt did not return any detectable signal for any of the samples. However, the chemical analysis revealed the presence of cobalt in 23 % of the samples. These findings are in accordance with the literature where XRF screening has been found to be inadequate for determination of cobalt in leather, especially at low concentrations.

Cobalt was found in all product categories. The highest amounts were found in handbags, and purses, and watch straps and bracelets. Concentrations were found in the range from <1 mg/kg to 153 mg/kg. However, the maximum concentration detected in leather from furniture was far lower than values reported in the literature when the furniture had been investigated as a potential source of cobalt allergy (Bregnback et al. 2017; Thysen et al. 2013). On the other hand, the concentrations found in footwear match the results from the Swedish study referred to above (Naturfredningsforening, 2009).

Only one pair of trousers and one pair of gloves were investigated. The amount of cobalt was below the detection limit in both cases. With this limited selection, it remains to draw any conclusions about leather clothing as a potential source of cobalt exposure. By wearing leather clothing a close contact with the skin is obtained, where sweat from the skin may promote the leaching of cobalt and therefore enhance exposure. Thus, a more extensive study on greater selection of products is recommended.

Some product categories were mentioned in Chapter 4, which have not been investigated in the present project, *e.g.* covers for mobile phones and iPads, products for automobiles and bycicles, products for animals, toys, etc. It is evident that no conclusions about cobalt content in these categories can be drawn yet.

6. Analysis of cobalt migration

Following the quantitative analysis of cobalt in the different leather products, the results were evaluated by Medico and Danish EPA. Subsequently, 10 leather products were selected for migration analysis according to DS/EN 1811:2011+A1:2015.

6.1 Selection of products for migration analysis

Ten products were selected for analysis of cobalt migration including the 7 samples which were found to contain more than 10 mg/kg. In addition, 3 samples were selected among those found to contain a detectable amount of cobalt. Thus, two products for children (sandals and shoes) were selected together with a product for which lengthy contact with the skin is anticipated (watch strap).

6.2 Method

A sample the size of 1 x 1 cm was cut out of the leather. The back of the leather was sealed with lacquer to allow migration to occur from the contact surface only. Any wax, fat, or grease was wiped off the surface. Subsequently, the leather piece was placed in a container and covered with artificial sweat, that is, an aqueous solution sodium hydroxide, lactic acid, and urea. The pH was adjusted to 6.5 with sodium hydroxide. The mixture was left for 168 hrs (7 days) at 30 °C after which the extract was analysed for cobalt by means of ICP-MS/MS.

6.3 Results from migrations analysis

The results from the migration experiments are shown in TABLE 7. For comparison, the column to the uttermost right provides the dry weight cobalt content from TABLE 6.

Cobalt was detected in the migration solution for 6 out of the 10 leather samples investigated. There was no correlation between leaching of cobalt and the amount of cobalt in the leather (FIGURE 3). The highest concentration of cobalt in the extract (corresponding to 0.44 µg/cm^2/week), was found for a ladies' boot with a dry weight content of 12 mg/kg. On the other hand was cobalt concentration in the extract from upholstery leather, which had the highest dry weight content, as low as 0.09 µg/cm^2/week.

TABLE 7 Migration of cobalt from different leather products

Sample # - cf. Appendix 3	Product	Cobalt migration (µg/cm^2/week)	Cobalt content (mg/kg dry weight)
Footwear			
75	Nubuck shoe sole	<0.05	42
76	Baby's shoe, dark blue	<0.05	1.8
87	Children's sandal, black, inner sole	<0.05	2.3
92	Man's shoe, black, inner sole	0.27	73
115	Ladies' boot, vamp	0.44	12
Bags and purses			
74	Belt bag, black	<0.05	11
Belts and straps			
125	Bracelet, black	0.33	13

128	Watch strap, red	0.07	6.4
Furniture			
11.A	Upholstery, nubuck, grey	0.09	153
18.A	Upholstery, Royal, beige	0.13	54

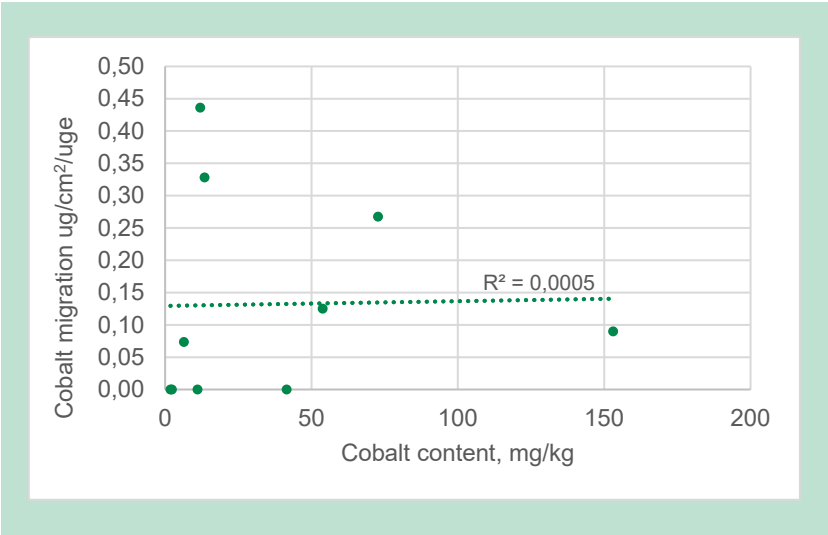

FIGURE 3 Correlation between migration of cobalt into artificial sweat and cobalt content in the dry matter.

7. Risk assessment

In this chapter the knowledge of the health risks and dose-response relationships are related to the results from the migration analysis in order to assess the risks posed to the consumers from using leather products.

7.1 Dose-response relationship

As enumerated in TABLE 4, Chapter 3, cases has been reported in Denmark of cobalt allergy being induced from contact with upholstery in leather furniture containing cobalt amounting to 802 mg/kg and 1250 mg/kg, respectively (Bregnbak et al. 2017). However, the measurements reported above indicate that there is no proportional relationship between the amount of cobalt in the leather and the leaching from there. Thus, it is not possible to assess the risk for the development of skin allergy solely from the amount of cobalt in the product. Induction of skin allergy as well as the subsequent provocation of dermatitis upon repeated exposure will therefore be estimated on the basis of the amount of cobalt/cm^2 which the skin is exposed to.

No data exists allowing for an estimate of the critical exposure required for induction of the allergic condition (Chapter 3). However, the minimum exposure needed to trigger the symptoms in the allergic patients has been determined. This is called the *minimum elicitation threshold*. Since elicitation is considered to be more sensitive than induction, a risk assessment based on the minimum elicitation threshold will also be protective against induction.

