Ministry of Environment of Denmark
Environmental Protection Agency

Survey and risk assessment of chemicals in knitting yarn

Survey of chemical substances in consumer products No. 184

March 2021

Publisher: The Danish Environmental Protection Agency

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ISBN: 978-87-7038-290-8

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Introduction

With this project, the Danish Environmental Protection Agency wants to map whether knitting yarns to the same extent as finished textiles contain chemicals, and whether knitting yarn complies with the legislation applying to textiles and yarns.

The purpose is to assess whether there may be a health risk to consumers under realistic expected use of the products. In addition, products sold in Denmark will be compared with products purchased online within and outside the EU.

Summary and conclusion

In recent years, Danes have been knitting more and more. Accordingly, the Danish Environmental Protection Agency has a desire to map the market for knitting yarns and investigate whether knitting yarns contain chemicals to the same extent as finished textiles, and whether yarn complies with the legislation applying to textiles and yarns.

Purpose
The purpose of the project is to assess whether there may be a health risk to consumers by realistically expected use of knitting yarn. In addition, products sold in Denmark must be compared with products purchased online within and outside the EU.

Mapping and selection of knitting yarn samples
Based on examination of the market and visits to web shops domiciled in Denmark, in other EU countries and countries outside the EU, 51 yarn samples were purchased for the project. The samples were divided into cotton, wool and superwash yarns.

Of the 51 yarn samples, 45 were selected for content and migration analyses; 15 bought in Denmark, 17 bought in the EU (other EU countries than Denmark) and 13 bought outside the EU. Of these samples, 13 were cotton yarns, 11 wool yarns (not superwash quality) and 21 superwash wool yarns. Yarn samples were selected with as much variation as possible in terms of quality (organic and non-organic), colours and price level (prices from DKK 7 per yarn to DKK 120 per yarn).

Based on previous reports on textiles and yarns, a number of substances problematic to health were identified that have previously been found in different qualities of wool and cotton, and which were therefore found relevant to be included in the analytical chemical programme.

Chemical analyses
All 45 yarn samples were tested for content of nonylphenol and nonylphenol ethoxylates as well as azo dyes and aromatic amines, as these substances are subject to regulation of content in textiles. Next, migration analyses were performed of all yarn samples in artificial sweat for a series of metals and also for formaldehyde and permethrin. In addition, migration of cyclic siloxanes was examined for 12 selected superwash wool yarn samples, and migration of bisphenol A (BPA) for 10 selected yarn samples.

None of the yarn samples contained nonylphenol above the detection limit. Nonylphenol ethoxylates were found above the detection limit in 6 yarn samples, one of which was above the upcoming limit of 100 mg/kg. The remaining 5 yarn samples were significantly below the limit value, with the highest concentration being 62 mg/kg.

In 4 yarn samples content of the regulated aromatic amines was detected. However, the measured concentrations were significantly below the limit value.

In the migration analyses, smaller concentrations of heavy metals were measured. Zinc and copper were found in both the largest number of samples (89% and 67%, respectively) and in the highest concentrations. The highest concentration in the migration fluid was 20 µg/g yarn for zinc and 7.5 µg/g yarn for copper. There was a tendency for higher zinc concentration in the migration liquid from wool yarn (both for superwash and non-superwash qualities) than from cotton yarn. There was also a tendency for increasing concentration in the migration fluid

with an increase in the price per yarn. The concentration and frequency of the other heavy metals in the migration fluid were significantly lower.

Chromium was found in the migration fluid of 4 samples at concentrations corresponding to the detection limit (0.1 µg/g). Due to the low total chromium concentration in the migration fluid, no analysis was performed for chromium (VI) as the detection limit for chromium (VI) was higher. However, supplementary content analyses have been performed on the 4 samples, where both content of total chromium and chromium VI were proven. Here, no chromium (VI) was found above the detection limit (3 µg/g), while total chromium was between 0.7 µg/g and 42 µg/g.

Formaldehyde was found in the migration fluid from 10 wool yarn samples in concentrations from 3.9 µg/g yarn to 21.5 µg/g yarn. None of the cotton yarn samples released formaldehyde to the migration fluid.

Neither permethrin, bisphenol A (BPA) nor cyclic siloxanes were found above the detection limit in the migration fluid.

Hazard assessment of analysed substances
The following substances found in the migration analyses were assessed as being of most concern regarding health risks and consequently selected for hazard and risk assessment.

- Formaldehyde (measured levels 3.9 - 21.5 µg/g yarn)
- Copper (measured levels 0.3 - 7.5 µg/g yarn)
- Zinc (measured levels 0.8 – 20 µg/g yarn)
- Cobalt (measured levels 0.1 - 0.6 µg/g yarn)
- Nickel (measured levels 0.1 - 0.5 µg/g yarn)
- Chromium (measured level 0.1 µg/g yarn)

When reviewing toxicological expert assessments of these substances, tolerable exposure levels (DN(M)EL values) were determined for the substances (see table below), both with regard to local effects for skin exposure and for systemic effects in connection with the substances being systemically absorbed.

Overview of DN(M)EL values for use in the risk assessment

	DN(M)EL skin contact ***µg/cm² and/or %***	**DN(M)EL skin contact** ***mg/kg bw/day***	**DN(M)EL oral** ***mg/kg bw/day***
Formaldehyde	20 µg/ cm² (allergic symptoms) 0.003 % (allergic symptoms)	-	0.15 (effects on the gastrointestinal)
Copper	1.4 % (irritation)	0.72 (enlarged spleen)	0.15 (enlarged spleen)
Zinc	0.03 % (irritation)	2 (neuro toxicity)	0.4 (neurotoxicity)
Cobalt	0.44 µg/cm² (allergic symptoms)	0.017 (effects on the blood)	0.0003 (effects on the blood)
Nickel	0.74 µg/cm² (allergic symptoms)	0.014 (reproductive toxicity)	0.00014 (allergic symptoms) 0.0055 (reproductive toxicity)

	DN(M)EL skin contact *µg/cm² and/or %*	DN(M)EL skin contact *mg/kg bw/day*	DN(M)EL oral *mg/kg bw/day*
Chromium (VI)*	0.02 µg/cm² (allergic symptoms)	0.0002 µg/kg bw/day (cancer risk)	0.0002 µg/kg bw/day (cancer risk)
Chromium (III)*	180 µg/cm² (allergic symptoms)	0.30 (no effects found)	0.30 (no effects found)

* As chromium (VI) could not be detected in the follow-up analyses, the chromium content is only assessed as chromium (III) in the risk assessment.

Risk assessment
Based on the highest measured migration values for the substances, exposure estimates were performed for two scenarios:

- Skin exposure locally (mg/cm²) and systemically (mg/kg bw/day) for a knitting person using 300 g of yarn per day, assuming migration of equal amounts of the substances per gram of yarn as measured in the migration analysis.

- Skin exposure locally (mg/cm²) and systemically (mg/kg bw/day) for an infant wearing a 200 g sweater as well as additional oral exposure by sucking on a small part (5 g) of the sweater.

When the exposure values obtained were compared with the tolerable exposure levels (DN(M)EL values), the following can be concluded regarding risk:

Overview of the risk assessments

	Risk: Skin contact local effects	Risk: Skin contact systemic effects	Risk: Oral exposure
Knitting person	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	No exposure
Infant wearing a sweater	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no

Local skin effects:
The substances formaldehyde, cobalt, nickel, chromium (VI) and chromium (III) are all skin sensitising substances.

The assessment of the effects of these substances is based on the lowest dose levels that have been reported to elicitate skin reactions in people sensitised to the substance. This value is compared with the estimated exposure at the highest measured value of the substances. In general, dose levels that can elicitate skin symptoms in the most sensitive allergic persons are considered to be significantly lower than the dose levels that cause the allergic condition itself.

When exposed to the found migration levels no unacceptable risk level of causing skin reactions in allergic persons was found.

For copper and zinc, which are not considered to be skin sensitisers, the critical effect is local irritation of the skin. The measured levels are not considered to pose a risk for local irritation neither to knitting persons nor to infants.

Systemic effects
For the estimated exposure levels of formaldehyde, copper, zinc, cobalt, nickel, and chromium (assessed as chromium (III)) no health risks were found for neither knitting persons nor infants.

Uncertainties
Follow-up analyses were performed of the chromium content found in the migration fluid to clarify whether the content originated from chromium (VI) or chromium (III). Unfortunately, the detection limit for this more specialised analysis for content in the yarn was higher than for the analysis of total chromium in artificial sweat. So even if chromium (VI) was not found in some of the yarn samples, it cannot be completely ruled out that there were low levels of chromium (VI) in the yarn and in the artificial sweat. However, the analysis results of the yarn samples suggest that most likely there is no chromium (VI) content in the migration fluid, which is why the risk assessment of chromium is based solely on toxicological data for chromium (III).

Overall assessment
Based on the examination of the selected yarn samples purchased in Denmark, from the remainder of the EU and outside the EU, it can be concluded that there is no risk skin effects or systemic effects when using the yarn in connection with knitting or wearing hand-knitted clothing.

The yarn samples examined represent only a very limited sample of the yarn available on the market, accordingly the conclusion cannot be applied generally to all yarns.

1. Introduction

1.1 Purpose

Danes are knitting more and more. With this project the Danish Environmental Protection Agency wants to map whether knitting yarns contain chemicals to the same extent as finished textiles, and whether the yarn complies with the legislation applying to textiles and yarns.

The purpose is to assess whether there may be a health risk to consumers under realistic expected use of the products. In addition, products sold in Denmark should be compared with products purchased online within and outside the EU.

1.2 Approach

To fulfil the above objectives, the project is divided into different phases with the following activities:

Mapping
The initial phase includes mapping of knitting yarns on the market in order to select relevant knitting yarn samples for chemical analysis and for risk assessment. In this phase, relevant analyses and exposure scenarios are also proposed for further use in the project.

Chemical analyses
In this phase, the relevant analyses for examining the knitting yarn samples are described. The purchased knitting yarn samples are analysed and the results are reported. Migration analyses of the yarn samples are performed and the results are used for risk assessment. In addition, content analyses are carried out to form the basis for assessing whether the products comply with the legislation for the content of azo dyes and aromatic amines as well as the legislation of the content of nonylphenol and nonylphenol ethoxylates.

Risk assessment of consumer scenarios
This phase consists of hazard assessment, exposure assessment and risk characterisation. Firstly, a hazard assessment of the chemical substances found by the chemical analysis is carried out to identify the most critical substances for exposure and risk assessment. Consumer exposure to the selected substances is then estimated using the results from the chemical analyses. Based on the hazard and exposure assessment, a risk characterisation is then made for the consumers and it is concluded whether there is a risk associated with the use of the individual yarn samples.

2. Mapping of knitting yarn and selection of samples

2.1 Mapping

For many years and through several consumer projects the Danish Environmental Protection Agency has focused on unwanted chemistry in textiles. However, the large assortment of different types of knitting yarn for home knitting has not previously been in focus. Due to the growing interest in home knitting, it is only natural to take a closer look at this area in terms of product consumer safety. Consequently, in the present project the content of chemical substances in non-synthetic yarn types will be looked at in more detail, covering cotton and wool yarn, and especially the new superwash wool yarn qualities will be in focus.

An initial web-based literature search has been conducted to obtain knowledge of the types of chemical substances that most probably can be found in the above yarn types. In this search, no studies have been found that have specifically examined and analysed for chemical substances in wool and cotton yarns.

In order to target the project, a selection of recent key publications regarding chemistry in textiles have been screened in order to identify substances of concern that could be most relevant to focus on with regard to further chemical analysis and risk assessment.

2.1.1 Use of chemical substances when producing superwash wool yarn and mercerised cotton

In connection with planning of the analyses, the Danish Environmental Protection Agency was interested to clarify whether particularly problematic chemicals are used during the production of the shrink-free superwash wool yarn quality and which may be present as residues in the final product.

Superwash quality

In order to prevent shrinkage when washing wool, the so-called directional frictional effect (DFE) exhibited by wool fibres must be broken. This can be done by mechanical processing (grinding) or by treatment with oxidizing agents or enzymes. During the mechanical processing, a part of the wool fibres is removed at the same time and a thinner and more glossy yarn is obtained.

In cases where the gloss is of minor importance, three types of treatment are used commercially (Rippon & Evans (2012):

- Treatment with chemicals
- Treatment with polymer
- Treatment with chemicals with subsequent addition of polymer

To achieve the lowest level of shrinkage, which is required to obtain a superwash quality, the last two methods are used, the cheapest and most common being chemical treatment with polymer addition.

Based on a detailed description of the production of superwash wool yarn by Hassan & Carr (2019), the processing can be summarized in the following steps:

The yarn is transported through a continuous process, in which treatment takes place in different reaction vessels with chemical processing.

1. To achieve superwash quality, the wool is first subjected to an oxidation process by treatment with either chlorine gas or sodium hypochlorite at low pH or with dichloroisocyanuric acid (DCCA). This treatment affects keratin structures in the yarn by breaking down disulfide bridges and removing the water-repellent 18-methyl eicosanoic acid surrounding the keratin. The treatment makes the yarn hydrophilic and available for treatment with surfactants. It is stated that this treatment results in a certain amount of organically bound chlorine in the effluent from the process.

2. Subsequently, the yarn is washed in a solution of metabisulfite and bicarbonate to increase the pH to a neutral value, which prevents yellowing of the yarn and makes the yarn more susceptible to the subsequent treatment with polymers.

3. Rinsing in water.

4. After rinsing, Hercosett synthetic polymer is added by an amount of approx. 1.2% of the yarn weight. Hercosett is a polymer consisting of poly (chloro-hydroxypropyl diethylene adipamide ammonium chloride).

5. When this polymer is added to the yarn and the solution is made basic, the chlorohydroxypropyl groups in the polymer are converted to epoxy compounds and poly(epoxypropyl diethylene adipamide ammonium chloride) is formed, which reacts and binds the polymer to carboxyl and hydroxyl groups in the yarn.

6. Finally, a silicone-based plasticizer, by an amount of approx. 0.2-0.3% of the yarn weight, is added to the yarn.

From this description of the manufacturing process it is most likely that the finished yarn product will have a certain content of the added silicone plasticizer as well as a possible residual content of unreacted Hercosett polymer (i.e. poly (chloro-hydroxypropyl diethylene adipamide ammonium chloride).

Mercerisation of cotton
In the production of cotton yarn, mercerisation of the cotton is the most common method to improve properties such as strength, gloss and dimensional stability and thus make the yarn suitable for machine washing.

The process is quite simple as the yarn is treated with strong base, whereby the fibres swell and some of the cellulose crystallizes (conversion from cellulose I to cellulose II). The process takes place under tension, whereby a smoother yarn and thus a glossier surface is obtained. Consequently, mercerisation is not considered to cause residues of chemical substances in the yarn.

2.1.2 Reports concerning chemicals in textiles

Listed below are a number of recent reports concerning residues of chemical substances in textiles. These reports have been screened to target the project at the most relevant substances.

ANSES (2018). Assessment of the skin sensitising/irritant effects of chemicals found in footwear and textile clothing.
In 2018, the French health authority institute ANSES published a project report to shed light on the presence of chemical substances in footwear and textiles. The report can be considered

the most up-to-date in the field, conducting a systematic literature search and reviewing a large number of European reports and collecting data from France, Denmark, Sweden, Germany, the Netherlands and the European Commission. On this basis, a large number of potential substances of concern were identified with the main emphasis placed on sensitising substances. The project analysed 25 different textiles with various forms of liquid extraction in a large analytical program, which included analyses for identification and quantification of more than 130 substances selected as critical substances covering 20 different substance groups (e.g. aromatic amines, azo dyes, metals, organic aldehydes , acids, etc.). Different solvents were used for the extractions to ensure optimal conditions for extraction of as many different types of chemical substances as possible.

However, only relatively few substances were found in the extractions. The following chemical substances were detected from the textile part of the products (i.e. substances found in connection with printed motifs and metal parts are not included below):

- 1,4- para-phenylene diamine (PPD)
- CI Disperse Yellow 23
- chromium
- nickel
- dibutyltin dichloride
- monobutyltin trichloride
- nonylphenols (NP)/ nonylphenol ethoxylates (NPEO)

A number of further substances (metals) were detected from metal and plastic accessories attached to the textile:

- cobalt
- cobber
- antimony
- lead
- arsenic
- cadmium
- mercury

Having a closer look, none of the 25 analysed textile products contained wool, only eight of the textiles contained cotton and the rest were based on synthetic material.

Chemical substances of potential concern were only found in two textiles containing cotton. In these products, nonylphenol ethoxylates were found in connection with print on the products, and in one, chromium was also found in connection with an elastic band. Thus, no of the found substances could uniquely be associated with a content in cotton.

