Survey of Chemical Substances in Consumer Products

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Survey of Chemical Substances in Paper Handkerchiefs and Toilet Paper

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Foreword

The Danish EPA has undertaken an initiative to examine consumer exposure to chemical substances in consumer products and the risks associated with such exposure. A variety of product categories within paper handkerchiefs and toilet paper are concerned.

The object of the project is to chart the significant constituent substances contained in paper handkerchiefs and toilet paper which have been manufactured based on new fibres or recycled paper. The object is also to undertake a human toxicological evaluation of selected substances. Moreover, the project is aimed at documenting the content of selected chemical substances through screening analyses of a number of products to be found in the market.

The project report "Survey of Chemical Substances in Paper Handkerchiefs and Toilet Paper" includes an examination of the market (producers, suppliers and products available on the Danish market), analyses of selected products, and a health evaluation of ten substances found in the products.

The project was carried out between November 2001 and November 2002.

The project was carried out by COWI. The project team consisted of Anne Abildgaard (project manager), Sonja Hagen Mikkelsen and Frank Stuer-Lauridsen (quality manager). The analyses were carried out by Miljøkemi (now Eurofins) by Jane Pors and René Fuhlendorff.

The project manager at the Danish EPA was Shima Dobel.

Summary and conclusions

Survey

Paper towels and toilet paper are consumer products which typically are marketed in supermarkets and other retail shops. Both paper towels and toilet paper can be assigned the official Nordic ecolabel, the Swan label, as the criteria cover both product groups. Toilet paper can also be assigned the European Union ecolabel, the EU flower.

Products can contain chemical residues from the production of paper, either from virgin cellulose fibres or from cleaning out recycled cellulose fibres. In addition chemical substances can be added in order to improve the properties of the of the finished product, e.g. softeners, perfume or lotion/balsam.

Use of the products may involve a risk for exposure to chemical substances by direct skin contact and by inhalation, when the paper (paper towels or toilet paper) is used as handkerchiefs. Therefore there is a need for a survey on the substances which may be found in the products in order to evaluate the risk.

There are four main producers in Germany, England, Sweden and Finland who deliver a considerable part of the products on the Danish market. Six of the toilet paper products have the Nordic ecolabel, the Swan, while only three paper towel products are carrying an ecolabel.

Almost all the chemical substances that can be found in the paper towels and toilet paper has its origin from tree. Some chemical substances are intentionally added to the paper product.

Analysis

Screening analyses show in general that it is simple hydrocarbons which are contained in the highest concentrations among the extractable constituents in toilet paper. The level is from 4 to 330 mg/kg. Other substances occur in concentrations below 30 mg/kg. Paper towels without balsam or menthol has a concentration of hydrocarbons in the interval from 35 to 250 mg/kg. The concentration of hydrocarbons in paper towels with menthol or balsam is in the interval 30 mg/kg to 19 g/kg, and the highest concentration is in paper towels with balsam. In the paper towels with perfume and softener added, perfume and softeners are detected in concentrations op to 770 mg/kg and 2.3 g/kg, respectively. No PCB, PAH, nitrosamines, EDTA, DPTA or acrylamide has been found in any of the tested products. Polyethoxylates are found in one of the analysed paper towels. Small amounts of colophonium are measured in one toilet paper product and one paper towel product.

Among metals it is only copper, magnesium and zinc which have been identified. Concentrations of magnesium are in all products considerably higher than the concentrations of the other two metals. Concentrations of copper are highest in the coloured products.

Results of the analyses do not show any differences between the content of chemical substances which in most cases can be attributed to naturally occurring substances in tree. Differences are most prominent between products with and without decoration, products with and without perfume and products with and without softeners (balsam).

Health evaluation

Ten of the identified substances in the screening analysis for extractable organic substances are selected for toxicological evaluation. The ten substances are: hydroxybiphenyl, isopropylmyristat, isopropylpalmitat, 9-octadecensyremethylester, 9,12-octadecadiensyre methylester, menthenol, menthol, sitosterol, stigmast-4-en-3-on og squalen.

Data collection has been carried out in a limited number of databases and only available literature from these sources has been examined. It is therefore likely that more information is available about the substances from other sources.