As mentioned in Chapter 3, provocation tests on cobalt allergics have demonstrated that exposure to 0.066 – 1.95 µg cobalt per cm^2 (corresponding to the action of a cobalt solution containing 31 – 259 mg cobalt/L) can trigger dermatitis in 10 % (ED10) of the most sensitive cobalt allergics (Fischer et al., 2015). Fisher et al. (2015) base their ED10 value on a closer inspection of 5 studies, in which provocation tests were performed using different levels of exposure. The low-end value ED of 0.066 µg cobalt per cm^2 originates from a study providing an exceptionally wide 95 % confidence interval (from 0.00035 to 0.,35 µg/cm^2, *i.e.* a factor of 1000), for which reason the ED quoted is subject to a great uncertainty (Study #4 in TABLE 8 below).

TABLE 8 ED10 values estimated by Fisher et al. 2015.

	Study #1	Study #2	Study #3	Study #4	Study #5
ED10 (µg/cm^2)	0.647	0.441	0.571	0.0663	1.95
95% confidence interval (µg/cm^2)	0.091 – 1.6	0.096 – 1.2	0.22 – 1.1	0.00035 -0.35	0.93-3.4
Width of confidence interval (97.5% value/ 2.5% value)	17.6	12.5	5	1000	3.6

The range for the other four (#1,2,3, and 5) ED10 values is from 0.441 to 1.95 µg/cm^2 and the width of the corresponding 95 % confidence intervals varies from 3.6 to 17.6. Thus, they are subject to much smaller uncertainty. An ED10 value in the interval 0.441 - 1.95 µg cobalt/cm^2 is therefore considered the most reliable estimate. Furthermore, Fisher et al (2015) report that the experience with nickel has demonstrated, that compliance with an ED10 threshold for induction of symptoms has served as a fairly efficient protection against induction of new instances of nickel allergy (Fisher 2015). The same effect can be expected for cobalt.

Since the migration tests described in Chapter 6 report the leaching from the leather in units of µg/cm^2, the release from the individual leather goods can be compared to the ED10 of 0.441 – 1.95 µg cobalt per cm^2 found to trigger dermatitis in 10 % of the most sensitive cobalt allergics.

If determination of a genuine *DNEL* value (Derived No Effect Level) is subject to great uncertainty, the REACH guidelines prescribe that it may be substituted with a *DMEL* value, *i.e.* a Derived Minimal Effect Level.

DMEL for cobalt in contact with skin is determined in the present project to 0.441 – 1.95 µg cobalt per cm^2.

7.2 Assessment of exposure

In this section the potential exposure to cobalt experienced by a user of the product is evaluated.
Referring to TABLE 7, the leaching of cobalt from the side of the leather in contact with the user was determined for different products as:

Man's shoe, black (inner sole):	*0.27 µg Co/cm^2 / week*
Ladies' boot (vamp):	*0.44 µg Co/cm^2 / week*
Bracelet, black:	*0.33 µg Co/cm^2 / week*
Watch strap, red:	*0.07 µg Co/cm^2 / week*
Upholstery leather, grey:	*0.09 µg Co/cm^2 / week*
Upholstery leather, beige:	*0.13 µg Co/cm^2 / week*

A number of circumstances must be considered when evaluating the risks of exposure from the individual products, *i.e.*:

- direct or indirect contact with the skin,
- frequency of skin contacts,
- duration of the individual skin contacts,
- part of the body/thickness of skin,
- risk of moistening (sweat) of the leather,
- migration potential (µg Co/cm^2/week) of the leather product.

These parameters (except migration potential) enter into the assessment by means of a subscore value from 1 to 3 assigned to each. A subscore value of 3 represents the highest potential for exposure whereas a value of 1 represents the lowest. The parameter scores for each product - except the migration score - are summed and multiplied by the migration score for the leather product.

The red watch strap is assigned a migration score of 1 corresponding the lowest migration (0.07 µg Co/cm^2/week) determined, whereas higher scores are assigned to other products relative to the red watch strap. For example, the vamp of the ladies' shoe is assigned the migration score 6.3, obtained as the ratio between the migration value for the ladies' shoe of 0.44 µg Co/cm^2/week and the migration value for the red watch strap of 0.07 µg Co/cm^2/week.

TABLE 9 shows the individual products and their subscore values for the parameters as outlined above. The sum is obtained as a quantitative expression of the relative potential for exposure which subsequently is multiplied by the migration score to provide an overall score.

TABLE 9 Evaluation of the potential for cobalt exposure for different leather products

	Man's shoe inner sole	**Ladies' shoe Vamp**	**Black bracelet**	**Red watch strap**	**Upholstery leather Grey**	**Upholstery leather, beige**
Direct/indirect contact (subscore 1-3)	Usually stockings 2	Usually stockings 2	Naked skin 3	Naked skin 3	Naked skin, hands arms 3	Naked skin, hands, arms 3
Frequency (subscore 1-3)	Every day 3	Every day 3	Every day 3	Every day 3	Every day 3	Every day 3
Duration each time used (subscore 1-3)	For hours each day 2	For hours each day 2	Constantly 3	Constantly 3	For hours each day 2	For hours each day 2
Part of body /thickness of skin (subscore 1-3)	Sole of the foot 1	Instep of foot 3	Wrist 3	Wrist 3	Hands, arms, thighs 3	Hands, arms, thighs 3
Moistening (subscore 1-3)	High 3	High 3	High 3	High 3	Medium 2	Medium 2
Sum of subscores above	11	13	15	15	13	13
Migration score	3	6.3	4.7	1	1.3	1.9
Overall score (Sum of subscores) x (migration score)	33	**82**	**71**	15	17	25

From this evaluation it is concluded that the ladies' shoe and the black bracelet (scores highlighted in **bold**) constitute the greatest potential for exposure to cobalt in the six leather products. It is evident that a risk assessment of these two products should be performed.

7.3 Risk assessment

The migration values for the leather products with the highest potential for exposure (TABLE 9) are compared with the DMEL limit values for cobalt (TABLE 10).
The migration parameter is expressed as µg cobalt released per cm^2 surface after extraction for one week, whereas the DMEL values are stated as µg cobalt per cm^2, being the concentration applied in the patch test, where the exposure time typically is 48 hrs.

Thus, the risk assessment represents a scenario where the person is exposed to the possible maximum dose of cobalt accumulated on the skin in a week by migration from the surface of 100 % soaked leather.
The risk assessment is made by comparing these values to each other and calculating the risk characterization ration (RCR = exposure / DMEL) from there. If the RCR value is above 1, this immediately indicates that the migration is higher than the DMEL value and therefore may pose a potential risk.

TABLE 10 Risk assessment of cobalt migration from ladies' boots and bracelets in relation to cobalt allergy and dermatitis.