However, the report referred to previous analytical reportings where formaldehyde has been found in connection with cotton and wool.

Kemi (2013). Hazardous chemicals in textiles – report of a government assignment. Report No 3/13.
In 2013, the Swedish Chemicals Agency KEMI published a report on hazardous chemicals in textiles.

This report identified a number of chemical substances that could potentially be found in the final product due to the use of these chemicals during the production of textiles.

It was considered possible to find the following substances from the production processes of wool and cotton:

Wool	Cotton
Acrylamide (previously used, shrink treatment)	Acrylamide (previously used)
Azo dyes and their cleavage products (arylamines)	Azo dyes and their cleavage products (arylamines)
1,4-dichlorobenzene (carrier for colours)	Zinc chloride (mercerisation, colouring)
Cr (VI) salts (pigments)	Bis(tributyltin)oxide (biocide)
Lead salts (dyes)	Hexabromocyclododecane (HBCDD) flame retardant

For acrylamide, it is stated that this is a substance that was previously used, and thus, it is not considered relevant to focus on this substance in this project. Similarly, it is not considered probable that knitting yarn has been treated with flame retardants as a possible treatment with flame retardants may only be relevant for very special uses of the final textile product.

Danish Environmental Protection Agency projects

Danish EPA (2014a): Survey of Selected Allergenic, Disperse Dyes in Clothes. Survey of chemical substances in consumer products No. 129, 2014.
In this report, azo dyes and degradation products are also listed as substances that may potentially occur in wool and cotton articles in connection with dyeing. The report selects 31 clothing products (mostly produced from synthetic textiles) where residues of azo dyes are found. Disperse Blue 124 was found in eight textiles and Disperse Yellow 49 in one piece of textile. None of these findings, however, were related to either cotton or wool.

Danish EPA (2014b): Survey and health and environmental assessments of biocidal active substances in clothing. Survey of chemical substances in consumer products No.128, 2014.
Mapping and health and environmental assessment of biocidal active substances in clothing. In connection with this project, 34 garments were analysed for content of biocides, including 21 of cotton and 5 of wool. In these analyses, residues of formaldehyde were found in three wool and three cotton products in the concentration range 3-23 mg/kg, and permethrin in a wool product at a concentration of 367 mg/kg.

Danish EPA (2013a): Survey and environmental and health assessment of nonylphenol and nonylphenlethoxylates in textiles. Survey on chemical substances in consumer products no. 120, 2013.
In this project, that performed chemical analytical examination for nonylphenol and nonylphenol ethoxylates in 15 clothing and bedding products (11 wool products and 4 synthetic textiles), nonylphenol ethoxylates were found in nine of the cotton products in the concentration range 3.2 - 311 mg/kg. The report found that the use of nonylphenol and nonylphenol ethoxylates was as an aid in cleaning and rinsing wool and cotton, for removing grease and other impurities and as an aid in bleaching, dyeing and wetting the textile.

Other data
In one recent publication, bisphenol A (BPA) was found in baby socks purchased in Spanish stores (Freire et al. 2019). Here, a tendency for increasing concentrations of BPA was observed with an increasing content of cotton. The findings were mainly related to very cheaply

purchased socks produced from cotton mixed with synthetic plastic fibres, and the authors assumed that a probable reason for this content could be the use of recycled plastic in the products.

Thus, it can be assumed that the use of recycled materials in particular could lead to residues of a number of different chemical substances as part of the content of the recycled products or associated contaminants. However, a further analysis of this aspect is not considered relevant, as this project focuses on yarn qualities sold as pure cotton and wool.

2.1.3 Selection of relevant substances for analysis/risk assessment

Based on the above information, it is considered relevant to focus on the following substances when performing chemical analysis of wool and cotton yarns:

- Nonylphenol og nonylphenol ethoxylates
- Azo dyes and degradation products (various arylamines)
- Metals (chromium, lead, nickel, zinc, tin and other particularly problematic metals such as cobalt and cadmium)
- Formaldehyde
- Permethrin
- Organotin

For superwash wool yarns it may further be relevant to focus on the use of silicone (here cyclic siloxanes D4, D5 and D6 are considered particularly critical) and Hercosett polymer (i.e. poly (chloro-hydroxypropyl diethylene adipamide ammonium chloride). For cotton it may be relevant to focus on possible residues of bisphenol A.

2.1.4 Hazard classification and regulation of substances of concern

Below in Table 1, the above substances are described on the basis of their hazard classification/ EU harmonised classification as well as on the basis of the relevant regulatory requirements in connection with possible content in knitting yarn.

TABLE 1. Regulatory data concerning potentially problematic substances in yarn

Substance	EU classification	Applicable regulation including textiles
Azo dyes (Benzidine CAS 92-87-5)	Aromatic amine: Carc. 1A, H350 Acute tox. 4, H302 Aquatic Acute 1, H400 Aquatic chronic 1, H410 (classification given for benzidine as an example of an aromatic amine from Appendix 10) Azo dye: Skin sens. 1 Aquatic Acute 1, H400 Aquatic chronic 1, H410 (classification of azo dye CAS 118685-33-9 included in Appendix 10)	REACH Annex XVII 43: All azo dyes capable of releasing more than 30 mg/kg (0.003%) of 22 specific aromatic amines are listed in Appendix 8 to Annex XVII. Azo dyes included in Appendix 9 to Annex XVII prohibited above 0.1% for dyeing textiles. REACH Annex XVII 72 (effective from 1 November 2020) 8 named azo dyes and aromatic amines as specified in Appendix 12.
Nonylphenol CAS 25154-52-3	Acute Tox. 4, H302 Skin Corr. 1B, H314 Aquatic Acute 1 H400	REACH Annex XVII 46 Prohibited at conc. ≥ 0.1% for textile processing

Substance	EU classification	Applicable regulation including textiles
	Aquatic Chronic 1, H410 Repr. 2, H361fd	
Nonylphenolethoxylates		REACH Annex XVII 46 Prohibited at conc. ≥ 0.1% for textile processing REACH Annex XVII 46a Prohibited in textiles at conc. ≥ 0.01% (effective from 3 February 2021)
Formaldehyde* CAS 50-00-0	Acute Tox. 3, H301, H311 Skin Corr. 1B, H314 Skin Sens. 1, H317 Acute Tox. 3, H331 Muta. 2, H341 Carc. 1B, H350	REACH Annex XVII 72 (effective from 1 November 2020) Prohibited in textiles (including yarn) ≥ 75 mg/kg
Lead CAS 7439-92-1	Repr. 1A, H360FD, C ≥ 0,03% Lact., H362 Suggestions for further harmonised classification as: Aquatic Acute 1, H400, M-factor=10, Aquatic Chronic 1, M-factor=10 (Repr. 1A, H360FD, C ≥ 0,03% Lact., H362 STOT RE 1 H372, C ≥ 0,5% Aquatic Acute 1, H400, M-factor=10, Aquatic Chronic 1, H410)	REACH Annex XVII, entry 63: Prohibited in consumer products at lead concentrations higher than 0.05% (equivalent to 500 ppm = 500 mg/kg) unless the migration can be shown to be less than 0.05 µg Pb/cm² per hour. Applies to articles or parts thereof, which children may put in the mouth under normal or reasonably foreseeable conditions of use. In addition, special Danish regulation applies for lead: Statutory order no. 856 of 05/09/2009. Prohibition on import and sale of products with lead content higher than 100 ppm (corresponding to 0.01% = 100 mg/kg). REACH Annex XVII 72 (effective from 1 November 2020): Prohibited in textiles (including yarn) at ≥ 1 mg/kg by extraction
Cadmium CAS 7440-43-9	Carc. 1B, H350 Muta. 2, H341 Repr. 2, H361fd Acute Tox. 2, H330 STOT RE 1, H372 Aquatic Acute 1, H400	Danish statutory order no. 858 of 05/09/2009 concerning ban on the import, sale and manufacture of cadmium-containing goods. Limit value 75 ppm (corresponding to 75 mg/kg = 0.0075%). On the REACH Candidate List for authorisation due to the carcinogenic effect of the substance. REACH Annex XVII 72 (effective from 1 November 2020): Prohibited in textiles (including yarn) at ≥ 1 mg/kg by extraction.
Chromate (CrVI)* Example: Sodium chromate CAS 7775-11-3	Acute Tox. 2 H330 Acute Tox. 3 H301 Acute Tox. 4 H312 Skin Corr. 1B, H314 Skin Sens. 1, H317 Resp. Sens 1, H317	REACH Annex XVII 72 (effective from 1 November 2020) Prohibited in textiles (including yarn) at ≥ 1 mg/kg by extraction

Substance	EU classification	Applicable regulation including textiles
	Muta. 1B, H340 Carc. 1B, H350 Repr. 1B, H360FD STOT RE 1, H372 Aquatic Acute 1, H400 Aquatic Chronic 1, H410	
Cobalt* CAS 7440-48-4	Skin Sens. 1, H317 Resp. Sens 1, H334 Muta. 2, H341 Carc. 1B, H350 Repr. 1B, H350 Aquatic Chronic 4, H413	No relevant regulation covering textiles
Nickel* CAS 7440-02-0	Skin Sens. 1, H317 Carc. 2, H351 STOT RE 1, H372 Aquatic Chronic 3, H412	No relevant regulation covering textiles
Zinc CAS 7440-66-6	Aquatic Acute 1, H400 Aquatic Chronic 1, H410	No relevant regulation covering textiles
Tin CAS 7440-31-5	See organic tin compounds	See organic tin compounds
Organic tin compounds Dibutyltinchloride CAS 683-18-1 as representative of a number of dibutyltin compounds	Muta. 2, H4341 Repr. 1B, H360FD Acute Tox. 2, H330 Acute Tox. 3, H301 Acute Tox. 4, H312 STOT RE 1, H372 Skin Corr. 1B, H314 Aquatic Acute 1, H400 Aquatic Chronic 1, H410	REACH Annex XVII, entry 20: Dibutyltin compounds banned in consumer products at tin concentrations above 0.1%
Permethrin CAS 52645-53-1	Acute Tox. 4, H302 Acute Tox. 4, H332 Skin Sens. 1, H317 Aquatic Acute 1, H400 Aquatic Chronic 1, H410	No relevant regulation covering textiles In 2016 approved as an active substance according to BPR for product type 8 (wood protection) and product type 18 (insecticides)
D4 Octamethyl-cyclotetrasiloxane CAS 556-67-2	Aquatic Chronic 4, H413 Repr. 2, H361 fertility	No relevant regulation covering textiles. Included on the REACH Candidate List as (very) persistent, bioaccumulative and toxic in the environment (PBT/vPvB).
D5 Decamethyl-cyclopentasiloxane CAS 541-02-6	No classification	No relevant regulation covering textiles. Included on the REACH Candidate List as (very) persistent, bioaccumulative and toxic in the environment (PBT/vPvB).
D6 Dodecamethylcyclohexasiloxane CAS 540-97-6	No classification	No relevant regulation covering textiles. Included on the REACH Candidate List as (very) persistent, bioaccumulative and toxic in the environment (PBT/vPvB).
Bisphenol A 80-05-7	Repr. 1B, H360F STOT SE 3, H335 Eye Dam. 1, H318 Skin Sens. 1, H317	No relevant regulation covering textiles. Included on the REACH Candidate List due to the reproductive harmful properties of the substance. Rated to be an endocrine disruptor both in terms of environment and health.

* It is important to note that currently (May 2020) there is a proposal to restrict the use of substances with an EU-harmonized classification for skin sensitisation with regard to their content in textiles, leather and furs. This proposal contains a number of limit values for the content of the various sensitising substances. For content in textiles, formaldehyde is included with a concentration limit of 30 mg/kg, nickel with a concentration limit of 120 mg/kg, cobalt with a concentration limit of 70 mg/kg and chromium (VI) with a concentration limit of 1 mg/kg (ECHA 2019).

2.2 Description of exposure scenarios

An important significant part of the risk assessment of the use of knitting yarn includes a realistic exposure assessment for the chemical substances that the knitting yarn may contain and release during use.

In the exposure assessment, it is important to distinguish between the different target groups for the risk assessment as the exposure may differ between the target groups. Taking into account relevant types of critical effects (such as local skin effects and/or systemic organ effects), exposure scenarios are made for the knitting person and for a person using the knitted garment. To include the most sensitive target groups, the exposure assessment includes a pregnant knitting women, whose unborn child may be particularly sensitive to harmful effects as one scenario and an infant wearing the knitted garment as the other scenario. Also, oral exposure is considered relevant for the infant when sucking on parts of the garment e.g. sucking on corners of the knitwear or yarn tassels.

The following target groups and exposure scenarios are considered relevant for the use of knitting yarn and knitted garments:

- skin exposure during knitting for a pregnant woman
- skin exposure for a child including the child’s sucking on the knitwear

It is expected that the exposure scenarios will differ widely, as a knitting, pregnant woman may have contact with new unwashed yarn for a certain number of hours daily for a longer period of time, while a child wearing the clothes will only be exposed to new yarn for a short period if the knitted garment has not been washed before use.

The exposure scenarios will be prepared as realistic worst-case estimates based on exposure parameters specified in the REACH guidelines combined with knowledge from scenarios previously used in the literature or in previous projects by the Danish Environmental Protection Agency. The exposure will be calculated in the unit "mg yarn/kg bw/day" and in the unit "mg yarn/cm^2".

2.2.1 Skin exposure of the knitting person

Exposure assessment of local exposure to the palms of the hand surface

The most intense skin exposure will occur on the person's hands during knitting. For this skin area, the potential risk from skin irritants or skin sensitisers is considered of concern, and is relevant to calculate exposure as amount of knitting yarn per cm^2 of skin.

Exposure (g yarn/cm^2) = consumption of knitting yarn per knitting period (g)/ area of the palms (cm^2)

As a worst-case scenario, it is estimated that 300 grams of yarn is used during a knitting period of 8 hours. Next, the touch and exposure of the yarn is considered to occur on a surface area corresponding to the palms. The Nordic Council of Ministers (2011) and RIVM (2014) state that the surface area of an adult woman's hands is 731 cm^2, which is why the inside of the hands is estimated at approx. half, i.e. 365 cm^2.

That is:

$$\text{Exposure (g yarn/ cm}^2\text{ skin)} = 300\text{ g}/365\text{ cm}^2 = 0.82\text{ g/ cm}^2$$

Based on chemical analytical results that determine the release of a chemical substance from the yarn into artificial sweat, knowledge is obtained about "mg substance released/g yarn", and the exposure to the substance can thus be calculated:

$$\text{Exposure (mg substance/ cm}^2\text{ skin)} = \text{Exposure (g yarn/cm}^2\text{)} \times \text{(mg substance released/g yarn)}$$

(1) $\text{Exposure (mg substance/cm}^2\text{ skin)} = 0.82\text{ g yarn/cm}^2 \times \text{(mg substance released/g yarn)}$

Exposure assessment relevant for systemic uptake

Chemicals released during knitting will be available for absorption in the body, as the specific substance to a greater or lesser extent will be able to penetrate the skin and into the blood-stream. To assess the risk for systemic organ effects, it is therefore relevant to calculate the exposure in mg substance/kg body weight per day.

Here, the exposure to the individual substance can be calculated from:

$$\text{Exposure (mg/kg bw/day)} = \text{amount of yarn (g/day)} \times \text{mg substance released/g yarn/ bw (kg)}$$

$$\text{Exposure (mg/kg bw/day)} = 300\text{ g/day} \times \text{mg substance released/g yarn/ }60\text{ kg}$$

(2) $\text{Exposure (mg/kg bw/day)} = 5\text{ g/kg bw} \times \text{mg substance released/g yarn}$

As a worst-case scenario, it is estimated as mentioned above that 300 grams of yarn are used in the course of one day. As default, a body weight of 60 kg is assumed for a woman (REACH 2012).

2.2.2 Exposure of infants, ½ - 1 year

Exposure of the infant's skin area

This scenario includes infants in the age group ½-1 year. In other words, an age with a high degree of sucking activity on objects within reach. It is assumed as a worst-case that the child is wearing one freshly knitted non-washed hoodie and that the child does is not wearing an undershirt under the knitted sweater, i.e. that the child's (sweaty) skin is in direct contact with the sweater. Furthermore, it is assumed that the child sucks on a pair of yarn tassels attached to the hood of the sweater.

Exposure per skin area can be calculated:

$$\text{Exposure per skin area (g substance/cm}^2\text{)} = \text{consumption of knitting yarn per hoodie (g)/body area torso, arms, part of the head of the child (cm}^2\text{)}$$

It is assumed that a thin hoodie for a 6-12-month old baby can be knitted using 200 grams of yarn. It is assumed that only a thin hoodie will be used without an undershirt, while a baby using a thicker sweater is expected to wear something under the sweater and therefore to a lesser extent is directly exposed to possible chemical substances in the yarn. Therefore, the use of 200 grams is considered a realistic worst-case scenario for the described scenario.