For a number of the substances the information is insufficient for an evaluation. A few substances are reasonably well documented. This is the case for hydroxybiphenyl, isopropylmyristate, menthol and sitosterol.

The health evaluation is based on the properties of the pure substances. The evaluation is therefore not necessarily the same for the actual concentration of the substances in the paper products. As mentioned the concentrations in the products are relatively low.

One of the substances (hydroxybiphenyl - a biocide) is on the 'Positive list' as a preservative for food. This is classified as irritant and on the list of dangerous substances. The substance is listed on the EU list of flavourings for food. The content of hydroxybiphenyl found in the products most properly has its origin from lignin in the tree.

The four substances - isopropylmyristate, isopropylpalmitate, 9-octadecenacid methyl ester and 9,12-octadecadienacid methyl ester - are very similar with regard to molecular structure. The substances isopropylmyristate, isopropylpalmitate and 9-octadecenacid methyl ester are used as softeners and surfactants. The substance 9,12-octadecadienacid methyl ester is used as a catalyst due to the oxidative properties.

Isopropylmyristate is studied in animal experiments. Among the subacute and chronic effects which have been found are effects on the skin and adverse effects on other organs following skin absorption. In addition skin and eye irritation has been shown. These health effects are also likely to be related to the other three substances isopropylpalmitate, 9-octadecenacid methyl ester and 9,12-octadecadienacid methyl ester. 9,12-octadecadienacid methyl ester seems to be more irritant and have a greater potential for sensitisation than the other three substances. The substances in this group occur in relatively low concentrations in the products and consequently the risk is considered insignificant.

Menthol is added as perfume in two of the tested paper towels in concentrations up to 770 mg/kg. Menthol may cause skin and eye irritation. It is reported that, products with up to 2% menthol cause allergic reactions in children treated with menthol in connection with treatment of cold. The

highest concentration of menthol detected in paper towels is 0.08% and menthol is therefore not considered to cause any problems in paper towels.

Menthenol is very similar to menthol and occurs in one of the paper towels along with menthol, but in rather low concentration and consequently the risk of menthenol is considered insignificant.

Two of the substances - sitosterol and stigmast-4-en-3-one are both sterols and steroid which are naturally occurring and used in the manufacture of synthetic hormones. Data are only available for one of the substances. These data do not indicate any health hazardous properties. There are however, no available data on mutagenicity and reproductive toxicity.

Squalene is a sterol as well and used as e.g. a natural medicine and in natural cosmetics. No data on health effects are available. The substance is similar to hormones as cortisone, estradiol and progesterone. Consequently, the substance may have hormone effects.

The analysed products are not expected to cause any adverse effects related to the use.

1 Introduction

Paper handkerchiefs treated with balsams, aromatic agents and dyes have appeared in the market during recent years, and thus consumers – both children and adults - risk being exposed to these substances through direct contact, especially with the skin and the mucous membranes, and via inhalation.

Similarly, toilet paper may expose consumers to undesirable substances during use, both via direct contact with the skin and mucous membranes and through inhalation if the paper is used as a paper handkerchief. Both paper based on new fibres and especially paper manufactured from recycled paper may contain a number of undesirable substances. These might be substances added during the manufacturing process, impurities or substances originating from the raw material. As a consequence, there is a need to chart the substances to which consumers may be exposed during use.

1.1 Purpose

The object of the project is to chart which constituent substances are contained in paper handkerchiefs and toilet paper with and without the addition of balsams, aromatic agents and dyes and toilet papers manufactured based on new fibres or recycled paper.

The purpose is also to undertake a health evaluation of certain substances selected from those found in the products and, if possible, to give an assessment of the extent of consumer exposure to these products. The health evaluation was undertaken with a view to producing input for a possible subsequent risk assessment. Great importance was attached to the possible exposure of children to the products.

Moreover, the project is aimed at documenting the content of selected chemical substances through screening analyses of a number of products to be found in the market. Screening included substances like bisphenol-A, perfumes and lotions. Finally, the purpose was to assess the need for further chemical analyses based on the results produced.

1.2 The method used in the project

The project was implemented in two phases, where phase 1 comprised the survey and the literature search. Phase 2 comprised chemical screening analyses, evaluation of the need for possible further analyses and human toxicological evaluation of the selected substances.