	Migration	DMEL	RCR
Brown ladies' boot (vamp)	0.44 µg Co/cm^2	0.441 – 1,95 µg Co/ cm^2	***0.23 - 1.00***
Black bracelet	0.33 µg Co/cm^2	0.441 – 1,95 µg Co/ cm^2	***0.17 – 0.75***

The RCR intervals are below the value 1, except for the upper part of the RCR interval for women's boot, which touch the critical level of 1. This is however not considered to be of a high concern, bearing in mind that the migration values express migration over 7 days, while the DMEL value is an expression of 48 hours exposure. In an exposure scenario for a user of women's boots, the migration would not occur for 7 days, but only for a shorter period corresponding to a few hours where the boots are wet or damp with sweat. The migration is therefore expected to be considerably lower in this shorter time course. Similarly, the DMEL value is based on 48 hours, which is much above the expected exposure time. A DMEL value based on shorter period, for example 2 hours, is considered to be substantially lower than a DMEL value for 48 hours of exposure. Using more realistic values for migration and DMEL would therefore result in significantly lower RCR values than the calculated, even for a worst-case multi-hour consumer scenario. However, the existing knowledge does not make possible to conduct more precise calculations of the RCR values, due to lack of more relevant data for migration and DMEL value.

On the background of these considerations it is concluded that there is no risk of inducing cobalt allergy from use of these particular ladies' boots and bracelets and the risk of triggering symptoms in cobalt allergics is marginal.

The same considerations apply to the other products for which migration of cobalt was found to be less than that observed for ladies' boots and the bracelet. Overall, it is assessed that there is no risk for induction of allergy nor for triggering of reactions among cobalt allergics by casual use of any of the products investigated in this project.

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Appendix 1. Questionnaire used in telephone interviews of producers and retailers of leather goods

"We are calling from Danish Environmental Analysis and would like to ask you a few questions as part of an ongoing project from Danish EPA, regarding the use of cobalt in leather goods. Your company markets some of these goods. But our questions are aimed at the specific products you produce or sell and eventually the processes involved in producing these products. Your answers will enter anonymously into our assessment of the risk for development of skin allergy due to the content of cobalt in leather goods marketed in Denmark."

Question
Which products do you produce?
How many tons do you produce a year?
How many different (number) leather products do you market in Denmark?
What are the origin countries of the leather? (DK/EU/non-EU)
In terms of processing, what is the condition of the leather you receive?
Do you dye the leather yourself? (Yes/No/Don't know)
Do you use premetallized dyes in your dyeing process? (Yes/No/Don't know)
Is cobalt used in you dyeing process? (Yes/No/Don't know)
Are other metals used in you dyeing process? (Yes/No/Don't know)
If "yes", how many tons cobalt are used a year? (kg pure chemical)
If you do not dye the leather yourself, do you know whether the leather you buy is dyed using cobalt? (Yes/No/Don't know)
If you do not dye the leather yourself, do you know what kind of dye was used? (Yes/No/Don't know)
Do you have any knowledge of cobalt being used in other processes in the production of leather (Yes/No/Don't know)
If "yes", which process?

Appendix 2. Codes being used in import / export transactions

Nace Rev 2 codes being used in data for production in Eurostat

Nace Rev 2 codes being used in data for production in Eurostat

Nace Rev 2 code	**Product categories in bold correspond to the categories in** Fejl! Henvisningskilde ikke fundet..
	Raw hides and skins
10114200	Raw hides and skins of bovine or equine animals, whole
10114300	Raw hides and skins of bovine or equine animals (excluding whole)
10114400	Skins of sheep or lambs
10114500	Raw hides and skins of goats or kids but not tanned, fresh or preserved
	Manufactured leather
15112100	Chamois leather and combination chamois leather
15112200	Patent leather; patent laminated leather and metallised leather
15113100	Leather, of bovine animals, without hair, whole
15113200	Leather, of bovine animals, without hair, not whole
15113300	Leather, of equine animals, without hair
15114130	Sheep or lamb skin leather without wool on; tanned but not further prepared (excluding chamois leather)
15114150	Sheep or lamb skin leather without wool on; parchment-dressed or prepared after tanning (excluding chamois, patent, patent laminated leather and metallised leather)
15114230	Goat or kid skin leather without hair on; tanned or re-tanned but not further prepared (excluding chamois leather)
15114250	Goat or kid skin leather without hair on; parchment-dressed or prepared after tanning (excluding chamois leather, patent leather; patent laminated leather and metallised leather)
15114330	Leather of swine without hair on, tanned but not further prepared
15144350	Leather of swine without hair on; parchment-dressed or prepared after tanning (excluding patent leather; patent laminated leather and metallised leather)
15115100	Leather of other animals, without hair on
15115200	Composition leather with a basis of leather or leather fibre; in slabs; sheets or strips
	Handbags, suitcases, purses, etc.
15121210	Trunks, suitcases, vanity-cases, briefcases, school satchels and similar containers of leather, composition leather, patent leather, plastics, textile materials, aluminium or other materials
15121220	Handbags of leather, composition leather, patent leather, plastic sheeting, textile materials or other materials (including those without a handle)
	Accessories incl, gloves, belts, watch straps, etc.,
32991130	Protective gloves, mittens and mitts for all trades, of leather or composition leather
14193175	Gloves, mittens and mitts, of leather or composition leather (excluding for sport, protective for all trades)
14193180	Belts and bandoliers, of leather or composition leather
14193190	Clothing accessories of leather or composition leather (excluding gloves, mittens and mitts, belts and bandoliers)

15121300	Watch straps, bands, bracelets and parts thereof (including of leather, composition leather or plastic; excluding of precious metal, metal or base metal clad/plated with precious metal)
32301510	Leather sports gloves, mittens and mitts
	Footwear
15201351	Men's town footwear with leather uppers (including boots and shoes; excluding waterproof footwear, footwear with a protective metal toe-cap)
15201352	Women's town footwear with leather uppers (including boots and shoes; excluding waterproof footwear, footwear with a protective metal toe-cap)
15201353	Children's town footwear with leather uppers (including boots and shoes; excluding waterproof footwear, footwear with a protective metal toe-cap)
15201361	Men's sandals with leather uppers (including thong type sandals, flip flops)
15201362	Women's sandals with leather uppers (including thong type sandals, flip flops)
15201363	Children's sandals with leather uppers (including thong type sandals, flip flops)
15201370	Slippers and other indoor footwear with rubber; plastic or leather outer soles and leather uppers (including dancing and bedroom slippers, mules)
15201380	Footwear with wood; cork or other outer soles and leather uppers (excluding outer soles of rubber; plastics or leather)
15201445	Footwear with rubber; plastic or leather outer soles and textile uppers (excluding slippers and other indoor footwear, sports footwear)
15201330	Footwear with a wooden base and leather uppers (including clogs) (excluding with an inner sole or a protective metal toe-cap)
15204020	Leather uppers and parts thereof of footwear (excluding stiffeners)
	Others
15121960	Articles of leather or of composition leather, n.e.c.