The hoodie will expose a surface area corresponding to arms, the upper body and half of the head. For 6-12 months old children, this will result in a surface area of 2287 cm^2 according to the recommended "deterministic default values" from RIVM (2014, table 32).

$$Exposure\ (g\ substance/\ cm^2) = 200\ g\ yarn/hoodie/\ 2287\ cm^2 = 0.087\ g/\ cm^2$$

Based on chemical analytical results that determine the release of a chemical ingredient from the yarn into artificial sweat, knowledge is obtained about "mg substance released/g yarn", and the exposure to the substance can thus be calculated:

$$Exposure\ (mg\ substance/\ cm^2) = Exposure\ (g\ yarn/\ cm^2) \times (mg\ substance\ released/g\ yarn)$$

$$(3) \quad Exposure\ (mg\ substance/\ cm^2) = 0.087\ g/\ cm^2 \times (mg\ substance\ released/g\ yarn)$$

Exposure assessment relevant for systemic uptake

In addition, the skin exposure in relation to body weight can be calculated:

$$Exposure\ (mg/kg\ bw) = (hoodie\ weight\ (g) \times mg\ substance\ released/g\ yarn/body\ weight\ (kg)$$

In this scenario, it is assumed that the sweater weighs 200 g and that the child weighs 8.0 kg, as this is stated by RIVM (2014) as the default value for the weight of ½-1 year old children.

$$Exposure\ (mg/kg\ bw) = 200\ g \times mg\ substance\ released/g\ yarn/8.0\ kg\ bw$$

$$(4) \quad Exposure\ (mg/kg\ bw) = 4\ g/kg\ bw \times (mg\ substance\ released/g\ yarn)$$

In addition to this skin exposure, it is estimated that the child may be exposed to substances released by oral ingestion in connection with sucking on the tassels, which are assumed to weigh 5 grams:

$$Oral\ exposure\ (mg/kg\ bw) = (tassels'\ weight\ (g) \times mg\ substance\ released/g\ yarn)/body\ weight\ (kg)$$

$$Oral\ Exposure\ (mg/kg\ bw) = 5\ g \times mg\ substance\ released/g\ yarn)/8\ kg\ bw$$

$$(5) \quad Oral\ Exposure\ (mg/kg\ bw) = 0.63\ g/kg\ bw \times (mg\ substance\ released/g\ yarn)$$

2.2.3 Methodological considerations for determining the release of chemical substances from the yarn

From the above exposure scenarios, it can be seen that mg of substance released per gram of yarn is a very significant factor in the calculations.

For this project it has been decided to perform extraction analysis of the yarn with an artificial sweat liquid (see further below) to determine the quantity of release.

When choosing circumstances for the extraction, it has been decided to avoid unrealistic worst-case assumptions for the release of substances from the knitting yarn. It was therefore decided to extract with artificial sweat for 2 hours at 37ºC without using shaking of the sample, as this is considered best to represent what a knitting person may be exposed to during knitting. The complete soaking of the yarn for 2 hours is considered to lead to a worst-case scenario for release, which is why further shaking to increase release from the yarn is not considered relevant. Furthermore, two hours of extraction is also assessed as worst-case, as exposure to the same piece of yarn is significantly less than two hours.

Similarly, a child's exposure is also considered to be a worst-case scenario when using this method, as it is considered unlikely that the child will wear a completely soaked sweater for a longer period of time.

A more detailed description of the extraction method is given below in section 2.3. and in Chapter 3.

It should be noted that it has been chosen not to perform extraction analyses in artificial saliva, as it is estimated that the analysis result for artificial sweat will be very similar to that of artificial saliva as extraction of the two liquids is considered to be very comparable. It is therefore estimated that small differences in the extraction using one or the other of the two liquids will be significantly within the quantitative uncertainties that many of the other exposure assumptions entail.

2.3 Description of relevant analyses

2.3.1 Selection of relevant substances and substance groups

The mapping of knitting yarns has identified the following substances and substance groups as relevant for analyses of cotton and wool yarns:

- Nonylphenol og nonylphenolehtoxylates
- Azo dyes and decomposition products (various arylamines)
- Metals (chromium, lead, nickel, zinc, tin and other particularly problematic metals)
- Formaldehyde
- Permethrin
- Organotin

In addition, it appears from the manufacturing method for superwash wool yarn that both Hercosett synthetic polymer and silicone-based substances are added. As a result, it is considered relevant to analyse superwash wool yarns for the cyclic siloxanes D4, D5 and D6, as they are often included in silicone mixtures, and the substances must be considered as problematic substances as they are included on the candidate list in the REACH Regulation. The Hercosett polymer is not included in the analysis program as it is evaluated that the probability of migration is low. Furthermore, it will be analytically very costly to structurally clarify the degradation products/residues that may occur from this polymer.

Finally, it is considered relevant to include bisphenol A (BPA). This substance is found in cotton products and the substance further cause reproductive effects and endocrine disrupting effects.

2.3.2 Analysis methods and analysis plan

As can be seen from the exposure scenarios, the focus is mainly on migration analyses of the above substances as this will provide the most suitable starting point for the subsequent risk assessment. For nonylphenol, nonylphenolethoxylates and azo dyes only content analyses are carried out, as regulatory limit values for the content of these substances exist. For these substances migration analyses and further risk assessment are not considered relevant.

In collaboration with the Danish Environmental Protection Agency, the project group has compiled an analysis plan as indicated in Table 2 below.

TABLE 1. Analysis plan

Substance	Analysis type	Number of yarn samples	Comment
Nonylphenol and Nonylphenolethoxylates	Content analysis	45	All yarn samples included in the analysis programme
Azo dyes and their cleavage products	Content analysis	45	All yarn samples included ion the analysis programme
Metals including chromium and organotin	Migration analyses	45	All yarn samples included in the analysis programme
Formaldehyde	Migration analyses	45	All yarn samples included in the analysis programme
Permethrin	Migration analyses	45	All yarn samples included in the analysis programme
Cyclic siloxanes (D4, D5 og D6)	Migration analyses	12	Samples selected from the purchased superwash wool qualities based on an assessment of the smoothness of the yarn.
BPA	Migration analyses	10	Cotton yarn samples

The migration analyses are performed on the basis of extraction of the yarn samples in artificial sweat. The artificial sweat is manufactured in accordance with ISO 105-E04, and the migration test is performed in accordance with ISO 71-3: 2013 + A2: 2017. All analyses are performed as true duplicate determinations. Detailed description of analysis methods can be found in section 3.1.1.

The metal analyses include lead, chromium, nickel, cadmium, arsenic, copper, zinc, mercury, boron, cobalt, tin, silver, antimony and vanadium. In case the metal analyses show the presence of chromium or tin, these samples will also be analysed for relative chromium (VI) and organic tin compounds.

As shown in Table 2, analyses for cyclic siloxanes and bisphenol A are performed only on a subset of the total number of yarn samples in the analysis program.

2.4 Selection of knitting yarn for testing

2.4.1 Criteria for selection of knitting yarn

When selecting knitting yarns for analysis and risk assessment the focus is on cotton yarns and wool yarns for home knitting (i.e. not yarns based on synthetic materials), and for wool yarns the focus is on the superwash quality. When buying products, 1/3 of the knitting yarn should be from the Danish market (physical stores or online stores), 1/3 from online stores from the rest of the EU and 1/3 from online stores outside the EU. In addition, the Danish purchases should represent purchases from specialty shops as well as from supermarkets/larger store chains. Thus, it is the registered home country of the web shop and the country from which the yarn is purchased that is decisive for grouping of the yarn, as the country of production often was not known before receipt of the yarn.

To obtain a more representative selection and to increase findings for metals and various azo dyes, the yar samples are selected so that they cover a wide range of colours (white, black, blue, red, yellow, green and possibly multicoloured yarn). Furthermore, the aim is to select different qualities within the yarn types as well as yarns in different price ranges.

2.4.2 Web-based searching

To obtain an overview of the yarn market, a web-based search has been made with the keyword "knitting yarn" to find online stores in Denmark. A similar search on "buy knitting yarn online" was made to find online stores in the rest of the EU and outside the EU. With regard to the Danish market, there was an equal search for yarn sold in physical stores and yarn sold only via online stores.

During the web search, within the categories wool, superwash wool and cotton, the following could be observed:

The general picture is that branded and expensive yarn types are sold primarily in specialty shops, while lot goods, own brands and "no-name" yarns are in the majority at the online stores and most significantly at foreign sites such as Amazon, eBay, AliExpress and Wish.

There is a tendency for the same brands to be sold in specialty shops and associated online stores, while there is a greater diversity in the pure online stores that also sell imported yarn in addition to own brands. In terms of price level, specialty shops are generally the most expensive, while it is harder to find a very expensive yarn at online stores. The supply of synthetic yarns and blended products (cotton/bamboo, cotton/milk fibres, wool/cotton, wool/silk, etc.) is greatest at the online stores that mainly deal with yarns from Asian countries.

Information about and description of the yarns is most detailed on the specialty shops' websites and at the Danish online stores. In the other online stores, there is usually only information about yarn type and weight and in a few cases information about yarn length and size of knitting pins.

2.4.3 New yarn types

Within cotton yarn, there are two newer types often advertised as "super soft" or "baby-soft". These are both blended products consisting of traditional cotton mixed with bamboo (bamboo cotton) or milk cotton (milk cotton) fibres.

For all these types of yarn, it must be assumed that both the manufacturing and dyeing process differ from the traditional methods, and that other residual chemicals may therefore be present in these products. This issue is not covered by this project.

Yarn types related to the environment and recycling and also sustainable design have also been found. These yarns are often blended products of natural fibres or contain recycled material. Examples include yarn produced from 100% recycled cotton from jeans and yarns produced from recycled plastic bottles (for example from Peru and India) consisting of 100% polyester.

The use of recycled materials in particular may lead to residues from a number of different chemical substances, either as part of the content of the recycled product or contaminants associated with it. Content of recycled materials is considered to be the most likely reason for the discovery of for instance bisphenol A in textile products, as stated by Freire et al. (2019), where bisphenol A was found in socks. The findings were mainly related to very cheaply purchased socks produced from cotton mixed with synthetic plastic fibres, and the authors assumed that a probable reason for this content could be the use of recycled plastic in the products.

2.4.4 Delimitation of selection and purchase

Within the framework of this project, a total of 51 yarn samples were ordered, including a certain surplus of products to ensure a sufficient number of samples were received for the analyses.

The purchased number of samples can only be considered as a random sample of the market, as it would require a significantly larger number of purchases to obtain a more representative sample of the global yarn market in terms of differences in yarn types, colours, qualities, etc. However, the aim has been to achieve a wide range of diversity by choosing different qualities of yarn types, colours and price ranges.

3. Analysis of knitting yarn

Based on the knowledge obtained in the mapping, a number of chemical substances have been selected for quantitative analysis (Table 2). In order to obtain the best background for the risk assessment, migration analyses were carried out for most of the selected substances. However, content analyses were performed in case of nonylphenols, nonylphenolethoxylates, and azo dyes. For those chemicals content limit values are already existing and further risk assessment was therefore not prioritized.

Out of 51 purchased yarn samples, 45 were selected for content- and migration analyses, including 15 yarn samples purchased from Danish web pages, 17 yarn samples from other EU-countries (inclusive England and Norway) and 13 yarn samples purchased from web pages outside EU. The purchases were thus classified according to the country of origin of the web pages and not according to the country of production of the yarn. Often, the country of production could not be identified on the web page, but only when the yarn had been received. The yarn samples included 13 samples cotton yarn, 11 wool yarns of non-superwash quality, and 21 superwash wool yarns. Furthermore, the yarns have been selected to obtain the best variation among the samples including yarns of different quality (organic and non-organic), yarn in different colours and yarn within a wide range of prices (from 7 DKK for a skein to 120 DKK for a skein).

All analyses were performed as duplicates and the results are shown as an average of the two values.

3.1 Quantitative content analyses

3.1.1 Existing content limit values

As described in Table 1, nonylphenolethoxylates will be banned in textiles at a concentration equal to or greater than 0.01% by weight. The ban applies from the 3rd of February 2021 ((REACH[1] Annex XVII, entry 46a[2]). There are currently no restrictions on the content of nonylphenol in the final product. But the use of both nonylphenol and nonylphenol ethoxylates in textile processing is prohibited, if the concentration in the solution or the mixture is equal to or greater than 0.1% by weight.

The import, sale or use of the blue azo dye (EF No 405-665-4) is prohibited when it is intended to dye textiles and leather goods. Impurities in solutions or mixtures up to 0.1% by weight are permitted.

Some azo dyes can release carcinogenic aromatic amines (also called PAAs). It is therefore prohibited to dye textile and leather goods with azo dyes which may release one or more of the 22 aromatic amines listed in the REACH Appendix VIII, entry 43[3]. The limit of the total content of the 22 aromatic amines is 0.003% by weight, corresponding to 30 ppm (mg/kg) in the

[1] Regulation (EC) No 1907/2006 of the European Parliament and oft he Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

[2] Annex XVII to Regulation (EC) No 1907/2006. Entry 46a Nonylphenol ethoxylates

[3] Appendix 8, Entry 43: Azocolourants — List of aromatic amines

coloured parts of the textile- or leather article. Further 8 amines will be regulated from November 1st 2020 (REACH Annex XVII, entry 72[4]) with limit values for the individual substances between 30 and 50 ppm.

3.1.2 Analysis methods

3.1.2.1 Nonylphenol and nonylphenol ethoxylates

The content of nonylphenol ethoxylates (NPE) is determined as described in standard method ISO 18254-1:2016. The method covers the nonylphenol ethoxylate from NPE-2 to NPE-16.

The samples were extracted according to the method and subsequently analysed for NPE-2 to NPE-16 by means of LC-ESI-MS (Liquid Chromatography Electrospray Ionization Mass Spectrometry). NP and NPE-1 were analysed by means of GC-MS (Gas Chromatography Mass Spectrometry). The content of NPE-2 to NPE-16 was quantified from the analytical standard IGEPAL® CO-630 as described in the standard method. NP and NPE-1 were quantified from certified reference standards and deuterium labelled NP was used as an internal standard. A control standard was run for every 10th sample or less.

The detection limit was 1 mg/kg for every congener and the expanded uncertainty (calculated from RSD with a covering factor 2) was 20%.

3.1.2.2 Azo dyes

Azo dyes are dyes that contain one or more azo-groups. The azo-group is a chemical functional group where two nitrogen atoms are connected by a double bound. The first step of the analysis consists of an extraction of the dye from the sample (textile/yarn) followed by a chemical reduction of the azo dye. The reduction splits the double bound between the two nitrogen atoms and the azo dyes are converted into two primary, aromatic amines (Figure 1) (PAAs), which are identified and compared to the EU list of 22 regulated PAAs.

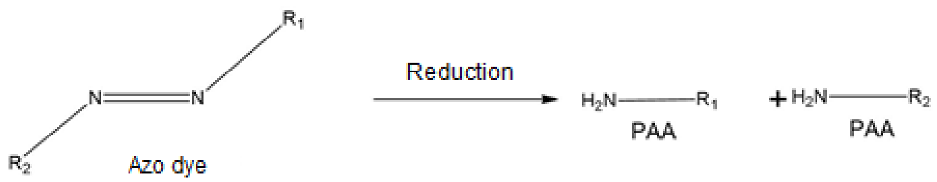

FIGURE 1. Reduction of Azo dye to PAA

The content of primary aromatic amines was determined according to DS/EN ISO 14362-1:2017. The yarn was weighed into a glass and added hot citrate buffer. After 30 minutes at 70°C, the colour was reduced with sodium dithionite at 70°C. To the reaction mixture was added sodium hydroxide (NaOH). The solution was shaken and treated with a sorbent material. The PAA was extracted with tert-butylether (MTBE) containing a deuterium labelled internal standard. The extract was analysed on a GC-MS in SIM-mode. The concentration of the amines was determined from a reference standard and the internal standard.

The detection limit of each amine was 0.2-1.5 mg/kg (ppm). The expanded uncertainty was 20%.

[4]Annex XVII to Regulation (EC) No 1907/2006. Entry 72. The substances listed in Appendix 12, Entry 72 — restricted substances and maximum concentration limits by weight in homogeneous materials.

The dyes and amines listed in REACH annex 9 entry 43 and annex 12 entry 72 were analysed according to ISO 16373-2, Textiles — Dyestuffs — Part 2: General method for the determination of extractable dyestuffs including allergenic and carcinogenic dyestuffs (method using pyridine-water). The sample was weighed into a glass and added a mixture of pyridine and water. The glass was closed and heated to 100°C for 35 minutes. The sample was cooled to room temperature and split in two parts. One part was analysed for the dyes Navy Blue 018112, Disperse Blue 1, Basic Red 9, and Basic Violet 3 on LC-MS according to method described in ISO 16373-2, Annex D, method example 1.