During Phase 1 a list of suppliers/producers of relevant products and already known constituents was drawn up. The list was drawn up based on

information available on the Internet and contacts with suppliers and producers.

Attempts were made to obtain information on the content of chemical substances in paper products from paper product manufacturers, from suppliers of additives such as balsams, aromatic agents and dyes, from the literature and via information available on the Internet.

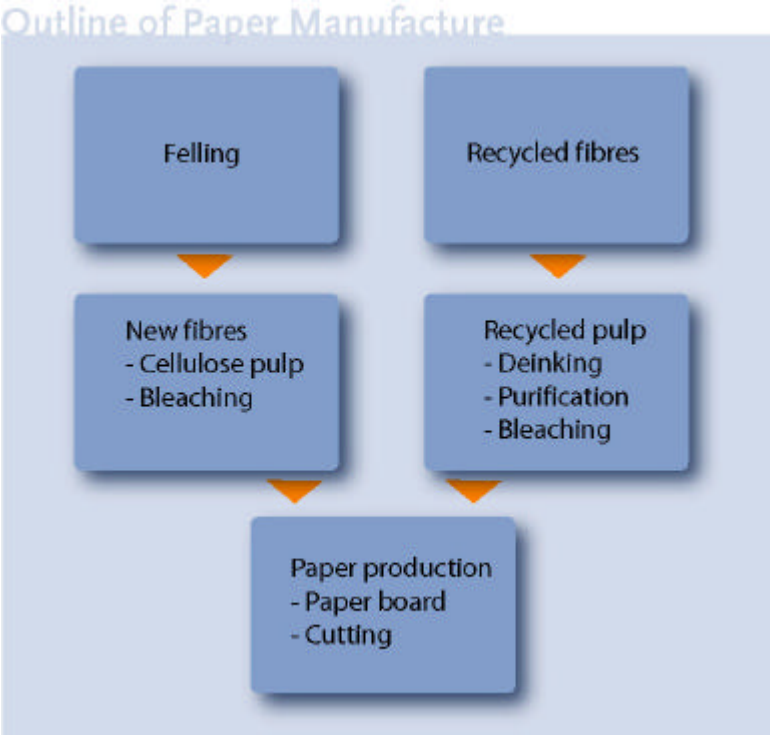
During Phase 2, chemical screening of selected products in the market was carried out. Subsequently, supplementary analyses of selected chemical substances were carried out. In the case of ten of the substances found, data searches were carried out to obtain information on them and to evaluate any possible toxic effects they might have.

2 The manufacture of paper handkerchiefs and toilet paper

Paper handkerchiefs and toilet paper are produced from pulp based on new cellulose fibres, recycled fibres or a combination of the two. The products are classified according to properties such as softness, purity, high absorption capacity and strength.

Manufacturing processes are illustrated in Figure 1 below.

Figure 1 Outline of paper manufacture



In the manufacture of pulp from virgin cellulose fibres, fresh wood (softwood and hardwood) is converted to pulp either through a chemical or a mechanical process. In the chemical process the lignin of the wood is dissolved by using the sulphate or the sulphite method. The lignin is the bonding substance that holds the fibres together. This process results in a fibre pulp and a solution consisting of chemicals and wood substances. In both processes the chemicals in the fluid can be recovered. The method used depends on the type of wood. For example, the sulphate method can be used for wood such as pine, oak, beech and birch /4/.

A number of chemicals are used to dissolve the wood. The sulphite method makes use of sulphites such as sodium sulphite, magnesium sulphite and calcium sulphite. Following this process the sulphite pulp is greyish yellow. Hydrogen peroxide is typically used to bleach the sulphite pulp. But the paper

pulp can also be bleached with oxidizing chlorine compounds such as chlorine dioxide, hypochlorite or other bleaching agents /1/.

The sulphate process makes use of such chemicals as sodium sulphide, sodium hydroxide, sodium sulphate and anti-slime agents (slimicides). The latter are used to prevent microbial growth and the consequent formation of slime. Following this process the sulphate pulp is dark brown and it can now be bleached. Bleaching agents include hydrogen peroxide, chlorine gas, chlorine dioxide, hypochlorite, sodium hypochlorite, sodium hydroxide, and others.