CN8 codes i data for import og eksport from Statistics Denmark

CN8 Code	**Product categories in bold correspond to the categories in** Fejl! Henvisningskilde ikke fundet.**.**
	Raw hides and skins
41041110	Full grains, unsplit and grain splits, in the wet state incl. wet-blue, of the whole hides and skins of bovine incl. buffalo animals, with a surface area of <= 2,6 m², tanned, without hair on (excl. further prepared)
41041151	Full grains, unsplit and grain splits, in the wet state incl. wet-blue, of the whole hides and skins of bovine incl. buffalo animals, with a surface area of > 2,6 m², tanned, without hair on (excl. further prepared)
41044159	Full grains leather, unsplit and grain splits leather, in the dry state crust, of hides and skins of bovine incl. buffalo animals, with a surface area of > 2,6 m² 28 square feet, without hair on (excl. further prepared and whole hides)
41044190	Full grains leather, unsplit and grain splits leather, in the dry state crust, of hides and skins of equine animals, without hair on (excl. further prepared)
41044919	Whole hides and skins of bovine incl. buffalo animals, with a surface area of <= 2,6 m² 28 square feet, in the dry state crust, without hair on, whether or not split (excl. further prepared and full grains, unsplit, grain splits)
41044951	Whole hides and skins of bovine incl. buffalo animals, with a surface area of > 2,6 m² 28 square feet, in the dry state crust, without hair on, whether or not split (excl. further prepared and full grains, unsplit and grain split)
41044959	Hides and skins of bovine incl. buffalo animals, with a surface area of > 2,6 m² 28 square feet, in the dry state crust, without hair on, whether or not split (excl. further prepared and whole hides and skins and full grains.
41044990	Hides and skins of equine animals, in the dry state crust, without hair on, whether or not split (excl. further prepared and full grains, unsplit and grain splits)
41053010	Indian hair sheep skins, in the dry state crust, without wool on, vegetable pre-tanned, whether or not having undergone certain treatments, but obviously unsuitable for immediate use for the manufacture of leather articles
41062210	Indian goat or kid skins, in the dry state crust, without wool on, vegetable pre-tanned, whether or not having undergone certain treatments, but obviously unsuitable for immediate use for the manufacture of leather articles
	Manufactured leather
41071111	Boxcalf full grains leather, unsplit, of whole calfhides and calfskins, with a surface area of <= 2,6 m² 28 square feet

41071119	Full grains leather "incl. parchment-dressed leather", unsplit, of the whole hides and skins of bovine "incl. buffalo" animals, with a surface area of <= 2,6 m² "28 square feet", without hair on (excl. boxcalf, chamois leather, patent leather, patent laminated leather and metallised leather)
41071190	Full grains leather "incl. parchment-dressed leather", unsplit, of the whole hides and skins of bovine "incl. buffalo" or equine animals, further prepared after tanning or crusting, without hair on (excl. of bovine "incl. buffalo" animals with a surface area of <= 2,6 m² "28 square feet", chamois leather, patent leather and patent laminated leather, and metallised leather)
41071211	Boxcalf grain splits leather, of whole calfhides and calfskins, with a surface area of <= 2,6 m² 28 square feet
41071219	Grain splits leather "incl. parchment-dressed leather", of the whole hides and skins of bovine "incl. buffalo" animals, with a surface area of <= 2,6 m² "28 square feet", without hair on (excl. boxcalf, chamois leather, patent leather, patent laminated leather and metallised leather)
41071291	Grain splits leather "incl. parchment-dressed leather", of the whole hides and skins of bovine "incl. buffalo" animals, further prepared after tanning or crusting, without hair on (excl. of bovine "incl. buffalo" animals with a surface area of <= 2,6 m² "28 square feet", chamois leather, patent leather and patent laminated leather, and metallised leather)
41071299	Grain splits leather "incl. parchment-dressed leather", of the whole hides and skins of equine animals, further prepared after tanning or crusting, without hair on (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41071910	Leather "incl. parchment-dressed leather" of the whole hides and skins of bovine "incl. buffalo" animals, with a surface area of <= 2,6 m² "28 square feet", without hair on (excl. unsplit full grains leather, grain splits leather, chamois leather, patent leather, patent laminated leather and metallised leather)
41071990	Leather "incl. parchment-dressed leather" of the whole hides and skins of bovine "incl. buffalo" or equine animals, further prepared after tanning or crusting, without hair on (excl. of bovine "incl. buffalo" animals with a surface area of <= 2,6 m² "28 square feet", unsplit full grains leather, grain splits leather, chamois leather, patent leather and patent laminated leather, and metallised leather)
41079110	Full grains sole leather "incl. parchment-dressed leather", unsplit, of the portions, strips or sheets of hides and skins of bovine "incl. buffalo" or equine animals, further prepared after tanning or crusting, without hair on (excl. chamois leather, patent leather and patent laminated leather, and metallised leather
41079190	Full grains leather "incl. parchment-dressed leather", unsplit, of the portions, strips or sheets of hides and skins of bovine "incl. buffalo" or equine animals, further prepared after tanning or crusting, without hair on (excl. sole leather, chamois leather, patent leather and patent laminated leather, and metallised leather)
41079210	Grain splits leather "incl. parchment-dressed leather", of the portions, strips or sheets of hides and skins of bovine "incl. buffalo" animals, further prepared after tanning or crusting, without hair on (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41079290	Grain splits leather "incl. parchment-dressed leather", of the portions, strips or sheets of hides and skins of equine animals, further prepared after tanning or crusting, without hair on (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41079910	Leather "incl. parchment-dressed leather" of the portions, strips or sheets of hides and skins of bovine "incl. buffalo" animals, further prepared after tanning or crusting, without hair on (excl. unsplit full grains leather, grain splits leather, chamois leather, patent leather and patent laminated leather, and metallised leather)
41079990	Leather "incl. parchment-dressed leather" of the portions, strips or sheets of hides and skins of equine animals, further prepared after tanning or crusting, without hair on (excl. unsplit full grains leather, grain splits leather, chamois leather, patent leather and patent laminated leather, and metallised leather)
41120000	Leather further prepared after tanning or crusting "incl. parchment-dressed leather", of sheep or lambs, without wool on, whether or not split (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41131000	Leather further prepared after tanning or crusting "incl. parchment-dressed leather", of goats or kids, without wool or hair on, whether or not split (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41132000	Leather further prepared after tanning or crusting incl. parchment-dressed leather, of pigs, without hair on, whether or not split (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41133000	Leather further prepared after tanning or crusting incl. parchment-dressed leather, of reptiles, whether or not split (excl. chamois leather, patent leather and patent laminated leather, and metallised leather)
41139000	Leather further prepared after tanning or crusting "incl. parchment-dressed leather", of antelopes, deer, elks, elephants and other animals, incl. sea animals, without wool or hair on, and leather of hairless animals, whether or not split (excl. leather of bovine and equine animals, sheep and lambs, goats or kids, swine and reptiles, and chamois leather, patent leather, patent laminated leather and metallised leather)
41141010	Chamois leather, incl. combination chamois leather, of sheep or lambs (excl. glacé-tanned leather subsequently treated with formaldehyde and leather stuffed with oil only after tanning)