The detection limit was 5 mg/kg, and the uncertainty was 20%.

The second part was analysed for the amines of the salts in REACH Annex 9 entry 43, including quinoline. To the extract was added a solution of sodium hydroxide and dichlormethane containing an internal standard. The mixture was shaken, and the dichloromethane phase was analysed on GC-MS.

The detection limit was 1.5-2.6 mg/kg calculated as amino-salts, and the uncertainty was 20%.

3.1.3 Results of content analyses

3.1.3.1 Nonylphenol and nonylphenol ethoxylates

The concentration of nonylphenol was below the limit of detection of 1mg/kg in all yarn samples investigated.

Concentration of the sum of nonylphenol ethoxylates (NPE-1 to NPE-16) was above the limit of detection of 1 mg/kg in 6 yarn samples, corresponding to 13% of samples investigated. Results for those samples are shown in Table 3. Three of the 6 samples with concentrations above the detection limit were purchased in countries outside EU. The highest concentration was found in sample no 42, which was white organic yarn purchased in Russia. It was the only sample, where the concentration was above the upcoming limit value of 0.01%.

TABLE 3. Concentration of nonylphenol ethoxylates in the investigated yarn samples.

Sample no.	Description	Concentration in the sample, mg/kg
Samples purchased from Denmark		
7	White 100% wool yarn; purchased from DK; 11 kr. per skein	11
Samples purchased from EU		
25	Green classic superwash yarn; purchased from UK; 49 kr. per skein	4.8
40	Yellow/white cotton yarn; Oeko-Tex; purchased from LV; 62 kr. per skein	41
Samples purchased from outside EU		
42	White 100% organic wool yarn; purchased from RU; 20 kr. per skein	318 corresponding to 0.03%
45	Dark blue (navy) 100% organic cotton yarn; purchased from USA; 52 kr. per skein	62
49	Red yarn; purchased from China	51

3.1.3.2 Azo Dyes
Concentrations of the 22 regulated aromatic amines were below the detection limit (0.2-1.5 mg/kg) in all but 4 yarn samples. In these samples, however, the concentration was safely below the limit value of 30 mg/kg. In Sample 49 (red yarn, purchased from China), o-toluidine (2-aminotoluene, CAS No.: 95-53-4) was found in a concentration of 1.1 mg/kg. A detectable content of 4-chloroaniline (CAS no.: 106-47-8) was found in 3 black yarn samples: 1) Sample 8 (black wool yarn; purchased from DK), 2) sample 12 (black 100% wool yarn - superwash; purchased from DK), and 3) sample 18 (black cotton yarn; purchased from the UK). The concentrations found were 1.5 mg/kg, 0.7 mg/kg, and 2.2 mg/kg, respectively. No detectable content of this amine was found in the fourth black yarn sample examined (sample 24 - black superwash wool; purchased from the UK). 4-chloroaniline is produced when Acid Red 119:1 dye, Pigment Red 184, Pigment Orange 44 (WHO, 2003) are reduced. But no 4-chloroaniline was detected when any of the red yarn samples were examined.

None of the investigated yarn samples showed detectable concentrations of the 8 amines, which will be subjected to limits from November 1st, 2020, according to REACH Annex XVII, entry 72.

3.2 Migration analyses
All tests were performed as real duplicates.

3.2.1 Sample preparation
The migration test was performed in artificial sweat based on an assessed realistic worst-case scenario. 1 g of sample was weighed into a glass. The weighing was performed in a fume hood and nitrile gloves were used to avoid contamination of siloxanes.

25 mL of artificial sweat was added to the weighed sample. The artificial sweat was prepared according to DS/EN ISO 105-E04, Textiles - Test for color fastness - Part E04: Color fastness to perspiration. The artificial sweat was made with L-histidine monohydrochloride monohydrate, sodium chloride and sodium dihydrogen orthophosphate dihydrate. The pH was adjusted to 5.5 with a 0.1M NaOH solution. A sample/sweat ratio 1/25 was used in accordance with the migration test described in DS/EN 71-3:2019, Safety of toys – Part 3: Migration of certain elements.

The migration test was performed in a heat bath at 37 °C for two hours, without shaking, as this was found to be a scenario too violent and unrealistic. After two hours the yarn sample was removed from the sample glass. The migration was subsequently analysed for the selected parameters, as described in the following section

3.2.2 Analysis methods

3.2.2.1 Metals
The concentration of heavy metals in the migration solution was determined by subjecting the fluid directly into an ICP-MS (Inductively coupled plasma mass spectrometer). The following metals were analysed: Lead (Pb), mercury (Hg), chromium (Cr), cobalt (Co), nickel (Ni), cobber (Cu), zinc (Zn), vanadium (V), arsenic (As), cadmium (Cd), tin (Sn), and antimony (Sb).

The detection limits (micrograms of metal per gram of yarn) for the migration analysis were: <0.05 µg/g for Co, As and Sn; 0.1 µg/g for V, Cr, Ni, Cd and Hg; 0.3 µg/g for Cu; 0.5 µg/g for Pb and Sb, and 0.8 µg/g for Zn. The expanded uncertainty for the analysis was 20% for each metal. Concentrations close to the detection limit may have an expanded uncertainty up to 50%.

Chromium (VI): According to the analysis plan, yarn samples with a total chromium concentration in the migration solution above the detection limit of chromium (VI), should be analysed for chromium (VI). But since chromium was detected in the migration solution in only four of the yarn samples in concentrations corresponding to the detection limit (0.1 µg/g yarn), chromium (VI) analysis was not performed initially.

However, the risk assessment for chromium (VI) revealed that even these low concentrations could be a problem if the chromium in the migration solution was present exclusively as Cr (VI). Therefore, in order to address this issue, the four yarn samples were analysed for content of both total chromium and chromium (VI).

The concentration of total chromium was determined according to MCL method DMA101. The yarn was weighed and extracted in a diluted aqua regia solution and heated in a microwave oven. The extract was analysed by means of ICP-MS. The detection limit was 0.5 ppm. The expanded uncertainty was 20%. Concentrations close to the detection limit may have an expanded uncertainty up to 50%.

The concentration of chromium (VI) was determined according to MCL method DMA113. The yarn was extracted in a boiling solution of sodium hydroxide and sodium carbonate. The mixture was vortexed and put into an ultrasonic bath. The extract was filtrated and acidified with dilute sulfuric acid. A solution of diphenylcarbazide in acetone was added. The concentration of chromium (VI) was determined using a spectrophotometer at 540 nm. The detection limit for chromium (VI) was 3 ppm, and the expanded uncertainty was 30%.

Organotin compounds: Like the chromium (VI) analysis, quantitative organotin analyses should only be performed if tin concentrations in the metal analysis were found to exceed the detection limit for organotin. Since this was not the case, no organotin analysis was performed on the migration solutions.

3.2.2.2 Permethrin

The migration solution was filtrated and analysed by means of LC-ESI-MS in accordance with a method described by Wang et al. (2003). In this method, permethrin is identified and quantified from the mother-ion (MH^+ = 391.1 m/z). Identification is further confirmed by occurrence of the two fragments, $[MH-Cl]^+$ and $[MH-2Cl]^+$ with m/z 319 and 355, respectively.

The content of permethrin was quantified by comparison with a certified standard solution. An internal standard was used to adjust for losses during sample preparation and analysis. At the minimum a control solution was run for every 10th sample.

Detection limit was 1 µg/g and the expanded uncertainty was 20%.

3.2.2.3 Formaldehyde

Formaldehyde was determined according to ISO 14184-1, Textiles — Determination of formaldehyde — Part 1: Free and hydrolyzed formaldehyde (water extraction method). A subsample from the migration solution was transferred to a sample vial and acetylacetone reagent was added. The mixture was allowed to react for 30 minutes at 40°C. The concentration was determined by measuring the absorption at 412 nm.

If there was any doubt whether the absorption was coming from the formaldehyde reaction or colour from the yarn, a dimedon confirmation test was carried out. In this test, dimedon reagent was added to the migration solution before the acetylacetone reagent. Dimedon prevents colour reaction from formaldehyde and a false positive could be detected.

The method covers the range from 3.75 µg/g to 820 µg/g. Concentrations below 3.75 µg/g were reported as not detected. The expanded uncertainty was 25 %.

3.2.2.4 Bisphenol A
Analyses for bisphenol A were conducted for 10 selected cotton yarn samples. To the migration solution was added D-16 BPA as an internal standard. The migration solution was then filtrated and analysed by means of LC-ESI-MS in negative mode. The concentration was quantified from a certified standard solution. The LS-MS analysis was done according to Freire et al. (2019). At the minimum a control solution was run for every 10th sample. The detection limit was 1 µg/g and the expanded uncertainty was 20%.

3.2.2.5 Siloxanes
Twelve selected superwash wool yarns were analysed for siloxanes D4, D5 and D6. The analysis was done according to ”Quantification of residual amounts of cyclic volatile methyl siloxanes in fully formulated personal care products, CES – Silicones Europe”, issue date September 2018, revised January 2019”, modified to migration solution.

To the migration solution was added cyclohexane containing an internal standard followed by liquid-liquid extraction. To the organic cyclohexane fraction was subsequently added N-trimethylsilyl trifluoracetamid (MSTFA), and the mixture was allowed to react for 30 minutes at 80 °C. The MSTFA treatment had three aims:

1. to derivatize silanol end-groups to prevent generation of cVMS by back biting
2. to silylate reactive species that might facilitate the generation of cVMS by back biting
3. to derivatize co-extracted species that might interfere with the chromatographic analysis

After derivatization, the cyclohexane phase was analysed by means of GC-MS (although the method recommends GC-FID), in order to achieve better selectivity.

The siloxanes were quantified by comparison with analytical standards for each component. The detection limit was 0.02-0.03 µg/g and the expanded uncertainty was 20%.

3.2.3 Results of migration analyses

3.2.3.1 Metals
Concentrations of heavy metals in the migration solution for the samples investigated are shown in Table 4.

TABLE 4. Concentration of heavy metals in the migration solution for the investigated yarn samples. "-" means that the concentration was below the limit of detection.

Sample no.	Description	Average concentration in the migration solution recalculated to µg/g yarn											
		V	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Sb	Hg	Pb
Samples purchased from Denmark													
1	Dark green cotton yarn; purchased from DK; 7 kr. per skein	-	0.1	-	-	0.3	1.4	0.02	-	-	0.9	-	-
2	Sky-blue cotton yarn; purchased from DK;	-	0.1	-	0.2	7.5	1.6	-	-	-	0.8	-	-
3	Cotton yarn in colour Fire Opal; purchased from DK; 120 kr. per skein	-	-	-	0.1	-	2.6	-	-	-	0.7	-	-
5	Green cotton yarn; purchased from DK; 15 kr. per skein	0.1	-	-	-	1.5	2.3	0.02	-	-	0.7	-	-
6	Organic red cotton yarn; purchased from DK; 31 kr. per skein	-	-	-	0.2	0.6	3.8	-	-	-	0.6	-	-
7	White 100% wool yarn; purchased from DK; 11 kr. per skein	0.1	-	-	-	-	2.8	0.02	-	-	0.6	-	-
8	Black wool yarn; purchased from DK; 110 kr. per skein	0.1	-	-	0.1	0.4	8.4	-	-	-	-	-	-
9	Yellow merino wool yarn; Øko-tex; purchased from DK; 45 kr. per skein	-	-	-	0.1	0.4	11	0.02	-	-	0.5	-	-
10	100% organic Shetlands wool in dusty blue; purchased from DK; 30 kr. per skein	-	0.1	-	-	0.4	3.0	-	-	-	-	-	-
11	White 100% merino wool superwash; purchased from DK; 34 kr. per skein	0.2	-	-	0.1	0.4	13	-	-	-	-	-	-
12	Black 100 % wool yarn – superwash; purchased from DK; 19 kr. per skein	-	-	-	-	0.6	16	-	-	-	-	-	-
13	Yellow wool yarn superwash; purchased from DK; 32 kr. per skein	-	-	0.6	0.1	0.5	11	0.02	-	-	-	-	-
14	Army-green 100% wool superwash yarn; purchased from DK; 20 kr. per skein	0.1	-	0.1	0.1	0.7	2.6	0.02	-	-	-	-	-
15	Dark blue extra soft superwash merino wool; purchased from DK; 25 kr. per skein	-	-	-	0.1	0.3	14	-	-	-	-	-	-
16	Dark blue 100% wool superwash; purchased from DK; 30 kr. per skein	0.2	-	-	0.1	0.4	11	-	-	-	-	-	-
Samples purchased from EU													

Sample no.	Description	Average concentration in the migration solution recalculated to µg/g yarn											
		V	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Sb	Hg	Pb
17	Blue (40) cotton Øko-tex; purchased from NL; 19 kr. per skein	-	-	-	0.1	0.3	4.7	-	-	-	-	-	-
18	Black cotton yarn; purchased from UK; 20 kr. per skein	-	-	-	-	-	1.3	-	-	-	-	-	-
20	70% cotton and 30 % polyacrylic dusty blue yarn; purchased from DE; 30 kr. per skein	-	-	-	0.1	3.1	1.8	-	-	-	-	-	-
21	White merino superwash wool; purchased from NL; 37 kr. per skein	-	-	-	-	-	1.2	-	-	-	-	-	-
22	Yellow 100% Scandinavian wool; purchased from NO; 32 kr. per skein	-	-	-	-	0.4	17	-	-	-	-	-	-
23	Red superwash wool; purchased from SE; 27 kr. per skein	-	-	-	-	0.3	4.5	-	-	-	-	-	-
24	Black superwash wool; purchased from UK; 25 kr. per skein	-	-	-	-	0.4	3.7	-	-	-	-	-	-
25	Green classic superwash yarn; purchased from UK; 49 kr. per skein	-	-	-	-	0.5	14	-	-	-	-	-	-
26	Yellow 100 % merino superwash wool; purchased from SE; 32 kr. per skein	-	0.1	0.1	-	0.5	1.0	-	-	-	-	-	-
31	Red 100 % alpaca (superfine) wool yarn; Oeko-Tex; purchased from DE; 38 kr. per skein	-	-	-	-	0.8	3.7	0.03	-	-	-	-	-
34	Blue superwash wool; purchased from UK; 37 kr. per skein	-	-	-	0.1	0.5	10	-	-	-	-	-	-
35	55 % Polyacrylicand 45 % cotton green yarn; purchased from DE; 10 kr. per skein	-	-	-	0.1	1.0	2.2	-	-	-	-	-	-
36	Rainbow superwash wool yarn; purchased from DE; 45 kr. per skein	-	-	-	-	0.5	13	-	-	-	-	-	-
37	Green (Myrtle) 100 % pure new British wool; purchased from UK; 57 kr. per skein	-	-	0.3	-	1.3	20	-	-	-	-	-	-
39	Red 100% wool; Øko-tex; purchased from LV; 22 kr. per skein	-	-	-	-	0.3	12	-	-	-	-	-	-
40	Yellow/white (7414) cotton; Øko-Tex; purchased from LV; 62 kr. per skein	0.2	-	-	0.1	-	2.3	0.1	-	-	-	-	-
43	Yellow superwash wool; purchased from UK; 37 kr. per skein	0.1	-	-	-	-	-	-	-	-	0.6	-	-
Samples purchased from outside EU													

Sample no.	Description	Average concentration in the migration solution recalculated to µg/g yarn											
		V	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Sb	Hg	Pb
29	White mercerised cotton yarn; purchased from USA; 43 kr. per skein	-	-	-	0.1	-	0.8	-	-	-	-	-	-
30	Red extra soft superwash merino wool yarn; purchased from USA; 91 kr. per skein	-	-	-	-	0.3	15	-	-	-	-	-	-
32	Yellow natural soft superwash wool yarn; purchased from USA; 26 kr. per skein	-	-	-	-	0.4	13	-	-	-	-	-	-
33	Blue (ultra marine) extra softwool superwash; purchased from USA; 33 kr. per skein	-	-	-	-	3.3	4.5	-	-	-	-	-	-
38	Light blue (blue fog) 100% pure new wool; purchased from USA; 52 kr. per skein	-	-	-	-	0.5	9.0	-	-	-	-	-	-
42	White 100 % organic wool yarn; purchased from RU; 20 kr. per skein	0.1	-	-	-	-	8.8	-	-	-	0.8	-	-
45	Dark blue (navy) 100% organic cotton yarn; purchased from USA; 52 kr. per skein	0.1	-	-	-	-	-	0.02	-	-	0.6	-	-
46	White 100% superwash merino wool; purchased from USA; 68 kr. per skein	0.1	-	-	-	-	-	0.02	-	-	-	-	-
47	Green (jade) 100 % extra soft superwash merino wool; purchased from USA; 59 kr. per skein	0.1	-	-	0.1	-	6.8	-	-	-	-	-	-
48	Red cotton yarn; purchased from USA	0.2	-	-	0.5	-	-	0.03	-	-	-	-	-
49	Red yarn; purchased from China	0.2	-	-	-	-	6.2	0.02	-	-	-	-	-
50	Green (06) 100% superwash extra soft merino wool; purchased from USA;	0.1	-	-	-	-	10	0.02	-	-	0.5	-	-
51	Red (11) 100 % superwash extra soft merino wool; purchased from USA;	0.1	-	-	-	-	-	0.02	-	-	-	-	-

Copper was found in the migration solution from 30 samples corresponding to 67% of the samples investigated. Concentrations of copper (Cu) were between 0.3 µg/g yarn (detection limit) and 7.5 µg/g yarn. The highest concentration was measured in the migration solution from sample 2 – sky-blue cotton yarn, purchased from Denmark.