If manufacture is based on recycled paper or a proportion of recycled paper the printing ink must be removed from the paper and the paper must be reconverted to fibre. This takes place during the de-inking process during which soap bubbles absorb the printing ink, which is then centrifuged out. Both water and chemicals are used in the process. Sodium soap is added to the recycled pulp in suspension, after which impurities such as filler and printing ink can be skimmed off as sludge. The fibres are then washed a number of times. Sodium hydroxide, complexing agents, hydrogen peroxide and alkali silicates can be used in the purification of recycled fibres.

The next step in the process is the bleaching process, which can be carried out according to a variety of principles and using various chemical substances, e.g. hydrogen peroxide and sodium hydroxide.

After the paper has been produced it is rolled up in layers.

Chemicals may be used in the following processes:

- pulp production
- de-inking of recycled paper
- washing of recycled paper
- bleaching
- colouring of paper if used
- decoration of paper/print

Chapter 4 provides a short description of the various chemicals used in the processes and which can thus be integrated in the fibre or can occur as residual content in recycled fibres.

3 Survey of manufacturers and suppliers

Paper handkerchiefs and toilet paper are mostly sold through supermarkets and other convenience stores. These products are not manufactured in Denmark but by major international manufacturers.

3.1 Manufacturers and suppliers

The most important players in the Danish market were identified and contacted by telephone and/or mail. The following companies are involved:

Paper handkerchiefs and toilet paper		
Manufacturer	Country	www.addresses
Metsä	Germany/Sweden	www.metsatissue.com
Georgia Pacific	Finland	www.gp.com
SCA Hygienic Products	Sweden	www.sca.se
Cartiera san Marco	Italy	www.cartierasanmarco.com
WEPA Paierfabrick	Germany	www.wepa-hygiene.de
Kimberley-Clark	UK	www.euro.k-caway.com

Paper handkerchiefs
According to the retail trade, there are four major suppliers to the Danish paper handkerchief market. In addition, there may be other suppliers which supply private labels, i.e. whose name is specific to the chain in question, e.g. COOP or Dansk Supermarked.

The four major manufacturers supplying the Danish market are:

- SCA Hygienic Products, Danmark
- Metsä-Serla
- Kimberley-Clark
- Georgia-Pacific A/S

Table 1 provides a review of paper handkerchiefs in the Danish market with manufacturers, suppliers and dealers. Note that there may be more product dealers than those mentioned in the table.

Table 1 Survey of Manufacturers supplying paper handkerchiefs to the Danish market

Paper handkerchiefs				
Producer	Products	Labeling	Dealer	Fibre/Bleaching method/additives
Metsä	Bluecare	Swan label	FDB	100% new cellulose, hydrogen peroxide
Georgia Pacific	Lotus	None	Dansk Supermarked, Matas etc.	New cellulose + recycled pulp, DIP, eucalyptos menthol
Georgia Pacific	Lotus menthol	None	Dansk Supermarked	New cellulose + recycled pulp, DIP
SCA Hygienic Products	Edit Softis	Swan label	Dansk Supermarked etc.	100% new cellulose, bleaching without chlorine
SCA Hygienic Products	Edit Softis menthol	Swan label	Dansk Supermarked etc.	100% new cellulose, bleaching without chlorine, eucalyptos menthol
Cartiera san Marco	Et godt køb	None	FDB	100% new cellulose, hydrogen peroxide
WEPA papirfabrik	Silk	None	Fakta	New cellulose, no bleaching
Kimberly - Clark	Kleenex	None	Dansk Supermarked, Matas etc.	New cellulose, ECF
Kimberly - Clark	Kleenex + balsam	None	Dansk Supermarked, Matas etc.	New cellulose, ECF, mineral oil, ceresin, stearyl alcohol, isopropylpalmitate calendula oil
Kimberly - Clark	New Satin	None	Dansk Supermarked	New cellulose, ECF, mineral oil, ceresin, stearyl alcohol, isopropylpalmitate calendula oil

ECF (elementary chlorine free): oxygen compounds such as oxygen, ozone, hydrogen peroxide are used in bleaching

DIP: De-inked pulp

Toilet paper

Similarly, there are three major suppliers to the Danish toilet paper market. In addition, there may be other suppliers who supply private labels.