41141090	Chamois leather, incl. combination chamois leather (excl. that of sheep or lambs, glacé-tanned leather subsequently treated with formaldehyde and leather stuffed with oil only after tanning)
41142000	Patent leather and patent laminated leather, metallised leather (excl. lacquered or metallised reconstituted leather)
41151000	Composition leather based on leather or leather fibre, in slabs, sheets or strip, whether or not in rolls
41152000	Parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles, leather dust, powder and flour
	Handbags, suitcases, wallets, etc., with outer side of leather, artificial leather, or patent leather
42021110	Executive-cases, briefcases, portfolios, school satchels and similar containers with outer surface of leather, composition leather or patent leather
42021190	Trunks, suitcases, vanity cases and similar containers, with outer surface of leather, composition leather or patent leather (excl. executive-cases)
42022100	Handbags, whether or not with shoulder straps, incl. those without handles, with outer surface of leather, composition leather or patent leather
42023100	Wallets, purses, key-pouches, cigarette-cases, tobacco-pouches and similar articles carried in the pocket or handbag, with outer surface of leather, composition leather or patent leather
42029110	Travelling-bags, toilet bags, rucksacks and sports bags with outer surface of leather, composition leather or patent leather
	Clothing and accessories to clothing of leather or artificial leather
42031000	Articles of apparel, of leather or composition leather (excl. clothing accessories, footware and headgear and parts thereof, and goods of chapter 95, e.g. shin guards, fencing masks)
42034000	Clothing accessories of leather or composition leather (excl. gloves, mittens and mitts, belts, bandoliers, footware and headgear and parts thereof, and goods of chapter 95 [e.g. shin guards, fencing masks])
	Gloves of leather or artificial leather
42032100	Specially designed gloves for use in sport, of leather or composition leather
42032990	Gloves, mittens and mitts, of leather or composition leather (excl. special sports gloves and protective gloves for all trades)
	Industrial gloves of leather or artificial leather
42032910	Protective gloves of leather or composition leather, for all trades
	Belts and shoulder straps of leather or artificial leather
42033000	Belts and bandoliers, of leather or composition leather
	Other goods of leather or artificial leather
42050090	Leather further prepared after tanning or crusting "incl. parchment-dressed leather", of antelopes, deer, elks, elephants and other animals, incl. sea animals, without wool or hair on, and leather of hairless animals, whether or not split (excl. leather of bovine and equine animals, sheep and lambs, goats or kids, swine and reptiles, and chamois leather, patent leather, patent laminated leather and metallised leather)
	Footwear with vamp of leather
64031900	Sports footwear, with outer soles of rubber, plastics, leather or composition leather and uppers of leather (excl. ski-boots, cross-country ski footwear, snowboard boots and skating boots with ice or roller skates attached)
64032000	Footwear with outer soles of leather, and uppers which consist of leather straps across the instep and around the big toe
64034000	Footwear, incorporating a protective metal toecap, with outer soles of rubber, plastics, leather or composition leather and uppers of leather (excl. sports footwear and orthopaedic footwear)
64035105	Footwear with outer soles and uppers of leather, made on a base or platform of wood, covering the ankle, with neither an inner sole nor a protective metal toecap
64035111	Footwear with outer soles and uppers of leather, covering the ankle but not the calf, with in-soles of < 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, orthopaedic footwear and toy footwear))
64035115	Mens footwear with outer soles and uppers of leather, covering the ankle but not the calf, with in-soles of >= 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, and orthopaedic footwear)
64035119	Womens footwear with outer soles and uppers of leather, covering the ankle but not the calf, with in-soles of >= 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, and orthopaedic footwear)
64035191	Footwear with outer soles and uppers of leather, covering the ankle and calf, with in-soles of < 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, orthopaedic footwear and toy footwear)
64035195	Mens footwear with outer soles and uppers of leather, covering the ankle and calf, with in-soles of >= 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, and orthopaedic

	footwear)Damefodtøj, som dækker anklen og læggen, med ydersål og overdel af læder, med længste indvendige mål >= 24 cm (undtagen med indbygget beskyttelseståkappe af metal og undtagen sportsfodtøj og ortopædisk fodtøj)
64035199	Womens footwear with outer soles and uppers of leather, covering the ankle and calf, with in-soles of >= 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, and orthopaedic footwear)
64035911	Footwear with outer soles and uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of > 3 cm (excl. with uppers which consist of leather straps across the instep and around the big toe)
64035931	Footwear with outer soles and uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of <= 3 cm, with in-soles of < 24 cm in length (excl. with uppers which consist of leather straps across the instep and around the big toe, and toy footwear)
64035935	Men's footwear with outer soles and uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of <= 3 cm, with in-soles of >= 24 cm in length (excl. with uppers which consist of leather straps across the instep and around the big toe)
64035939	Women's footwear with outer soles and uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of <= 3 cm, with in-soles of >= 24 cm in length (excl. with uppers which consist of leather straps across the instep and around the big toe)
64035950	Slippers and other indoor footwear, with outer soles and uppers of leather (excl. covering the ankle, with a vamp or upper made of straps, and toy footwear)
64035991	Footwear with outer soles and uppers of leather, with in-soles of < 24 cm in length (excl. covering the ankle, incorporating a protective metal toecap, made on a base or platform of wood, without in-soles, with a vamp or upper made of straps, indoor footwear, sports footwear, orthopaedic footwear, and toy footwear)
64035995	Men's footwear with outer soles and uppers of leather, with in-soles of >= 24 cm in length (excl. covering the ankle, incorporating a protective metal toecap, made on a base or platform of wood, without in-soles, with a vamp or upper made of straps, indoor footwear, sports footwear, and orthopaedic footwear)
64035999	Women's footwear with outer soles and uppers of leather, with in-soles of >= 24 cm in length (excl. covering the ankle, incorporating a protective metal toecap, made on a base or platform of wood, without in-soles, with a vamp or upper made of straps, indoor footwear, sports footwear, and orthopaedic footwear)
64039105	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, made on a base or platform of wood, covering the ankle with neither an inner sole nor a protective metal toecap
64039111	Footwear with outer soles and uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of > 3 cm (excl. with uppers which consist of leather straps across the instep and around the big toe))
64039113	Footwear non-identifiable as men's or women's footwear, with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle (but not the calf), with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)
64039116	Mens footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle (but not the calf), with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)
64039118	Womens footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle (but not the calf), with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)
64039191	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle and calf, with in-soles of < 24 cm in length (excl. incorporating a protective metal toecap, sports footwear, ortho...
64039193	Footwear non-identifiable as men's or women's footwear, with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle, with in-soles of a length >= 24 cm (excl. 6403.1-00 to 6403.40.00)
64039196	Mens footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle, with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00 nor 6403.90-16)
64039198	Womens footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, covering the ankle, with in-soles of length >= 24 cm (excl. orthopaedical fodwear)
64039905	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, made on a base or platform of wood, with neither an inner sole nor a protective metal toecap (excl. covering the ankle)
64039911	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of > 3 cm
64039931	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, with a vamp made of straps or which has one or several pieces cut out, with a maximum sole and heel height of <= 3 cm, with in-soles of < 24 cm in length (excl. toy footwear)
64039933	Footwear non-identifiable as men's or women's footwear, with outer soles of rubber, plastics or composition leather, with uppers of leather (not covering the ankle), with a vamp made of straps or which has one or several pieces cut out, with sole and heel height <= 3 cm, with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)