Zinc was found in 40 yarn samples corresponding to 89% of the samples investigated. The concentration of zinc (Zn) was between 0.8 µg/g yarn (limit of detection) and 20 µg/g yarn. The highest concentration was measured in sample 37 - green wool yarn, purchased from the UK.

Cobalt (Co) was found in 4 samples with the highest concentration of 0.6 µg/g yarn. Antimony (Sb) was measured in the migration solution from 11 samples at concentrations between 0.5 µg/g yarn (corresponding to the detection limit) and 0.9 µg/g yarn. Lead (Pb), cadmium (Cd), tin (Sn) and mercury (Hg) were not found in quantities above the detection limit in the migration solution for any of the yarn samples investigated. Vanadium (V), chromium (Cr), nickel (Ni) and arsenic (As) were found in the migration solution from 4 yarn samples. However, the concentrations were low, i.e. equal to or close to the detection limit for the individual heavy metals.

Supplementary content analyses for total chromium and chromium (VI) were performed on the 4 yarn samples where chromium was found in the migration solution. They showed total chromium content below 1 ppm in sample 1 - dark green cotton yarn (0.8 ppm) and sample 2 – sky-blue cotton yarn (0.7 ppm). The content in sample 10 – 100% organic Shetland wool in dusty blue and sample 26 – Yellow100% merino superwash wool was higher, 42 ppm and 8.8 ppm, respectively. No chromium (VI) above the detection limit (3 ppm) was found in any of the samples examined.

Higher migration values for zinc (Zn) were found from wool and superwash wool yarns compared to cotton yarns. For the sum of the remaining heavy metals, the opposite trend was observed although less pronounced (Figure 2). Furthermore, a tendency towards increased zinc concentration with increasing yarn price was observed (Figure 3).

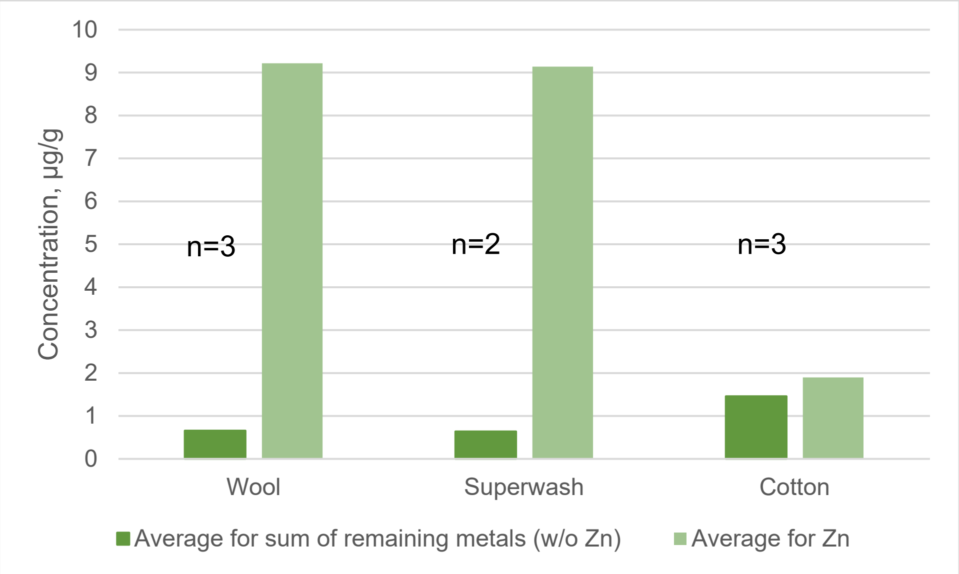

FIGURE 2. Metal content in wool, superwash wool, and cotton yarns. Average concentration (in µg/g yarn) for zinc (light green column) and average concentration for the sum of the remaining metals (dark green column) are shown for each yarn type. The median number (n) of heavy metals above the detection limit in each group is shown.

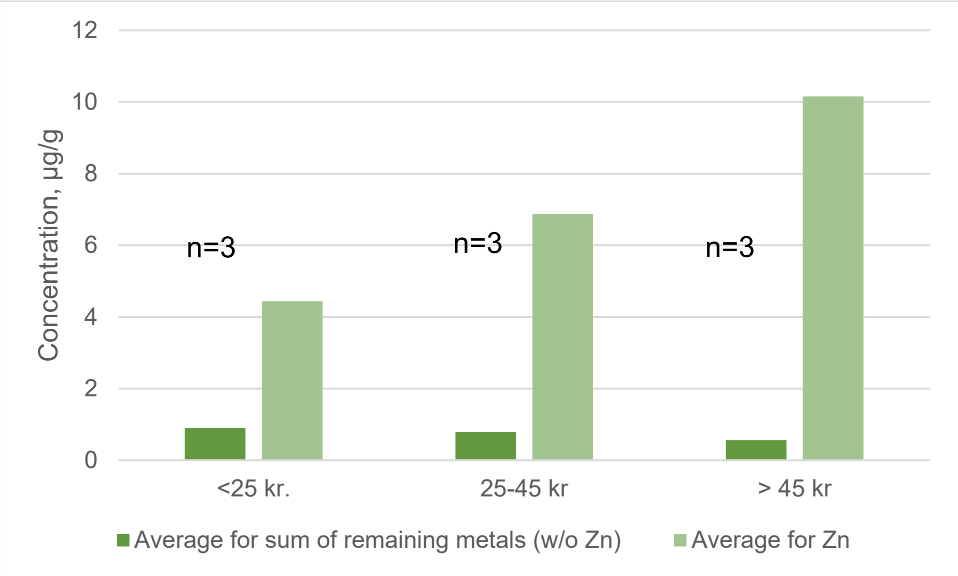

FIGURE 3. Metal content in relation to price level. Average concentration (in µg/g yarn) for zinc (light green column) and average concentration for the sum of the remaining metals (dark green column) are shown for each price range. The median number (n) of heavy metals above the detection limit in each group is shown.

The average concentration of zinc in the migration solution was slightly higher for samples purchased outside the EU, while the average sum of concentrations of the remaining heavy metals examined was slightly higher in the migration solution from the Danish samples. The overall number of heavy metals being detected was also found to be higher in the Danish samples compared to samples purchased elsewhere (Figure 4). However, the relevance of the country of purchase in regard to the concentration of heavy metals in the migration fluid and the number of metals measured above the detection limit seems minor when the uncertainties of the measurements are taken into account.

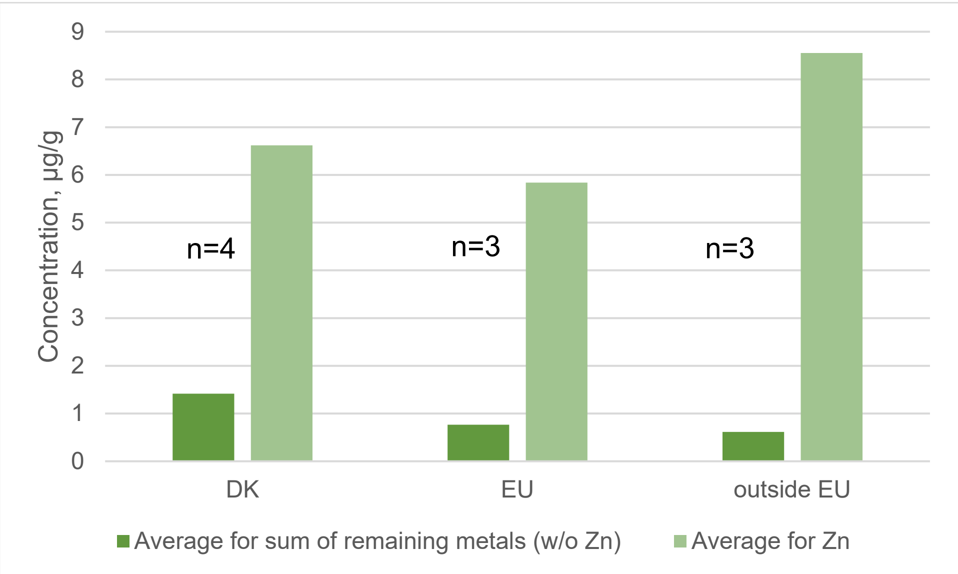

FIGURE 4. Metal content in relation to country of purchase; resp. DK, EU and outside EU. Average concentration (in µg/g yarn) for zinc (light green column) and average concentration for the sum of the remaining metals (dark green column) grouped by country of purchase. The median number (n) of heavy metals above the detection limit in each group is shown.

3.2.3.2 Permethrin

Permethrin was not found above the detection limit in the migration solution for any of the yarn samples investigated.

3.2.3.3 Formaldehyde

Formaldehyde was found in concentrations above the detection limit in the migration solutions from 10 out of 45 yarn samples, corresponding to 22% of the samples investigated. Analysis results for these samples are shown in Table 5, which displays average values for duplicate determinations performed on each yarn sample.

The concentration of formaldehyde in the migration solution for the examined yarn samples varies from just above the detection limit (3.7 µg/g yarn) to 21 µg/g yarn. Migration of formaldehyde was only found from the wool yarn samples, including both superwash (4 samples) and non-superwash (6 samples). The highest concentration was measured in sample 42, which was organic wool yarn purchased from Russia.

TABLE 5. Results for formaldehyde migration from the investigated yarn samples.

Sample no.	Description	Concentration in the migration solution recalculated to µg/g yarn
Samples purchased from Denmark		
9	Yellow (46129) merino wool yarn; Øko-tex, purchased from DK; 45 kr. per skein	6.9
10	100 % organic Shetlands wool, dusty blue; purchased from DK; 30 kr. per skein	4.4
13	Yellow wool superwash yarn; purchased from DK; 32 kr. per skein	6.6
14	Army-green 100% wool superwash yarn; purchased from DK; 20 kr. per skein	11.3
Samples purchased from EU		
22	Yellow 100% Scandinavian wool; purchased from Norway, approx. 32 kr. per skein	4.9
25	Green classic superwash wool yarn; purchased from UK; approx. 50 kr. per skein	5.2
31	Red 100 % alpaca (superfine) wool yarn; Øko-Tex; purchased from DE; 38 kr. per skein	3.9
37	Green (Myrtle) 100% pure new British wool; purchased in UK; approx. 58 kr. per skein	10.7
43	Yellow superwash wool; purchased from UK; 37 kr. per skein	5.3
Samples purchased from outside EU		
42	White 100% organic wool yarn; purchased from RU; 20 kr. per skein	21.5

3.2.3.4 Bisphenol A

Migration of bisphenol A was investigated in a selection of 10 cotton yarn samples, including 3 yarns purchased in Denmark (sample no.: 1, 3, 6), 4 yarns purchased in other EU countries (sample no.: 17, 18, 27, 40) and 3 yarns purchased outside EU (sample no.: 29, 45, 48). Bisphenol A was not found above the detection limit in the migration solution for any of these yarn samples.

3.2.3.5 Siloxanes

Migration of D4, D5 and D6 siloxanes was investigated in a selection of 12 superwash wool samples. The selection included 4 yarns purchased in Denmark (sample no.: 11, 13, 15 and

16), 4 yarns purchased in other EU countries (sample no.: 21, 23, 24 and 26) and 4 yarns purchased outside EU (sample no.: 30, 32, 33 and 47). Neither D4, D5, nor D6 siloxanes were found above the detection limit in the migration solution from any of these yarn samples.

3.3 Summary of the results

45 yarn samples have been examined, including:

- 21 superwash wool yarn samples
- 11 wool yarn samples (not superwash)
- 13 cotton yarn samples.

None of the yarn samples contained nonylphenol above the detection limit. Nonylphenol ethoxylates were found above the detection limit in 6 yarn samples, one of which was above the upcoming limit value of 100 mg/kg. The remaining 5 yarn samples showed values significantly below this limit value, with a maximum concentration of 62 mg/kg being found.

Regulated aromatic amines were found in 4 yarn samples. However, the measured concentrations were significantly below the limit value.

Only low concentrations of heavy metals were detected in the migration analyses. In some samples, formaldehyde has been found. Neither permethrin, bisphenol A, nor cyclic siloxanes have been found in quantities above the detection limit in the migration solutions.

Zinc and copper were the two metals being found in both the greatest number of samples (89% and 67%, respectively) and in the highest concentrations. The highest concentrations found in the migration solutions was 20 µg/g yarn for zinc and 7.5 µg/g yarn for copper. There was a tendency towards higher zinc concentrations in the migration solutions from wool yarn (both superwash and non-superwash qualities) relative to those from cotton yarn. In addition, there was a tendency towards elevated zinc concentrations with increasing yarn price. The concentrations and frequency of the other heavy metals in the migration solutions were considerably lower. Chromium was found in only 4 samples at concentrations in the order of the detection limit. Lead, cadmium, tin and mercury were not found. Therefore, no analysis was performed for organotin compounds in the migration solutions, since this analysis should be performed only if total tin was detected in amounts above the detection limit of the organotin analysis.

In the risk assessment for chromium (VI), it was found that even concentrations as low as the detection limit could be a problem if the chromium was present only as chromium (VI). Supplementary content analysis for total chromium and chromium (VI) was performed on the 4 yarn samples where chromium was found in the migration solution. They showed total chromium contents below 1 ppm in two samples (sample no.: 1 and 2), while the content in sample 10 and sample 26 was higher, that is 42 ppm and 8.8 ppm, respectively. No chromium (VI) above the detection limit (3 ppm) was found in any other samples examined.

Formaldehyde was found in the migration solution from 10 wool yarns at concentrations ranging from 3.9 µg/g yarn to 21.5 µg/g yarn. None of the cotton yarns released formaldehyde into the migration solution.

4. Risk assessment for consumers

4.1 Hazard assessment

Based on the analytical chemical findings, it was decided to carry out hazard assessments of the following substances:

- Formaldehyde (measured levels 3.9 – 21.5 µg/g yarn)
- Copper (measured levels 0.3 – 7.5 µg/g yarn)
- Zinc (measured levels 0.8 – 20 µg/g yarn)
- Cobalt (measured levels 0.1 – 0.6 µg/g yarn)
- Nickel (measured levels 0.1 – 0.5 µg/g yarn)
- Chromium (measured level 0.1 µg/g yarn)

Although the latter three metals have only been found in very low concentrations, they are still included, as cobalt, chromium (especially Cr (VI)) and nickel are potent skin sensitisers.

Below is an overall overview regarding the health hazard classification of the above substances. For metals, the classification for easily soluble salts will be stated as the metals have been found as soluble metal ions in the migration liquid.

TABLE 6. Hazard classification of selected substances for hazard assessment

Substance/CAS no.	Classification according to IEU 1272/2008
Formaldehyde 50-00-0	Acute Tox 3 H301; H311; H331 Skin. Corr. 1B H314 Skin Sens 1 H317 (C ≥ 0,2%) Muta. 2 H341 Carc. 1B H350
Copper Copper sulphate 7758-98-7	Acute Tox. 4 H302 Skin Irrit. 2 H315 Eye Irrit. 2 H319
Zinc Zinc sulphate 7446-19-7	Acute Tox. 4 H302 Eye Dam. 1 H318
Cobalt Cobalt sulphate 10124-43-3	Acute Tox. 4 H302 Skin Sens 1 H317 Resp. Sens. 1 H334 Muta. 2 H341 Carc. 1B H350i Repr. 1B H360F
Chromium (VI) Chromium trioxide 1333-82-0	Acute Tox 3 H301, H311 Acute Tox 2 H330 Skin Corr. 1A Skin Sens 1 H317 Resp. sens.1 H334 Muta. 1B H340 Carc 1A H350 STOT RE 1 H372

Substance/CAS no.	Classification according to IEU 1272/2008
	Repr. 2 H361f
Chromium (III) Chromium (iii) chloride * 10025-73-7	Acute Tox. 4 H302 Skin Sens 1 H317
Nickel Nickel sulphate 7786-81-4	Acute Tox. 4 H302, H332 Skin Irrit. 2 H315 Skin Sens 1 H317 Resp. Sens. 1 H334 Muta. 2 H341 STOT RE 1 H372 Carc. 1A H350i Repr. 1B H360D

*Classification from the REACH registration. No harmonised classification.