The three major manufacturers supplying the Danish market are:

- SCA Hygienic Products, Danmark
- Metsä-Serla
- Georgia-Pacific A/S

Table 2 provides a review of toilet paper in the Danish market with appurtenant manufacturers, suppliers and dealers. Note that there may be more product dealers than those mentioned in the table.

Table 2 Survey of selected toilet paper suppliers and dealers

Toilet paper				
Producer	Products	Labeling	Dealer	Fibre/Bleaching method/additives
Metsä	Bluecare/tusindfryd	Swan label	FDB, Irma	80% bleached recycled pulp, 20% bleached new fibres, cullulose, hydrogen peroxide (TCF)
Kimberly – Clark	Kleenex Premium	None	Various supermarkets	New cellulose + recycled pulp, ECF/BCTMP, dry stregnth agent, pigments
Georgia Pacific	Lotus	Swan label	Various supermarkets	New cellulose
SCA Hygienic Products	Edit White	Swan label	Various supermarkets	100% new cellulose, bleaching without chlorine
SCA Hygienic Products	Edit Soft	Swan label	Various supermarkets	100% new cellulose, bleaching without chlorine
SCA Hygienic Products	Edit Natur	Swan label	Various supermarkets	100% new cellulose, bleaching without chlorine
Metsä	Daily bløde	None	FDB	100% bleached recycled pulp, formamidine sulfonic acid (FAS), sodium thionite
Metsä	Soft	None	FDB	New cellulose, bleaching without chlorine
Metsä	Lambi	Swan label	Dansk Supermarked etc.	New cellulose, bleaching without chlorine

BCTMP: Bleached-Chemi-Thermo-Mechanical-Pulping

TCF (total chlorine free): oxygen compounds such as oxygen, ozone and hydrogen peroxide are used

ECF (elementary chlorine free): oxygen compounds such as oxygen, ozone, hydrogen peroxide are used in bleaching

Retail chains

Table 3 below contains a list of the most important retail chains in the Danish market which are dealers in these products.

Table 3 Survey of selected dealers

Forhandlere	**www.adresser**
Matas	www.matas.dk
Supervib I/S	www.edeka.dk
FDB	www.fdb.dk
Dansk Supermarked	www.dansksupermarked.dk
F-Gruppen	www.fdb.dk
Fakta A/S	www.fakta.dk
Irma A/S	www.irma.dk
Aldi Marked K/S	

4 Survey of chemical constituents

Retail chains and manufacturers were contacted by telephone or by post with a questionnaire and comments on statements. The purpose was to obtain information about the substances which are actively added to the products and to obtain analysis results on constituent substances from the manufacturers.

The data collected from the manufacturers has in general been of a very limited nature. Only very few of the retail chains possess any knowledge in the form of analyses of which substances are contained in the products. Information was of a general nature. For example, we were informed that there is no active addition of chemical substances, but they suppose that there might be chemical residues from recycled fibres and from the purification process when using recycled fibres.

Data collection was supplemented with data from available literature.

A number of chemical substances are used in the manufacture of paper. According to the description of paper production in Europe /6/, the so-called BREF (BAT reference document) under the IPPC directive, up to 800 different chemical substances may be used in paper manufacture. In the case of paper produced for use as toilet paper and paper handkerchiefs, the range is assessed as being somewhat narrower, as fewer types of substance in fewer process steps are used.

The synthetic chemical substances used in paper production can be divided according to the parts of the process and the finished product, as shown in table 4.