64039936	Men's footwear with outer soles of rubber, plastics or composition leather, with uppers of leather (not covering the ankle), with a vamp made of straps or which has one or several pieces cut out, with sole and heel height <= 3 cm, with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)
64039938	Women's footwear with outer soles of rubber, plastics or composition leather, with uppers of leather (not covering the ankle), with a vamp made of straps or which has one or several pieces cut out, with sole and heel height <= 3 cm, with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00)
64039950	Slippers and other indoor footwear, with outer soles of rubber, plastics, or composition leather and uppers of leather (excl. covering the ankle, with a vamp made of straps or which has one or several pieces cut out, and toy footwear)
64039991	Footwear with outer soles of rubber, plastics or composition leather, with uppers of leather, with in-soles of < 24 cm in length (excl. covering the ankle, incorporating a protective metal toecap, made on a base or platform of wood, without in-soles, with a vamp made of straps or which has one or several pieces cut out, indoor footwear, sports footwear, orthopaedic footwear and toy footwear)
64039993	Footwear non-identifiable as men's or women's footwear, with outer soles of rubber, plastics or composition leather and uppers of leather, with in-soles of a length of >= 24 cm (excl. footwear covering the ankle; with a protective metal toecap; with a main sole of wood, without in-sole; footwear with a vamp made of straps or which has one or more pieces cut out; indoor, sports or orthopaedic footwear)
64039996	Mens footwear with outer soles of rubber, plastics or composition leather, with uppers of leather (not covering the ankle), with in-soles of a length >= 24 cm (excl. 6403.11-00 to 6403.40.00, 6403.99.11, 6403.99.36, 6403.99.50)
64039998	Footwear with outer soles of rubber, plastics or composition leather and uppers of leather, with in-soles of a length of >= 24 cm, for women (excl. footwear covering the ankle; with a protective metal toecap; with a main sole of wood, without in-sole; footwear with a vamp made of straps or which has one or more pieces cut out; indoor, sports or orthopaedic footwear; footwear which cannot be identified as men's or women's)
64042010	Slippers and other indoor footwear with outer soles of leather or composition leather and uppers of textile materials (excl. toy footwear)
64042090	Footwear with outer soles of leather or composition leather and uppers of textile materials (excl. indoor footwear and toy footwear)
64051000	Footwear with uppers of leather or composition leather (excl. with outer soles of rubber, plastics, leather or composition leather and uppers of leather, orthopaedic footwear and toy footwear)
64059010	Footwear with outer soles of rubber, plastics, leather or composition leather and uppers of materials other than leather, composition leather or textile materials (excl. orthopaedic footwear and toy footwear)
64061010	Uppers and parts thereof, of leather (excl. stiffeners)
64069060	Outer soles of shoes, of leather or composition leather
	Safety shoes with vamp of leather
64035905	Footwear with outer soles and uppers of leather, made on a base or platform of wood, with neither an inner sole nor a protective metal toecap (excl. covering the ankle)

Appendix 3. Outline of products and results of analysis

Sample #	Object	Part investigated	X-ray fluorescence Total chromium (mg/kg)	Chemical analysis Cr (VI) (mg/kg dry matter)		Chemical analysis Total Cr (mg/kg dry matter)		XRF Cobalt (mg/kg dry	Chemical analysis Cobalt (mg/kg dry matter)	
Footwear										
61	Black wooden shoes	Inner sole	5,662	<LOD	<LOD	23,000	21,000	<LOD	<LOD	<LOD
		Vamp	5,283	2.0	1.0	15,000	16,000	<LOD	<LOD	<LOD
65	Black man's shoes	Vamp	9,047	4.2	5.2	24,000	24,000	<LOD	<LOD	<LOD
67	White comfort shoes	Inner sole	5,066	<LOD	<LOD	20,000	20,000	<LOD	<LOD	<LOD
		Vamp	1,765	<LOD	<LOD	19,000	19,000	<LOD	<LOD	<LOD
68	Bronze coloured comfort shoes	Inner sole	6,659	<LOD	<LOD	17,000	18,000	<LOD	<LOD	<LOD
		Vamp	1,449	<LOD	<LOD	17,000	18,000	<LOD	1.1	1.1
71	White wooden shoes	Inner sole	5,805	<LOD	<LOD	24,000	18,000	<LOD	<LOD	<LOD
		Vamp	2,855	<LOD	<LOD	24,000	16,000	<LOD	<LOD	<LOD
72	White sandals	Inner sole	6,171	<LOD	<LOD	16,000	14,000	<LOD	<LOD	<LOD
		Vamp	< LOD	n.d.	n.d.	n.d.	n.d.	<LOD	n.d.	n.d.
75	Light brown insole	Material	3,813	<LOD	<LOD	16,000	19,000	<LOD	38.0	45.0
76	Dark blue baby' s shoes	Material	10,057	<LOD	<LOD	27,000	22,000	<LOD	1.3	2.3
77	Brown casual shoes	Inner sole	7,023	<LOD	<LOD	20,000	20,000	<LOD	<LOD	<LOD
		Vamp	7,898	<LOD	<LOD	24,000	23,000	<LOD	<LOD	<LOD