For formaldehyde, it is noted that even at low concentrations the substance is classified as a skin sensitiser (at concentrations ≥ 0.2%), and that the substance is classified for carcinogenic and mutagenic effects. In addition, the substance is classified for acute toxic and corrosive properties.

Copper and zinc are classified for acute oral toxicity and for skin irritating and eye irritating properties. The substances are not skin sensitisers like the other substances in the table.

For the other metals, it is noted that they all have a very comprehensive health classification, as they are all classified for skin and respiratory sensitisation, as carcinogenic and toxic to reproduction as well as for mutagenic properties - thus a wide range of critical effects.

Subsequently, a hazard assessment is made of the selected substances. Data are obtained primarily from already performed expert evaluations of the substances (e.g. from EU scientific committees and expert groups or from WHO expert groups). These data are supplemented with recent relevant data obtained by web-based searches and from the REACH registration dossiers of the substances.

The hazard assessments focus on harmful effects from *skin contact* and in connection with *oral ingestion* (infants sucking on parts of the knitwear), as this is considered the relevant exposure routes regarding exposure from knitting yarn. The possibility of *inhalation* of substances from the yarn is considered less likely, but in the case of content of particularly volatile substances this will be included in the assessment based on the specific findings.

Based on the toxicological data collected, the most critical effects of the substance and N(L)OAEL values for these effects are identified. If the expert assessments have derived a tolerable exposure level (corresponding to DNEL values, Derived No Effect Level) in the REACH regulation), these are stated. If tolerable exposure levels are not specified, the derivation of DNELs is carried out in accordance with the guidelines given in the REACH guideline document R8, (ECHA 2012).

It should be noted, for instance for skin sensitisers and genotoxic carcinogens, that data are rarely available to establish a safe level of exposure completely without risk of the harmful effects. Instead of a DNEL value, the risk assessment can be based on the determination of a DMEL value (Derived Minimal Effect Level), i.e. a level with a very low effect level.

For skin sensitisers, the DMEL may be based on an ED10 value, which corresponds to the concentration of the skin sensitiser triggering an allergic reaction in skin provocation tests in

10% of the test subjects known to be allergic to the substance. Such a concentration will usually be significantly below the concentration that can induce sensitisation. Thus, using a ED10 value in the risk assessment, will not only protect against sensitisation but will also to a wide extent protect already sensitised persons.

For carcinogens without a lower threshold value and based on the dose-response relationship at carcinogenic exposure levels, the risk of the carcinogenic effect at very low exposure levels can be calculated. Exposure levels corresponding to a 10^{-5} or 10^{-6} lifetime risk of developing cancer are often used as a tolerable DMEL value.

Finally, each hazard assessment for the individual substance is concluded with a selection/calculation of relevant D(M)NEL values for further use in the risk assessment.

4.1.1 Formaldehyde

The following references have been used as the basis for hazard assessment of formaldehyde:

- EFSA (2006). Use of formaldehyde as a preservative during the manufacture and preparation of food additives. Opinion of the Scientific Panel on food additives, flavorings, processing aids and materials in contact with food (AFC). The EFSA Journal (2006) 415, 1-10.

- Danish EPA (2014c). Survey of Formaldehyde. Part of the LOUS review Environmental project No 1618, 2014. https://www2.mst.dk/Udgiv/publications/2014/11/978-87-93283-23-7.pdf.

- SCCS (2014). Opinion on the safety of the use of formaldehyde in nail hardeners. SCCS/1538/14, Revision of 16 December 2014.

- WHO (2005a). Formaldehyde in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. WHO/SDE/WSH/05.08/48.

Skin contact

The sensitising effect of formaldehyde is considered to be the most critical effect in relation to skin contact. It is estimated that approx. 0.5% of the population in Europe show allergic reactions at skin contact with formaldehyde.

Formaldehyde has been found as a skin sensitiser in a number of experimental animal testin, including LLNA test in mice where a positive response (corresponding to an EC3 value) at a concentration of 0.29% formaldehyde solution.

In humans, skin sensitisation has been observed at exposure to 1% formaldehyde, whereas already sensitised persons may react at exposure to 0.003% formaldehyde in aqueous solutions and to 0.006% in products containing formaldehyde (SCCS 2008).

In human provocation experiments with sensitised persons allergy an exposure of 20.1 µg per cm^2 causes an allergic reaction in the 10% most sensitive formaldehyde perssons allergy sufferers (ECHA 2020).

Oral exposure
No systemic absorption of formaldehyde has been reported, as formaldehyde upon exposure reacts rapidly with the surface of the mucous membranes and is thus no longer available for systemic uptake (Danish EPA 2014c).

Based on animal experimental data, WHO (2004) and EFSA (2006) set a NOAEL of 15 mg/kg bw/day based on a long-term study in rats, with higher exposure levels having effects on the gastric mucosa. Based on this, WHO (2004) and EFSA (2006) determined a TDI value of 0.15 mg/kg bw/day using an uncertainty factor of 100.

Other data
SCCS (2014) further assessed the respiratory tract irritation and carcinogenic effects of formaldehyde as critical effects by inhalation. Formaldehyde has been shown to be carcinogenic by inhalation when the exposure exceeds a certain threshold value. For humans 100 µg/m^3 is considered a tolerable exposure level without risk of carcinogenic effects and/or irritation of the eyes and respiratory tract.

However, these data are not considered relevant for this risk assessment, partly as evaporation from the yarn is not measured and partly because evaporation can be considered negligible due to the very low measured concentrations in the yarn. Empirical evidence shows that evaporation from building materials with such a low content of formaldehyde will not result in a concentration of 100 µg/m^3 in a room even with large surfaces involved.

Conclusion
The following tolerable exposure levels (DN(M)ELs) are used as a basis for further risk assessment.

<u>DN(M)EL skin contact, formaldehyde sensitised persons:</u>

DMEL*, skin contact, symptoms = 20 µg per cm^2 (ECHA 2020)
DMEL*, skin contact, symptoms = 0.003 % ** (SCCS 2014)

* The DMEL term is used instead of the DNEL term, as the value refers to an effect level (Derived Minimal Effect Level) corresponding to the reaction of the 10% most sensitive sensitised persons in a provocation experiment.

** For comparison: when applying a 1 mm layer of a 0.003% formaldehyde solution to the skin, this would correspond to an exposure of 30 µg per cm^2 of skin.

<u>DNEL, skin contact systemic effects:</u>

DNEL for skin contact cannot be calculated for systemic effects as formaldehyde is not absorbed systemically through the skin.

<u>DNEL oral exposure:</u>

DNEL, orally = 0.15 mg/kg bw/day (with regards to effects on the gastric mucosa)

4.1.2 Copper
The following references have been used as the basis for hazard assessment of copper:

- EFSA (2018). Peer review of the pesticide risk assessment of the active substance copper compounds copper(I), copper (II) variants namely copper hydroxide, copper

oxychloride, tribasic copper sulphate, copper(I) oxide, Bordeaux mixture. EFSA Journal 2018;16(1):5152, 1- 25.

- EFSA (2008). Conclusion on pesticide peer review. Conclusion regarding the peer review of the pesticide risk assessment of the active substance Copper (I), copper (II) variants namely copper hydroxide, copper oxychloride, tribasic copper sulphate, copper (I) oxide, Bordeaux mixture. EFSA Scientific Report (2008) 187, 1-101.

- REACH registration dossier for copper sulphate (ECHA, Copper sulphate 2020).

Skin contact
Water-soluble copper sulphate in a concentration of 42% has shown moderate skin irritating effects in rabbit experiments. Four hours of exposure caused reversible redness, but without causing edema (REACH registration).

In a rabbit skin sensitisation test (GPMT test), copper sulphate did not show a skin sensitising effect (REACH registration).

EFSA (2008) found that there were no suitable experimental data to assess the dermal absorption of copper ions and used a dermal absorption of 10% as a conservative estimate for risk assessment.

Oral exposure
EFSA (2008) stated that copper is an essential mineral for the human organism and that the natural daily intake of copper through food in Europe is in the range of 1-2 mg/day.

After oral dosing, the lowest NOAEL value of 15 mg Cu/kg bw/day was found in a reproduction study in rats, where higher dose levels resulted in reduced spleen weight in both the parent generation and the offspring. However, the preferred basis for calculating a tolerable exposure level was a NOAEL value of 15 mg Cu/kg bw/day from a 1-year study in dogs. From this a tolerable exposure level of 0.15 mg/kg bw/day was calculated using a safety factor of 100 (EFSA 2008)

Furthermore, EFSA found that human data with a high copper intake of up to 10-12 mg daily (equivalent to 0.2 mg/kg bw/day) were without adverse effects, so the human data thus supported an upper tolerable exposure level of 0,15 mg Cu/kg bw/day.

EFSA (2008) found that approx. 50% copper is absorbed by oral ingestion, and calculated a tolerable systemic exposure level of 0.072 mg/kg bw/day.

Other data
EFSA (2008) did not find it possible from the available *in vitro* and *in vivo* studies to conclude whether copper can be considered genotoxic. Copper was not considered to possess carcinogenic properties based on long-term studies in rats.

Conclusion
The following tolerable exposure levels (DNELs) are used as a basis for further risk assessment.

<u>DNEL for skin contact:</u>

DNEL, skin contact (irritation) = LOAEL/AF1 x AF2 x AF3
DNEL, skin contact (irritation) = 42 %/1 x 10 x 3
DNEL, skin contact (irritation) = 1.4 %

where

AF1 is set to 1 for local irritation effects, as human skin is not considered more sensitive to irritation than the skin of experimental animals (ECHA 2012)
AF2 is set to 10 for differences in human susceptibility
AF3 is set to 3 to extrapolate from effect level to a no-effect level

<u>DNEL, for skin contact, systemic effects:</u>

DNEL, skin contact (syst. tox.) = NOAEL syst./abs. dermal
DNEL, skin contact (syst. tox.) = 0.072 mg/kg bw/day/0,1
DNEL, skin contact (syst. tox.) = 0.72 mg/kg bw/day

<u>DNEL for oral exposure:</u>

DNEL, oral (syst. tox.) = 0.15 mg/kg bw/day

4.1.3 Zinc

The following references have been used as a basis for hazard assessment of zinc:

- EFSA (2014a). Scientific Opinion on Dietary Reference Values for zinc. EFSA Journal 2014;12(10):3844, 76 pp.

- SCCS (2017). Opinion on water-soluble zinc salts used in oral hygiene products20 - Submission I. Scientific Committee on Consumer Safety. SCCS/1586/17.

Skin contact
Water-soluble zinc compounds are highly irritating to the skin. In experimental animals, skin irritation was at 1% aqueous zinc solutions (SCCS 2017).

Oral
EFSA (2014a) stated that zinc is an essential mineral for the organism, and a daily need for zinc intake is in the range of 6.2-12.7 mg/day for adults.

The body regulates the uptake of zinc according to the needs of the organism. In people with normal zinc status, the oral absorption of zinc varies between 20 and 30%. In people with high and low zinc status, respectively, it can vary from 8 to 80% (SCCS 2017).

Chronic high zinc intake in humans may cause neurological damage due to copper deficiency, as zinc inhibits the body's uptake of copper. To address this, the EU has set a tolerable upper zinc intake of 25 mg/day (equivalent to 0.4 mg/kg bw/day) based on a NOAEL of 50 mg/day from human data and using an uncertainty factor of 2 (EFSA 2014a).

Other data
SCCS (2017) assessed that zinc possesses neither mutagenic, reproductive toxic or carcinogenic properties.

Conclusion
The following tolerable exposure levels (DNELs) are used as a basis for further risk assessment.

<u>DNEL for skin contact:</u>

DNEL, skin contact (irritation) = LOAEL/AF1 x AF2 x AF3
DNEL, skin contact (irritation) = 1 %/1 x 10 x 3
DNEL, skin contact (irritation) = 0.03 %

where

AF1 is set to 1 for local irritation effects, as human skin is not considered more sensitive to irritation than the skin of experimental animals.
AF 2 is set to 10 for differences in human susceptibility
AF 3 is set to 3 to extrapolate from effect level to a no-effect level

DNEL, skin contact, systemic effects:

DNEL, skin contact (syst. tox.) = NOAEL oral x oral abs./abs. dermal
DNEL, skin contact (syst. tox.) = 0.4 mg/kg bw/day x 0.5/0.1
DNEL, skin contact (syst. tox.) = 2 mg/kg bw/day

DNEL, oral exposure:

DNEL, oral (syst. tox.) = 0.4 mg/kg bw/day

4.1.4 Cobalt

The following references have primarily been used as the basis for hazard assessment of cobalt:

- Danish EPA (2013b). Cobalt (II), inorganic and soluble salts Evaluation of health hazards and proposal of a health based quality criterion for drinking water. Danish Environmental Protection Agency Environmental Project. No. 1520.

- Danish EPA (2019). Chromium VI and cobalt in leather goods. Control of chromium and risk evaluation of cobalt. Survey on consumer products No. 177.

Skin contact
Cobalt is both a skin sensitiser in animals and humans and cobalt allergy occurs in approx. 6% of female and 2% of male eczema patients. Cobalt allergy often coincides with allergy to chromium (VI) and nickel (Danish EPA 2019, source: website from the National Allergy Research Center 2018).

Based on clinical provocation tests of cobalt sensitised persons, it has been shown that cobalt exposure of the skin corresponding to 0.441 - 1.95 µg cobalt per cm^2 can trigger allergic skin reactions in the 10% most sensitive people among the test persons (Danish EPA 2019, source: Fisher et al. 2015).

In connection with a restriction proposal for skin sensitisers in leather and textiles, ECHA (2020) has subsequently assessed 0.44 µg of cobalt per cm^2 as the most relevant starting point for a risk assessment.

The skin absorption is reported to a maximum of 1% for the cobalt (II) ion based on skin exposure experiments with guinea pigs (Danish EPA 2013b, source: ATSDR 2004 with reference to Inaba and Suzuki-Yasumoto 1979).

Oral exposure
Cobalt is part of the body's essential B12 vitamin. Through the diet, the population consumes approx. 5-40 µg cobalt per day. Human oral absorption is reported to be in the range of 18-97% depending on the cobalt compound and the nutritional status (Danish EPA 2013b, source: ATSDR 2004 with reference to Harp and Scoular 1952, Smith et al. 1972, Sorbie et al. 1971, Valberg et al 1969). Based on these data, an average absorption rate of 50% will be used in this report.

There are no recent assessments regarding tolerable oral exposure to cobalt. The Danish EPA (2013) concluded that the influence on blood parameters is the most critical effect in both humans and animals. In rats, an NOAEL of 0.6 mg Co/kg bw/day was found in an oral experiment over 6 weeks, while in humans a LOAEL of 1 mg Co/kg bw/day was found (Danish EPA 2013b, source: ATSDR 2004 with reference to Stanley et al. 1947 and Davis & Fieldes 1958). Based on a human LOAEL of 1 mg/kg bw/day and using an uncertainty factor of 3000 (10 for differences in sensitivity between humans and 300 due to the use of an effect level (LOEL) in the calculation and due to a lot of major deficiencies in the database), a tolerable daily intake of 0.00033 mg/kg bw/day was set (Danish EPA 2013b). The assessment is in line with the assessment of the US EPA (2008), which similarly calculated a tolerable exposure level of 0.0003 mg/kg bw/day.

In addition, reproductive toxic effects of cobalt have been found in studies with experimental animals, but at higher levels than the effect on blood parameters (Danish EPA 2013b source: ATSDR 2004).

Other data
In addition, water-soluble cobalt compounds have been shown to have mutagenic, carcinogenic and reprotoxic properties. The carcinogenic and mutagenic properties are only considered relevant for risk assessment in connection with inhalation of cobalt, as cobalt is not considered carcinogenic by other routes of exposure (ECHA 2016a).

Conclusion
The following tolerable exposure levels are used as a basis for further risk assessment.