Table 4 Distribution of synthetic chemical substances in paper goods (average at global level)/6/

Use/function	Percentage of total consumption
Coating, binding agent and auxiliary substances	50
Sizing incl. starch	25
Wet strength agents	8
Bleaching agents	6
Retention and flocculation	5
Dyes and optical brightening	3
Biocides	1
Anti-foaming agents	1
Other	1

Processing chemicals used in paper manufacture are:

- De-inking agents (recycled fibres)
- Bleaching agents
- Auxiliary substances to retain substances in paper (retention/flocculation)
- Complex agents
- Surfactants
- Biocides (slimicides)
- Anti-foam agents

Product chemicals are:

- Fillers
- Sizing (makes the paper water-repellent)
- Fixing (increases adsorption of chemicals to the fibres)
- Dry strength agents (increases paper strength in dry state)
- Wet strength agents (increases paper strength in wet state)
- Dyes
- Optical brightening
- Coating (surface properties)

All the mentioned groups of chemicals may not necessarily be used in the manufacture of toilet paper and paper handkerchiefs. The following types of chemical substances are used in the production of toilet paper and paper handkerchiefs.

- Bleaching agents/de-inking agents
- Auxiliary substances to retain substances in paper (retention/flocculation)
- Wet strength agents
- Dyes
- Dry strength agents
- Lotions/balsams
- Aromatic agents

The last two groups – lotions/balsams and aromatic agents – particularly apply to paper handkerchiefs, where lotions/balsams or aromatic agents can be intentionally added to the paper handkerchiefs.

4.1 Chemical residues in paper

The chemicals used in the manufacture of paper can be discharged into water environment, the air, as waste or may remain contained in the paper. Distribution depends on the process and the additives used.

The trend among manufacturers is towards ensuring that as great a part as possible is retained in the paper in order to protect the external environment against the discharge of chemicals, cf. BAT reference document /6/. In addition, in general efforts are made to limit the use of chemical substances as much as possible, and to use substances which are not harmful to the

environment or to health. Particular attention is paid to bio-degradability, toxicity, and bio-accumulation.

The chemicals used may be divided into process-related auxiliary substances and substances intended to enhance the properties of the product.

4.1.1 Fillers

This group consists of kaolin (China clay), calcium carbonate, titanium dioxide, talcum and plastic microspheres. The first two products predominate. The substances may be added to soften the surface or as an economical way to give the impression of increased fibre length (higher quality).

Typically, up to 300 kg per ton are added. 50-80 % is retained in the paper.

Fillers are not used in the production of paper handkerchiefs and toilet paper.

4.1.2 Bleaching agents

Bleaching agents can consist of hydrogen peroxide, chlorine dioxide, hypochlorite, sodium hypochlorite and sodium hydroxide.

Bleaching agents may be used in quantities of up to 30 kg per ton. It is assessed that most of them are discharged in the waste/process waters. Moreover, the remaining bleaching agent in the paper is inactive after use.

4.1.3 Retention and flocculation agents

The most frequently used substances are synthetic polymers such as modified polyacrylamide in quantities of the border of 0.1 – 0.5 kg per ton or polyethylenamine in 1-2 kg per ton.

Most of these products are retained in the paper – up to 97-99%, i.e. approx. 0.1 kg per ton.

4.1.4 Wet strength agents

Wet strength agents may consist of several different types of polymer. For example, these may include urea formaldehyde binding agent, melamine formaldehyde or polyamidoamine-epichlorohydrin binding agent.

Approx. 50 kg per ton are used. Of this, it is assessed that over 90% is retained in the paper, i.e. up to approx. 45 kg per ton. Formaldehyde can be released in processes related to the treatment of recycled paper. It is thought that formaldehyde can be released through use as toilet paper or handkerchiefs if binding agents based on urea formaldehyde are used. This is known from other types of product where this substance is used as binding agent.

4.1.5 Dry strength agents

Starch or modified cationic starch is used in quantities of approximately 10 kg per ton and a further up to 50 kg is used in the pressing of the paper. A major part is discharged into the process water. It is assessed that up to 90% of the 10 kg is retained in the paper, i.e. up to 9 kg per ton, and up to 54 kg per ton if pressing is carried out.

4.1.6 Dyes/coating

Various types of dye may be used. These may include triphenyl methane, xanthene, acridine, quinoline, thiazolidine, anthraquinone, indigo and phthalocyanine dyes. Consumption is typically from 0.1 kg per ton up to 100 kg per ton for extremely dark colours. 70-98 % is retained in the paper, i.e. a residual content of between 0.07-0.1 and 70-98 kg per ton.