Sample #	Object	Part investigated	X-ray fluorescence Total chromium (mg/kg)	Chemical analysis Cr (VI) (mg/kg dry matter)		Chemical analysis Total Cr (mg/kg dry matter)		XRF Cobalt (mg/kg dry	Chemical analysis Cobalt (mg/kg dry matter)	
79	Pink baby's shoes	Vamp	4,002	2.5	1.1	20,000	20,000	<LOD	<LOD	<LOD
80	Black wooden shoes	Inner sole	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD	n.d.	n.d.
		Vamp	7,933	<LOD	2.4	18,000	19,000	<LOD	<LOD	<LOD
81	Black sandals	Inner sole	8,290	<LOD	<LOD	25,000	26,000	<LOD	<LOD	<LOD
82	Light brown slippers	Inner sole	2,970	1.9	2.6	9,100	8,400	<LOD	<LOD	<LOD
		Vamp	16,487	3.4	3.3	31,000	30,000	<LOD	<LOD	<LOD
83	Black baby's shoes	Vamp	9,065	2.5	1.5	31,000	30,000	<LOD	<LOD	<LOD
84	Black/snakeskin ladies' sandals	Vamp	8,547	<LOD	<LOD	15,000	8,300	<LOD	<LOD	<LOD
85	Black ladies' boots	Inside of shaft	1,689	<LOD	<LOD	5	7	<LOD	<LOD	<LOD
86	Brown babies' boots	Vamp	13,423	<LOD	<LOD	16,000	19,000	<LOD	1.9	2.2
87	Black children’s sandals	Vamp	7,399	<LOD	<LOD	16,000	15,000	<LOD	<LOD	<LOD
		Inner sole	n.d.	<LOD	<LOD	11.000	11.000	<LOD	2.3	2.3
88	Red sandals	Inner sole	6,540	<LOD	<LOD	13,000	14,000	<LOD	<LOD	<LOD
		Vamp	9,270	<LOD	<LOD	14,000	15,000	<LOD	<LOD	<LOD
89	Blue babies' shoes with elephant	Vamp, elephant	8,644	4.6	3.4	18,000	18,000	<LOD	<LOD	<LOD
90	Man's shoes, brown	Blue Inner sole	7,604	5.3	5.4	21,000	22,000	<LOD	<LOD	<LOD
		Vamp	5,057	<LOD	<LOD	15,000	15,000	<LOD	<LOD	<LOD
91	Brown sandals	Inner sole	13,094	<LOD	<LOD	24,000	23,000	<LOD	<LOD	<LOD
		Vamp	9,580	<LOD	<LOD	25,000	25,000	<LOD	<LOD	<LOD
92	Man's shoes, black	Vamp	12,095	<LOD	<LOD	22,000	16,000	<LOD	<LOD	<LOD
		Inner sole	n.d.	1.9	1.4	18,000	16,000	<LOD	70.6	74.9
93	Brown shoes	Vamp	6,175	<LOD	<LOD	19,000	18,000	<LOD	1.7	1.4

Sample #	Object	Part investigated	X-ray fluorescence Total chromium (mg/kg)	Chemical analysis Cr (VI) (mg/kg dry matter)		Chemical analysis Total Cr (mg/kg dry matter)		XRF Cobalt (mg/kg dry	Chemical analysis Cobalt (mg/kg dry matter)	
94	Blue shoes	Vamp	11,293	1.3	<LOD	16,000	16,000	<LOD	<LOD	<LOD
95	Dark blue shoes	Vamp	11,900	<LOD	<LOD	22,000	24,000	<LOD	<LOD	<LOD
		Inner sole	5,516	<LOD	<LOD	12,000	12,000	<LOD	2.9	3.0
96	Light grey shoes	Inner sole	11,211	<LOD	<LOD	23,000	28,000	<LOD	<LOD	1.0
		Vamp	9,163	1.7	2.3	10,000	13,000	<LOD	<LOD	<LOD
102	Man's shoe, Black	Vamp	6,942	<LOD	<LOD	6,500	6,100	<LOD	<LOD	<LOD
		Inner sole	5,204	<LOD	<LOD	16,000	16,000	<LOD	<LOD	<LOD
103	Black children’s sandals	Inner sole	5,644	<LOD	<LOD	23,000	21,000	<LOD	<LOD	<LOD
104	Pink sandals	Inner sole	12,168	<LOD	<LOD	25,000	26,000	<LOD	<LOD	<LOD
		Vamp	5,860	<LOD	<LOD	18,000	17,000	<LOD	<LOD	<LOD
105	Brown children's sandals	Inner sole	10,806	<LOD	<LOD	19,000	19,000	<LOD	<LOD	<LOD
		Vamp	7,524	<LOD	<LOD	20,000	21,000	<LOD	<LOD	<LOD
106	Grey-blue sandals	Inner sole	8,610	2.7	3.1	30,000	33,000	<LOD	<LOD	<LOD
		Vamp	7,887	<LOD	<LOD	16,000	18,000	<LOD	<LOD	<LOD
107	Black sandals	Inner sole	9,754	<LOD	<LOD	23,000	24,000	<LOD	<LOD	<LOD
108	Pink ladies' shoes	Vamp	7,995	<LOD	<LOD	19,000	20,000	<LOD	<LOD	<LOD
109	Blue casual shoes	Inner sole	6,141	<LOD	<LOD	22,000	22,000	<LOD	<LOD	<LOD
		Vamp	8,473	<LOD	<LOD	20,000	19,000	<LOD	<LOD	<LOD
110	Bordeaux casual shoes	Vamp	11,860	<LOD	<LOD	15,000	15,000	<LOD	1.3	1.2
115	Beige/Black button boots	Light coloured leather	6,292	2.1	3.0	20,000	21,000	<LOD	11.6	12.4
116	Light brown shoes	Vamp	8,105	2.6	1.3	15,000	10,000	<LOD	1.6	1.2
117	Dark brown boots	Vamp	7,180	<LOD	<LOD	19,000	21,000	<LOD	6.3	7.5
121	Orange sandals with rivets	Inner sole	7,691	<LOD	<LOD	18,000	23,000	<LOD	5.3	7.0
		Vamp	7,143	5.1	5.3	16,000	16,000	<LOD	<LOD	<LOD
122	Gold sandals	Inner sole	3,032	<LOD	<LOD	18,000	18,000	<LOD	<LOD	<LOD