<u>DMEL, skin contact, cobalt allergy sufferers:</u>

DMEL, skin contact, allergic symptoms = 0.44 µg cobalt per cm^2

<u>DNEL, skin contact, systemic effects:</u>

DNEL, skin contact (syst. tox.) = NOAEL oral x oral abs/dermal abs.
DNEL, skin contact (syst. tox.) = 0.00033 mg/kg bw/day x 0.5/0.01
DNEL, skin contact (syst. tox.) = 0.017 mg/kg bw/day

<u>DNEL, oral exposure:</u>

DNEL, oral (syst. tox.) = 0.0003 mg/kg bw/day

4.1.5 Nickel

As a basis point for hazard assessment of nickel, the following references have primarily been used:

- Danish EPA (2013b). Nickel, inorganic and soluble salts Evaluation of health hazards and proposal of a health based quality criterion for drinking water. Environmental Project No. 1522, 2013.

- EU RAR (2008). European Union Risk Assessment Report NICKEL; NICKEL CARBONATE; NICKEL CHLORIDE; NICKEL DINITRATE; NICKEL SULPHATE. (https://echa.europa.eu/documents/10162/cefda8bc-2952-4c11-885f-342aacf769b3).

- EFSA (2020). DRAFT: Update of the risk assessment of nickel in food and drinking water. Public consultation on the draft scientific opinion on update of the risk assessment of nickel in food and drinking waterhttps://www.efsa.europa.eu/en/consultations/call/public-consultation-draft-scientific-opinion-update-risk.

Skin contact
The skin sensitising effect of nickel is considered the most critical effect in connection with skin contact. There is no data on a limit to skin sensitisation, while there are numerous data at dose levels that induce symptoms in nickel sensitised persons.

In connection with restriction proposals for skin sensitisers in leather and textiles, ECHA (2020) has assessed ED10 for nickel to be at 0.74 µg per cm^2, corresponding to the dose that produces effects in the 10% most sensitive nickel sensitised persons.

Based on *in vitro* studies with human skin, the skin absorption is estimated to be approx. 2% for water-soluble nickel ions (Danish EPA 2013c, EU RAR 2008).

Oral exposure
A single oral exposure to nickel can aggravate dermal symptoms in nickel sensitised persons. Based on an oral LOAEL of 0.012 mg/kg bw, the Danish EPA (2013c, EU RAR 2008) calculated a tolerable exposure level of 0.0012 mg/kg bw for this effect. EFSA (2020), on the other hand, used a LOAEL of 0.0043 mg/kg bw for exacerbation of symptoms in nickel sensitised persons and assessed that the exposure should be at least 30 times lower, equivalent to 0.00014 mg/kg bw to protect nickel sensitised persons.

For repeated oral dosing, the Danish EPA (2013c, EU RAR 2008) set a NOAEL value of 1.1 mg/kg bw/day based on a 2-generation study in rats showing increased mortality among the newborn pups at higher dose levels. From this, a tolerable daily intake of 0.0055 mg/kg bw/day was calculated. Besides the standard factors of 10 x 10, an additional uncertainty factor of 2 was included due to the severity of the effect.

EFSA (2020) calculated a BMDL10 of 1.3 mg/kg bw/day based on the same animal experimental data, and on the basis of this set a tolerable daily intake of 0,013 mg/kg bw/day using a safety factor of 100.

The oral absorption in the animal experiments is estimated to be 5% when converted to a systemic dose (Danish EPA 2008, EU RAR 2008).

Conclusion
The following tolerable exposure levels are used as a basis for further risk assessment:

DMEL, skin contact, nickel sensitised persons:

DMEL, skin contact, allergic symptoms = 0.74 µg nickel per cm^2[i]

DNEL, oral exposure, nickel sensitised persons:

DNEL, skin contact, allergic symptoms = 0.00014 mg/kg bw

DNEL, for skin contact, systemic effects:

DNEL, skin contact (syst. tox.) = NOAEL oral x oral abs/dermal abs.
DNEL, skin contact (syst. tox.) = 0.0055 mg/kg bw/day x 0.5/0.02
DNEL, skin contact (syst. tox.) = 0.014 mg/kg bw/day

DNEL, oral, systemic effects:

DNEL, oral (syst. tox.) = 0.0055 mg/kg bw/day

4.1.6 Chromium

Since the toxicology of chromium is different, depending on whether chromium is present as the chromium (III) ions or chromium (VI) ions, each of these ions is described separately.

4.1.6.1 Chromium (VI)

As a basis for hazard assessment of chromium, the following references have primarily been used:

- SCHER (2015). Opinion on chromium VI in toys. https://ec.europa.eu/health/sites/health/files/scientific_committees/environmental_risks/docs/scher_o_167.pdf.

- ECHA (2012). Background document to the Opinion on the Annex XV dossier proposing restrictions on Chromium VI in leather articles. Committee for Risk Assessment (RAC). Committee for Socio-economic Analysis (SEAC). https://echa.europa.eu/documents/10162/8ff2f208-c6a7-4ab8-8573-4100ac8214df.

Skin contact

Chromium (VI) allergy is reported to occur in 0.5-1.7% of the population in Europe. Chromium sensitised persons are reported to react to chromium (VI) solutions down to a concentration of 4-5 mg/kg (4-5 µg/g SCHER 2015).

Based on provocation tests of chromium (VI) sensitised persons, ECHA (2012) and most recently ECHA (2020) have identified a skin exposure of 0.02 µg chromium (VI) per cm^2 as the most relevant ED10 value for use in risk assessment.

In terms of dermal absorption, an EU risk assessment report indicates an absorption of 1-4% based on guinea pig skin exposure (EU RAR 2005).

Oral exposure

In connection with oral dosing in experimental animals, chromium (VI) has shown a carcinogenic effect in the gastrointestinal tract. Chromium (VI) is thought to be carcinogenic via a mutagenic/genotoxic mechanism of action without a lower effect threshold. In a dose-response analysis SHER (2015) calculated an acceptable exposure level (virtual safe dose) of 0.0002 µg/kg bw/day. A lifelong, daily exposure at this level corresponds to an increased lifetime risk of cancer of 10^{-6} or one in a million.

Data for oral absorption are lacking, but WHO (2005b) states that up to 6% is absorbed in experimental animals.

Conclusion

The following tolerable exposure levels are used as a basis for further risk assessment:

<u>DMEL, skin contact, chromium (VI) sensitised persons:</u>

DMEL, skin contact, allergic symptoms = 0.02 µg chromium (VI) per cm^2

<u>DMEL, skin contact, cancer:</u>

DNEL, skin contact (syst. tox.) = 0.0002 µg/kg bw/day

The DMEL value with regard to skin sensitisation is considered to be the most relevant value for assessment of knitting yarn, thereby protecting against an *acute effect* that may occur after *single or repeated exposure*. The DMEL value for cancer, on the other hand, is based on *lifelong daily exposure*, where exceedances over shorter periods have less significance for the overall risk.

<u>DMEL, oral, cancer:</u>

DNEL, oral (syst. tox.) = 0.0002 µg/kg bw/day

As can be seen, the DMEL values for skin contact and oral exposure are similar in terms of systemic effects (cancer), as it is not possible to differentiate the degree of absorption from the two exposure routes due to lack of precise data. However, the values given indicate approximately the same absorption ranges.

4.1.6.2 Chromium (III)

As a basis for hazard assessment of chromium (III), the following references have primarily been used:

- EFSA (2014b). Scientific Opinion on the risks to public health related to the presence of chromium in food and drinking water. EFSA Journal 2014;12(3):3595

- Bregnbak et al. (2015). Chromium allergy and dermatitis: prevalence and main findings. Contact Dermatitis,73, 261–280

In addition, data from the REACH registration for chromium trichloride are used (ECHA, Chromium trichloride 2020).

Skin contact
Chromium trichloride has shown to cause skin sensitisation in experimental animal, while the substance does not show to result in irritation in skin irritation tests (REACH registration).

Chromium (III) allergy is significantly less studied than chromium (VI) allergy. Bregnbak et al. (2015) indicate that the chromium (III) ion has significantly lower skin permeability than the chromium (VI) ion but do not indicate any quantitative measures for this. In provocation experiments, doses of chromium (III) approx. 6 times higher compared to chromium (VI) are required to cause an allergic reaction in chromium sensitised persons. In an experiment with chromium sensitised persons, it was found that MET10%[5] for chromium (III) and chromium (VI) were 0.18 mg/cm^2/48h (corresponding to a 6 ppm solution) and 0.03 mg/cm^2/48h (corresponding to a 1 ppm solution), respectively (Bregnbak et al. 2015; Hansen et al. 2003). This is the lowest MET10% value stated for chromium (III), as other and somewhat older studies indicate significantly higher values (Bregnbak et al. 2015).

Oral exposure
In a 2-year oral experimental animal study with chromium (III), neither carcinogenic effects nor other adverse effects were found in the experimental animals at the highest dose of 286 mg/kg bw/day. Based on this EFSA calculated a tolerable exposure level of 0.3 mg/kg bw/day, using in addition to the standard uncertainty factors of 10 x 10 for inter- and intraspecies variation a further uncertainty factor of 10 to compensate for the lack of data on reproductive toxic effects (EFSA 2014b).

EFSA (2014b) stated the oral absorption of chromium (III) to be in the range 0.4 - 2.8%, i.e. somewhat lower than for chromium (VI).

Conclusion
The following tolerable exposure levels for chromium (III) are used as a basis for further risk assessment:

[5] MET 10% (Minimal Elicitation Threshold): dose that causes symptoms in the 10% most sensitive allergic persons.

DMEL, skin contact, chromium (III) sensitised persons:

DMEL, skin contact, allergic symptoms = 180 µg chromium (III) per cm^2 or 6 mg/L corresponding to 0.0006%

DNEL, skin contact, systemic effects:

DNEL, skin contact (syst. tox.) = 0.30 mg/kg bw/day

DNEL, oral, systemic effects, cancer:

DNEL, oral (syst. tox.) = 0.30 mg/kg bw/day

As can be seen, the DNELs for skin contact and oral exposure are similar, as it is not possible to differentiate the degree of absorption from the two routes of exposure due to lack of precise data. However, the information provided indicates approximately the same oral and dermal absorption.

4.1.7 Summery

The table below provides an overview of the established DN(M)EL values for further use in the risk assessment.

TABLE 7. Overview of DN(M)EL values for use in the risk assessment

Substance	**DN(M)EL skin contact** ***µg/cm² and/or %***	**DN(M)EL skin contact** ***mg/kg bw/day***	**DN(M)EL orally** ***mg/kg bw/day***
Formaldehyde	20 µg/ cm^2 (allergic symptoms) 0.003 % (allergic symptoms)	-	0.15 (gastrointestinal effects)
Copper	1.4 % (irritation)	0.72 (enlarged spleen)	0.15 (enlarged spleen)
Zinc	0.03 % (irritation)	2 (neurotoxicity)	0.4 (neurotoxicity)
Cobalt	0.44 µg/cm^2 (allergic symptoms)	0.017 (effects on the blood)	0.0003 (effects on the blood)
Nickel	0.74 µg/cm^2 (allergic symptoms)	0.014 (reproductive toxicity)	0.00014 (allergic symptoms) 0.0055 (reproductive toxicity)
Chromium (VI)*	0.02 µg chromium (VI)/cm^2 (allergic symp-toms)	0.0002 µg/kg bw/day (cancer risk)	0.0002 µg/kg bw/day (cancer risk)
Chromium (III)*	180 µg chromium (III)/cm^2 (allergic symptoms)	0.30 (no critical effects identified)	0.30 (no critical effects identified)

The table lists both tolerable exposure levels for chromium (III) and chromium (VI). As can be seen the values for chromium (VI) are lower than for chromium (III).

It was therefore considered important to clarify whether the chromium content measured in the migration fluid from four of the yarn samples (indicated in Table 4) consisted of chromium (III), chromium (VI) or a mixture thereof. This led to follow-up analyses of the content in yarn. However, no content of chromium (VI) could be detected above the detection limit of 3 mg/kg in any of the samples. On this basis, it is assumed that the chromium content measured in the migration analyses consists only of chromium (III), which is why the hazard assessment of chromium (VI) will not be included in the subsequent risk assessment.

4.2 Exposure assessment to the migrating substances

In the exposure assessment, the highest measured values (see section 4.1) for the individual substances are used to calculate the highest exposure to the substances.

4.2.1 Exposure of a knitting person

Dermal exposure, mg/cm²

This exposure is calculated from expression (1) in section 2.2.1:

Exposure (mg substance/cm² skin) = 0.82 g/cm² x (mg substance released/g yarn)

By inserting the highest measured values for the migrating substances, the following exposure of the knitting person is obtained:

TABLE 8. Dermal exposure of hands on a knitting person (mg/cm²)

Substance	Highest measured value in yarn *mg/g*	Dermal exposure of hands *mg/cm²*
Formaldehyde	21.5×10^{-3}	18×10^{-3}
Copper	7.5×10^{-3}	6.2×10^{-3}
Zinc	20×10^{-3}	16×10^{-3}
Cobalt	0.6×10^{-3}	0.50×10^{-3}
Nickel	0.5×10^{-3}	0.41×10^{-3}
Chromium	0.1×10^{-3}	0.08×10^{-3}

Dermal exposure, mg/kg bw/day

This exposure is calculated from expression (2) in section 2.2.1:

Exposure (mg/kg bw/day) = 5 g/kg bw x mg substance released/g yarn

By inserting the highest measured values for the migrating substances, the following exposure of the knitting person is obtained:

TABLE 9. Dermal exposure of knitting person (mg/kg bw/day)

Substance	Highest measured value in yarn *mg/g*	Dermal exposure of hands *mg/kg bw/day*
Formaldehyde	21.5×10^{-3}	11×10^{-2}
Copper	7.5×10^{-3}	3.8×10^{-2}
Zinc	20×10^{-3}	10×10^{-2}
Cobalt	0.6×10^{-3}	0.30×10^{-2}
Nickel	0.5×10^{-3}	0.25×10^{-2}
Chromium	0.1×10^{-3}	0.05×10^{-2}

4.2.2 Exposure of an infant

It is assumed as a worst-case consideration that the child is exposed daily to the measured levels of migration for the individual substances during first time use of the knitted garment (before washing).

Dermal exposure, mg/cm²

This exposure is calculated from expression (3) in section 2.2.2:

Exposure (mg substance/cm²) = 0.087 g/cm² x (mg substance released/g yarn)

By inserting the highest measured values for the migrating substances, the following exposure of the infant is obtained:

TABLE 10. Dermal exposure of infant (mg/cm²)

Substance	Highest measured value in yarn *mg/g*	Dermal exposure *mg/cm²*
Formaldehyde	21.5×10^{-3}	1.9×10^{-3}
Copper	7.5×10^{-3}	0.65×10^{-3}
Zinc	20×10^{-3}	1.7×10^{-3}
Cobalt	0.6×10^{-3}	0.05×10^{-3}
Nickel	0.5×10^{-3}	0.04×10^{-3}
Chromium	0.1×10^{-3}	0.01×10^{-3}

Dermal exposure, mg/ kg bw/day

This exposure is calculated from expression (4) in section 2.2.2:

Exposure (mg/kg bw) = 4 g/kg bw/day x (mg substance released/g yarn)

By inserting the highest measured values for the migrating substances, the following exposure of the infant is obtained:

TABLE 11. Dermal exposure of infant (mg/kg bw/day)

Substance	Highest measured value in yarn *mg/g*	Dermal exposure *mg/kg bw/day*
Formaldehyde	21.5×10^{-3}	11×10^{-2}
Copper	7.5×10^{-3}	3.0×10^{-2}
Zinc	20×10^{-3}	8×10^{-2}
Cobalt	0.6×10^{-3}	0.24×10^{-2}
Nickel	0.5×10^{-3}	0.20×10^{-2}
Chromium	0.1×10^{-3}	0.04×10^{-2}

Oral exposure, mg/kg bw/day

This exposure is calculated from expression (5) in section 2.2.2:

Oral exposure (mg/kg bw/ day) = 0.63 g/kg bw/day x (mg substance released/g yarn)

By inserting the highest measured values for the migrating substances, the following exposure of the infant is obtained:

TABLE 12. Oral exposure of infant (mg/kg bw/day)

Substance	Highest measured value in yarn *mg/g*	Oral exposure *mg/kg bw/day*
Formaldehyde	21.5×10^{-3}	14×10^{-3}
Copper	7.5×10^{-3}	4.7×10^{-3}
Zinc	20×10^{-3}	13×10^{-3}
Cobalt	0.6×10^{-3}	0.38×10^{-3}
Nickel	0.5×10^{-3}	0.32×10^{-3}
Chromium	0.1×10^{-3}	0.06×10^{-3}

5. Risk assessment

The risk assessment of the knitting yarn is carried out in accordance with the instructions set out in the REACH Regulation and its guidelines (ECHA 2016b).

The calculated exposure level and the tolerable exposure level for a given substance are compared by calculating an RCR value (risk characterisation ratio):

$$RCR = Exposure/DN(M)EL$$

If the calculated RCR value is> 1, it means that the exposure is higher than the tolerable exposure level. This indicates a potential increased risk of adverse effects from the exposure in question.