4.1.7 Other additives

These additives include:

- biocides (slimicides)
- optical brightening
- surfactants
- odoriferous substances
- lotions/balsams

Biocides are added to the process water (approx. 30 mg/l). In Denmark there are three approved anti-slime agents for paper production /9/. The approved slimicides go under the product names of: Myacide AS (2-bromo-2-nitropropane-1,3-diol), Microbiocide B-6012 (2,2-dibromo-2-cyanoacetamide) and Intace B 100 (2-bromo-2-nitropropane-1,3-diol).

As toilet paper and paper handkerchiefs are not manufactured in Denmark, products other than those approved for use in Denmark may be used. A review of Swedish statistics concerning the use of approved slimicides /7/ shows that consumption in Sweden is dominated by 2,2-dibromo-2-cyanoacetamide (76,5 t) and glutaraldehyde (78,4 t), which together account for 93 % of total consumption. Besides the substances mentioned above, 2-bromo-4-hydroxyacetophenone, 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one are also used in Sweden. 2-bromo-4-hydroxyacetophenone is an allergen.

According to the European BAT reference document /6/, slimicide residues in paper are assessed as being of an extremely limited nature. It is assessed that by far the major share is discharged with the process water. However, there are indications that there may be a theoretical risk of residues of between 0.008 and 0.08 kg per ton of paper.

Optical whitening may be added to give the paper a whiter appearance. Normally substances such as 4,4-diaminostilbene-2,2-sulfonic acid are used. 5-10 kg per ton are added, of which 50-90 % is retained in the paper, i.e. in the region of 2.5 to 9 kg per ton.

Aromatic agents may be added to alter the aroma. These might be substances such as eucalyptus oils and menthol. At present, amounts added are not known.

Lotions or balsams may be added to soften the paper upon use. Substance used may include ceresin, stearyl alcohol, isopropyl palmitate, dimethicone and mineral oils. The amounts added are not known at present. The declared constituent substances are listed in table 5.

Table 5 Aromatic agents, lotions and balsams in paper handkerchiefs and appurtenant physical-chemical properties (data from chemfinder). - indicates that the value is unknown.

Name of substance (formula)	Percentage content (%)	CAS no.	bp °C
Eucalyptus oil	-	8000-48-4	-
Menthol (Cyclohexanol- $C_{10}H_{20}O$)	-	89-78-1	212
Ceresin (wax)	-	8001-75-0	-
Stearyl alcohol (Octadecanol - $C_8H_{38}O$)	-	112-92-5	336
Isopropyl palmitate ($C_{19}H_{38}O_2$)	-	142-91-6	-
Dimethicone (silicone rubber)	-	9016-00-6	--
Mineral oil	-	8012-95-1	360

In many cases the manufacturers of paper handkerchiefs and toilet paper have their own requirements to the products in regard to the content of chemical substances. The demands could for instance be that the products may not contain optical brightening and formaldehyde releasing substances.

4.2 Screening of potential constituent substances

Table 6 below lists those substances which, based on a review of BAT note /6/, may occur as residues in paper goods. Table 6 does not include aromatic agents substances, lotions and balsams which may be added to paper handkerchiefs.

Table 6 Survey of chemical substances which may occur as residues in paper handkerchiefs and toilet paper

Substance group/name	Estimated residual content kg/t	CAS no.
Fillers	150-240	
- kaolin		1332-58-7
- calcium carbonate		471-34-1
Retention agents	0.1 – 0.5	
- polyethylenimine		26658-46-8
- polyacrylamide		9003-05-8
Wet strength agents	45 - 50	
- urea formaldehyde		9011-05-06
- melamine formaldehyde		-
- polyamidoamine-epichlorohydrin		(106-89-8)
Dry strength agents	9	
- modified starch		9005-25-8
Dyes/coating	0.07 - 98	
- diphenylmethane		101-81-5
- triphenylmethane		519-73-3
- xanthene		92-83-1
- acridine		290-94-6
- quinoline		91-22-5
- thiazolidine		504-78-9
- anthraquinone		84-65-1
- indigo		482-89-3
- phthalocyanine		574-93-6
Biocides	0.008-0.08	
- glutaral		111-30-8
- 2,2-dibromo-2-cyanoacetamide		

Chemical substances other than those appearing in the list of substance groups may have been used.