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		Vamp	3,145	<LOD	<LOD	7,700	7,600	<LOD	4.4	4.5
Bags and purses										
59	Blue shoulder bag	Material	11,175	16.1	14.8	25,000	25,000	<LOD	<LOD	<LOD
60	Black handbag	Handle or material	8,684	<LOD	1.5	23,000	22,000	<LOD	<LOD	<LOD
62	Black purse	Material	4,272	<LOD	<LOD	11,000	12,000	<LOD	<LOD	<LOD
63	Black bag	Material	7,041	1.6	1.0	21,000	20,000	<LOD	<LOD	<LOD
64	Brown shoulder bag	Material	12,465	30.1	25.6	24,000	26,000	<LOD	<LOD	<LOD
66	Black bag	Material	10,051	<LOD	1.2	21,000	22,000	<LOD	<LOD	<LOD
74	Black belt bag	Material	4,133	<LOD	<LOD	29,000	22,000	<LOD	11.7	10.4
97	Black shoulder bag	Material	6,682	<LOD	<LOD	17,000	14,000	<LOD	<LOD	<LOD
98	Brown cover for mobile phone	Material	6,618	<LOD	<LOD	20,000	20,000	<LOD	<LOD	<LOD
99	Blue-green card holder	Material	5,670	<LOD	2.3	18,000	18,000	<LOD	3.7	3.1
100	Grey note sleeve	Material	4,780	<LOD	<LOD	15,000	15,000	<LOD	2.7	2.3
113	Black purse	Material	7,261	2.2	<LOD	19,000	19,000	<LOD	<LOD	<LOD
123	Brown bag	Material	12,979	10.8	12.0	22,000	22,000	<LOD	1.3	1.5
129	Brown purse	Material	4,821	<LOD	<LOD	12,000	13,000	<LOD	2.6	2.7
130	Brown purse	Material	4,596	<LOD	<LOD	12,000	12,000	<LOD	2.0	2.3
131	Beige purse	Material	4,852	<LOD	<LOD	19,000	19,000	<LOD	<LOD	<LOD
Clothing and gloves										
114	Black suede trousers	Material	8,622	<LOD	<LOD	24,000	24,000	<LOD	<LOD	<LOD
112	Brown driving gloves	Material	8,637	<LOD	<LOD	27,000	20,000	<LOD	<LOD	<LOD
Belts and straps										
69	Brown belt	Material	497	4.2	3.9	22,000	23,000	<LOD	<LOD	<LOD
70	Black belt	Material	4,560	<LOD	<LOD	15,000	15,000	<LOD	<LOD	<LOD
73	Black belt	Material	2,052	<LOD	<LOD	5,500	5,400	<LOD	<LOD	1.1
101	Black belt	Material	<LOD	<LOD	<LOD	11	4	<LOD	<LOD	<LOD

Sample #	Object	Part investigated	X-ray fluorescence Total chromium (mg/kg)	Chemical analysis Cr (VI) (mg/kg dry matter)		Chemical analysis Total Cr (mg/kg dry matter)		XRF Cobalt (mg/kg dry	Chemical analysis Cobalt (mg/kg dry matter)	
111	Black belt with rivets	Material	62	<LOD	<LOD	120	120	<LOD	<LOD	1.0
118	Black belt	Material	n.d.	<LOD	<LOD	11	8	<LOD	<LOD	<LOD
119	Blue bracelet	Material	6,573	<LOD	<LOD	31,000	31,000	<LOD	<LOD	<LOD
120	Black watch strap	Strap	7,568	<LOD	<LOD	8,500	8,200	<LOD	8.9	8.6
125	Brown bracelet	Material	4,420	1.7	<LOD	13,000	13,000	<LOD	13.3	13.6
126	Brown bracelet	Material	6,980	<LOD	<LOD	22,000	21,000	<LOD	<LOD	<LOD
127	Black bracelet	Material	4,601	<LOD	1.6	8,800	8,500	<LOD	<LOD	<LOD
128	Red watch strap	Strap	6,564	4.8	4.7	9,400	8,700	<LOD	6.5	6.3
132	Black keystring	Material	6,330	1.9	1.4	21,000	20,000	<LOD	2.7	2.7
Others										
78	Black lambskin cushion	Skin	<LOD	<LOD	<LOD	11	14	<LOD	<LOD	<LOD
124	Grey kettle holder	Material	7,563	<LOD	<LOD	20,000	20,000	<LOD	<LOD	<LOD
Furniture										
1.A	Upholstery leather – Nubuck, Black		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
2.A	Upholstery leather – Nougat		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
3.A	Upholstery leather – Nubuck, Black		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
4.A	Upholstery leather – Dark brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
5.A	Upholstery leather – Red		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
6.A	Upholstery leather – Brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
7.A	Upholstery leather – ice		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
8.A	Upholstery leather – Cognac		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
9.A	Upholstery leather – White		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
10.A	Upholstery leather – Nubuck blue		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
11.A	Upholstery leather – Nubuck grey		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	151.3	154.8
12.A	Upholstery leather – Nubuck natural		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
13.A	Upholstery leather – Royal, white		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD

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14.A	Upholstery leather – Royal, Black		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
15.A	Upholstery leather – Royal, dark grey		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
16.A	Upholstery leather – Royal, Orange		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
17.A	Upholstery leather – Royal, Bordeaux		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
18.A	Upholstery leather – Royal, beige		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	53.3	54.3
19.A	Upholstery leather – Royal, dark brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
20.A	Upholstery leather – Royal, light brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
21.A	Upholstery leather – Royal, medium brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
22.A	Upholstery leather – King royal Sidney, light brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
23.A	Upholstery leather – King royal Sidney, red		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
24.A	Upholstery leather – King royal Sidney, medium brown		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
1	Upholstery leather – Split, red		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
2	Upholstery leather – Chocolate		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
3	Upholstery leather –Grey/silver		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	2.2
4	Upholstery leather –brandy		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.3
5	Upholstery leather –Silver/beige		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
6	Upholstery leather – Silver/beige		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
7	Upholstery leather – soft, Black		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
8	Upholstery leather – blue-grey		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
9	Upholstery leather –cognac		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	2.5
10	Upholstery leather –silver/grey		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD

n.d. – not determined; <LOD – below detection limit

Chromium VI and cobalt in leather goods - Control of chromium and risk evaluation of cobalt

Leather goods are the most common origin of chromium allergy in Denmark. As of May 2015
leather goods in contact with human skin must not be marketed if they contain chromium (VI) in concentrations of or higher than 3 mg/kg (0.0003%) based on the dry weight of the leather (REACH, appendix 17, section 47, points 5 and 6). Recent investigations show that leather goods also can contain cobalt which may cause cobalt allergy.

The overall conclusion of the market survey was that the industry associations, producers, and retailers of leather goods did not have any knowledge of the occurrence of cobalt in the products. Neither did they know whether the leather is dyed with premetallized dyes or whether cobalt was involved in other processes.

The concentration of chromium (VI) was below the detection limit in 74 out of 94 leather samples being analyzed. In 10 samples the concentration of chromium (VI) was higher than the limit value of 3 mg/kg dry matter, though was one result within the uncertainty of the analysis method and was thereby not regarded as a violation af the limit value. The highest measured values of 28 mg/kg, 16 mg/kg, and 11 mg/kg, respectively, were found in handbags. Chromium (VI) content exceeding the detection limit was found in 3 out of 8 shoes for babies and children. In one of these shoes the concentration was higher than 3 mg/kg.

From the measure cobalt concentrations it is estimated that there are no risks for initiation of cobalt allergy or risk for induction of symptoms when cobalt allergics are wearing these analyzed goods is considered to be low.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
5000 Odense C

www.mst.dk