If the calculated RCR value is <1, it means that the exposure is lower than the tolerable exposure level. This indicates that the exposure is acceptable and has no adverse health effects.

When calculating the RCR value, uncertainties and limitations must always be taken into account regarding the estimated exposure values and tolerable exposure values before the risk of use can be definitively concluded. This is especially important in borderline cases where an RCR value is just below or above 1.

5.1 Risk assessment for knitting consumer

When assessing the risk for local irritating effects and allergic symptoms on the skin of a knitting person, an RCR value is calculated based on the estimated exposure of the hands per cm^2 of skin (Table 8) and the estimated tolerable exposure levels (DN(M)EL-values expressed in mg/cm^2). RCR values for the migrating substances into the artificial sweat are indicated below in Table 13.

TABLE 13. Risk calculation for local skin effects on a knitting person

Substance	Highest measured value in yarn *mg/g*	Dermal exposure of hands *mg/cm²*	DN(M)EL skin contact *µg/cm²* *%*	RCR value
Formaldehyde	21.5×10^{-3} corresponding to 0.0022 %	18×10^{-3} 0.0022 %	20 µg/cm² (allergic symptoms) 0.003 % (allergic symptoms)	1.1 0.73
Copper	7.5×10^{-3} corresponding to 0.00075 %	6.2×10^{-3} 0.00075 %	- 1.4 % (irritation)	- 0.0005
Zinc	20×10^{-3} corresponding to 0.002 %	16×10^{-3} 0.002 %	- 0.03 % (irritation)	- 0.07
Cobalt	0.6×10^{-3}	0.50×10^{-3}	0.44 µg/cm² (allergic symptoms)	1.1
Nickel	0.5×10^{-3}	0.41×10^{-3}	0.74 µg/cm² (allergic symptoms)	0.55

Substance	Highest measured value in yarn *mg/g*	Dermal exposure of hands *mg/cm²*	DN(M)EL skin contact *µg/cm²* *%*	RCR value
Chromium (III)	0.1 x 10^{-3}	0.08 x 10^{-3}	180 µg chromium (III)/cm^2 (allergic symptoms)	0.0004

Based on the calculated RCR values for copper and zinc, where the most critical effect is skin irritation, the values 0.0005 and 0.07 are significantly below 1, and there is no risk of skin irritation due to exposure to the measured contents of the two substances in the knitting yarn.

For the other substances, where the critical effect is skin symptoms in people who are already sensitised to the substances, RCR values have been found in the range 0.0004 - 1.1. This indicates at first look an increased risk to people who are already sensitised to formaldehyde and cobalt, where the RCR values are in the range 1.1 - 4. When assessing chromium (as chromium (III)), a very low RCR value of 0.0004 is obtained.

However, having a further look at the RCR value of 1.1 this is not considered to cause an unacceptable risk. This is because the basis for the DMEL values for cobalt and formaldehyde is from provocation experiments with sensitised people. In such experiments, the test substance is typically exposed for 48 hours under an occlusive dressing to keep the skin moist. In the knitting scenario exposure to the yarn will be over a limited number of hours during a day and on bare uncovered hands, which are usually washed several times a day. In addition, the exposure will not be to soaked yarn, which is the basis for the migration volumes used for the exposure calculation. Both factors - partly underestimation of DMEL and partly overestimation of the exposure - will contribute to a significant overestimation of the RCR value. Therefore, an RCR value of 1.1 is not considered to represent a risk.

Risk assessment for systemic effects

In the risk assessment for systemic effects in connection with uptake of the substances through the skin, an RCR value is calculated from the dermal exposure calculated as "mg/kg bw/day" (Table 9) and the estimated tolerable dermal exposure levels (DN(M)EL values also expressed in "mg/kg bw/day"), see Table 7. This results in RCR values for the migrated substances as indicated below in Table 14.

TABLE 14. Risk assessment for systemic effects in a knitting person

Substance	Highest measured value in yarn *mg/g*	Dermal exposure *mg/kg bw/day*	DN(M)EL skin contact *mg/kg bw/day*	RCR value
Formaldehyde	21.5 x 10^{-3}	11 x 10^{-2}	-	-
Copper	7.5 x 10^{-3}	3.8 x 10^{-2}	0.72 (enlarged spleen)	0.05
Zinc	20 x 10^{-3}	10 x 10^{-2}	2 (neurotoxicity)	0.05
Cobalt	0.6 x 10^{-3}	0.30 x 10^{-2}	0.017 (effects on the blood)	0.18
Nickel	0.5 x 10^{-3}	0.25 x 10^{-2}	0.014 (reproductive toxicity)	0.18
Chromium (III)	0.1 x 10^{-3}	0.05 x 10^{-2}	0.30 (no critical effects identified)	0.002

For the calculated RCR values up to 0.18, calculated on the basis of the highest measured values for formaldehyde, copper, zinc, cobalt, nickel and chromium (as chromium (III)), it can be concluded that there is no risk for systemic effects from these substances by daily knitting.

5.2 Risk assessment for infant

Risk for local effects on skin

When assessing the risk for local irritation and allergic symptoms in an infant wearing an unwashed sweater, RCR values are calculated based on the estimated exposure of the skin per cm^2 (Table 10) and the estimated tolerable exposure levels, i.e. DN(M)EL values expressed in mg/cm^2 (Table 7). It should be noted that the use of DMEL for sensitising substances can be discussed and must be considered a conservative approach, as one would not expect infants to already have developed allergy towards the substances. In general, it is considered that significantly higher exposure is required to induce the allergic condition than to provoke symptoms in people who are already allergic. Therefore, RCR values around or just above 1 must to a great extent be considered to provide protection against sensitisation of the infants.

TABLE 15. Risk calculation for local skin effects on infant wearing knitwear

Substance	Highest measured value in yarn *mg/g*	Dermal exposure *mg/cm²*	DN(M)EL Skin contact *µg/cm²* *%*	RCR value
Formaldehyde	21.5×10^{-3} corresponding to 0.0022 %	1.9×10^{-3}	20 µg/ cm^2 (allergy symptoms) 0.003 % (allergy symptoms)	0.095 0.73
Copper	7.5×10^{-3} corresponding to 0.00075 %	0.65×10^{-3}	1.4 % (irritation)	0.0005
Zinc	20×10^{-3} corresponding to 0.002 %	1.7×10^{-3}	0.03 % (irritation)	0.067
Cobalt	0.6×10^{-3}	0.05×10^{-3}	0.44 $µg/cm^2$ (allergy symptoms)	0.11
Nickel	0.5×10^{-3}	0.04×10^{-3}	0.74 $µg/cm^2$ (allergy symptoms)	0.054
Chromium (III)	0.1×10^{-3}	0.01×10^{-3}	180 µg chromium $(III)/cm^2$ (allergy symptoms)	0.00006

All calculated RCR values are below 1 and therefore not considered to indicate an unacceptable risk to the infant in terms of local irritant effects or skin sensitisation due to skin contact with the yarn.

Risk for systemic effects

Skin exposure

For risk assessment for systemic effects linked to uptake of the substances through the skin, RCR values are calculated based on the estimated dermal exposure calculated as “mg/kg bw/day” (Table 11) and the estimated tolerable exposure levels, i.e. dermal (DN(M) EL values also expressed in “mg/kg bw/day” (Table 7). RCR values obtained for the migrated substances are indicated below in Table 16.

TABLE 16. Risk assessment for systemic effects in infant wearing knitwear, dermal exposure

Substance	Highest measured value in yarn *mg/g*	Dermal exposure *mg/kg bw/day*	DN(M)EL skin contact *mg/kg bw/day*	RCR value
Formaldehyde	21.5×10^{-3}	11×10^{-2}	-	-
Copper	7.5×10^{-3}	3.0×10^{-2}	0.72 (enlarged spleen)	0.04
Zinc	20×10^{-3}	8×10^{-2}	2 (neuro toxicity)	0.04
Cobalt	0.6×10^{-3}	0.24×10^{-2}	0.017 (effects on the blood)	0.14
Nickel	0.5×10^{-3}	0.20×10^{-2}	0.014 (reproductive toxicity)	0.14
Chromium (III)	0.1×10^{-3}	0.04×10^{-2}	0.30 (no critical effects stated)	0.001

For all the RCR values up to a value of 0.14 calculated from the highest measured values for formaldehyde, copper, zinc, cobalt, nickel and chromium (such as chromium (III)), it can be concluded that there are no risk for systemic effects from these substances in relation to skin contact with an unwashed knitted sweater.

Oral exposure

In the risk assessment for systemic effects linked to uptake of the substances when sucking on parts of a sweater, RCR values are calculated based on the estimated oral exposure calculated as “mg/kg bw/day” (Table 12) and the estimated tolerable exposure levels, i.e. oral (DN(M)EL values, also expressed in “mg/kg bw day” (Table 7). RCR values obtained for the migrated substances are given below in Table 17.

TABLE 17. Risk assessment for systemic effects in infant wearing knitwear, oral exposure

Substance	Highest measured value in yarn *mg/g*	Oral exposure from sucking *mg/kg bw/day*	DN(M)EL orally *mg/kg bw/day*	RCR value
Formaldehyde	21.5×10^{-3}	14×10^{-3}	-	-
Copper	7.5×10^{-3}	4.7×10^{-3}	0.72 (enlarged spleen)	0.007
Zinc	20×10^{-3}	13×10^{-3}	2 (neuro toxicity)	0.007
Cobalt	0.6×10^{-3}	0.38×10^{-3}	0.017 (effects on the blood)	0.022
Nickel	0.5×10^{-3}	0.32×10^{-3}	0.014 (reproductive toxicity)	0.022
Chromium (III)	0.1×10^{-3}	0.06×10^{-3}	0.30 (no critical effects stated)	0.0002

All the calculated RCR values are approx. a factor 6 lower than the RCR values calculated from skin contact, which is due to the fact that exposure through sucking is calculated to be approx. 6 times lower or about 16% of the dermal exposure.

The total risk of both dermal and oral exposure can be calculated by adding the RCR values for the two exposure routes for a given substance. As contributions from the oral exposure only result in a total RCR value approx. 16% higher than the dermal RCR value, this will not change the conclusions as stated for the dermal exposure.

5.3 Overall conclusion

Risk assessments have been made for local effects on the skin and systemic effects in connection with the use of knitting yarn in two different scenarios (a knitting person and an infant wearing a newly knitted, unwashed sweater). Selected yarn samples have been analysed for the content of selected chemical substances of concern. The risk assessment was carried out from the highest measured concentration levels for a number of substances that in migration testing were been found to migrate into artificial sweat.

Of the substances measured in the migration fluid, the following six substances were found to be the most critical substances based on their potential hazard:

- Formaldehyde (measured levels 3,9 – 21,5 µg/g yarn)
- Copper (measured levels 0,3 – 7,5 µg/g yarn)
- Zinc (measured levels 0,8 – 20 µg/g yarn)
- Cobalt (measured levels 0,1 – 0,6 µg/g yarn)
- Nickel (measured levels 0,1 – 0,5 µg/g yarn)
- Chromium (measured level 0,1 µg/g yarn)

The results of the risk assessments for the highest measured levels of these sub stances are indicated in Table 18 below:

TABLE 18. Overview of risk assessments

	Risk: Skin contact local effects	**Risk: Skin contact systemic effects**	**Risk: Oral exposure**
Knitting person	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	No exposure
Infant wearing a sweater	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no	Formaldehyde: no Copper: no Zinc: no Cobalt: no Nickel: no Chromium (III): no

Local skin effects

The substances formaldehyde, cobalt, nickel, and chromium are all substances that can cause skin sensitisation/ allergy.

The critical exposure levels for these substances are based on the lowest dose levels observed to cause skin reactions in already sensitised persons in clinical tests. This value is compared with the estimated exposure at the highest measured values of the substances. In general, dose levels causing skin symptoms in the most sensitive individuals in a group of sensitised persons are considered to be significantly lower than the dose levels causing the allergic condition itself.

As can be seen from the table the migration levels of the identified skin sensitising sub substances are not considered to result an unacceptable increased risk of skin reactions in sensitised persons or in infants.

For copper and zinc, which are not considered as skin sensitisers, the critical effect is local irritation of the skin. The measured levels of these substances are not found to result in risk for skin irritation in the knitting person or in the infant wearing a new unwashed sweater.

Systemic effects
As seen in Table 18, no risk of adverse health effects was found when using knitting yarn neither for the knitting person nor for the infant wearing a new unwashed sweater. This was found for systemic exposure to formaldehyde, copper, zinc, cobalt, nickel and chromium at the levels found in the migration analyses.

Overall assessment
On the basis of the study of selected yarn samples purchased in Denmark, the rest of the EU and outside the EU, it can be concluded that there is no risk for local skin effects or systemic effects from the investigated substances when using the yarn in connection with knitting or wearing the knitted garment.

5.4 Uncertainties and limitations

As part of the risk assessment, it is important to assess the validity by discussing the uncertainties in relation to the assumptions and estimates made during the process. Below, the discussion is divided into uncertainties for estimating the DN(M)EL values for the substances and uncertainties for estimating the exposure.

Estimation of DN(M)EL values
The basis for the toxicological assessment and the determination of DN(M)EL values are mainly recent assessments and conclusions from expert groups within the EU, such as EFSA, SCCS and ECHA assessments as well as WHO expert group assessments. The uncertainties when determining DN(M)EL values are therefore considered to be rather limited.

Exposure assessment based on migration testing in artificial sweat
The exposure assessment is based on the amount of a specific substance that migrates in connection with an experimental setup, where the yarn is in an artificial sweat liquid at 37ºC for two hours. Although no shaking was used in the experiment, the experimental set-up is considered to lead to a higher degree of migration than will occur when the yarn is in contact with sweaty skin.

The exposure assessment assumes that the migration of a specific substance, per gram of yarn during knitting or per gram of yarn during wearing a knitted sweater, is at the same level as the migration found in the migration testing.

In addition, the exposure assessment is based on a knitting person that daily is exposed on the skin to the migration of substances from 300 grams of yarn, or an infant being daily exposed on the skin to the migration from a 200-gram sweater and oral exposure from sucking on 5 grams of the sweater. In the case of the infant scenario, the exposure is estimated to only occur for a few days until the sweater is washed for the first time. An assessment based on a tolerable systemic dose in relation to long-term repeated exposure is therefore a cautious approach.

Especially estimation of systemic dose is considered to be uncertain due to uncertainties regarding absorption and systemic uptake through the skin, whereas local exposure of the skin surface and risk assessment of local skin reactions does not imply this uncertainty.

Use of the highest measured migration values from the 45 different yarn samples for the risk assessment are considered as a realistic worst-case in the current project.

The uncertainties described in combination with the assumptions overall indicate that the exposure estimates may be considered as worst-case and thereby exceeding a more realistic average exposure. This means that risks based on an RCR value with a limited exceedance of the value 1 has to be concluded with great caution. Only exposures that give rise to significant exceedances in the form of an RCR value >> 1 can be concluded to pose a health risk.

Concerning the chromium measurements, follow-up analyses were performed to clarify whether the content in the migration liquid originated from chromium (VI) or chromium (III) in the yarn. The results of the analyses of the yarn samples itself indicated that chromium (VI) was not present in the yarn, and therefore most likely not present in the artificial sweat where the analytical method was not able to detect chromium (VI) and therefore, the risk assessment of chromium is based on toxicological data for chromium (III). It should be noted, however, that the detection limit for this more specialised analysis for content in the yarn was higher than for the analysis of total chromium in artificial sweat, so, even if no chromium (VI) was found in the yarn samples, it cannot be completely ruled out that low levels of chromium (VI) were present in the yarn and in the migration fluid.

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Survey and risk assessment of chemicals in knitting yarn

In recent years, Danes have been knitting more and more. Accordingly, the Danish Environmental Protection Agency has a desire to map the market for knitting yarns and inves-tigate whether knitting yarns contain chemicals to the same extent as finished textiles, and whether yarn complies with the legislation applying to textiles and yarns.

All 45 yarn samples were tested for content of nonylphenol and nonylphenol ethoxylates as well as azo dyes and aro-matic amines, as these substances are subject to regulation of content in textiles. Next, migration analyses were per-formed of all yarn samples in artificial sweat for a series of metals and also for formaldehyde and permethrin. In addi-tion, migration of cyclic siloxanes was examined for 12 se-lected superwash wool yarn samples, and migration of bi-sphenol A (BPA) for 10 selected yarn samples.

Based on the examination of the selected yarn samples purchased in Denmark, from the remainder of the EU and outside the EU, it can be concluded that there is no risk skin effects or systemic effects when using the yarn in con-nection with knitting or wearing hand-knitted clothing.

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