As table 6 shows, dyes, wet strength agents and dry strength agents account for the largest potential residues. Residues of retention agents, dyes and biocides may be supposed to be significantly lower than for the three above mentioned groups. It should be noticed that no dyed to the grain paper goods were found, though some products were printed on one side. Therefore, the dye content of toilet paper and paper handkerchiefs was assessed as being relatively low.

Wet strength agents consist of a variety of binding agents, of which some probably release formaldehyde in small quantities during use just as chipboards and mineral wool insulation are known to do. Formaldehyde is classified as toxic (T;R23/24/25), corrosive (C;R34) and category 3 carcinogenic (Carc3;R40 R43). Some of the dyes used can be harmful to health and carcinogenic. If the substances are not bound to the fibres, they may cause skin irritations upon contact.

It should be noted that manufacturers failed to produce any precise list of the substances used in production. According to information received, heavy metals do not occur in concentrations above 100 ppm (= 100 mg/kg). Moreover, according to the manufacturers the paper products fulfil German requirements for products used in contact with food, BgVV Recommendation 36/10/. We were informed that benzidine based dyes, o-anisidine based dyes or toluidine based dyes are not used in paper handkerchiefs and toilet paper.

4.3 Eco-labelling of paper handkerchiefs and toilet paper

Under the Nordic Swan eco-label and the EU Flower eco-label, criteria have been established for the eco-labelling of both toilet paper and paper handkerchiefs. There exist criteria for the awarding of the EU Flower eco-label to toilet paper and paper handkerchiefs. There are 8 European manufacturers producing toilet paper with the EU Flower label. The manufacturers are: Cartiera Lucchese S.p.A., Dalle Hygiene SA, Delicarta SpA, Georgia-Pacific GB Ltd, Industrie Cartarie Tronchetti, Metsä Tissue GmbH, Tishu MFG Ltd and Trascarta SpA (cf. www.svanen.nu). Metsä also has toilet paper bearing the EU Flower in the Danish market (cf. www.ecolabel.dk).

Within the paper handkerchief product group, in August 2002 there were two products on the Danish market which carried the Nordic Swan eco-label. In the toilet paper product group, by August 2002 there were more than 20 products in Denmark carrying the Nordic Swan label (cf. www.ecolabel.dk). These included white, natural (unbleached) and decorated products. Table 7 reproduces a list of some eco-labelled products produced by major manufacturers.

Table 7 Examples of eco-labelled toilet paper products on the Danish market (all with the Swan)

Manufacturer	Product name	Colour/decoration
Georgia Pacific	Lotus soft Lotus Royal Lotus Maxi	
SCA Hygienic	Edet Maxi Edet Natur Edet Ultra Edet Soft Uniline	

Metsä-Serla	Leni	
	Lambi	
	Daisy	
	Bluecare	
	Irma toilet, blue	X
	Irma toilet, yellow	x
	FDB Supersoft	
	Irma Soft	
	Daily Soft	

As the table shows, this group of products also includes some provided with coloured decoration.

Swan eco-labelled products must comply with a series of criteria related to the use and residual content of chemical substances /3/.

There are requirements related to bleaching agents, wet strength agents, antifoaming agents, complexing agents, and requirements concerning product safety. Products may contain a maximum of:

- Formaldehyde max. 1mg/dm^2
- Glyoxal max. 1.5 mg/dm^2
- PCB max. 2 mg/dm^2

In addition, the biocide contents of the product, dyes and optical brightening must not rub off in accordance with test methods EN 646 and 648.

In order to be awarded the eco label, test documentation of the above mentioned substances must be submitted.

Printed on decoration must not be carried out with dyes from which a number of selected amines might be discharged.

Perfumes and other aromatic agents must not be actively added to the product.

Corresponding requirements are also included in the EU Flower criteria /2/.

5 Test products

5.1 Selection of products

Five products within the area of tissues and six products within the area of toilet paper have been selected. The products represent a broad section of the market available products. Products with and without colour decoration have been selected, as have products with and without odorants and softeners (tissues). The products have been produced of a new cellulose, return mass, or a combination of both the latter stated in the table as partly under column return mass.

Five tissue products have been analysed (P-1 to P-5) and six toilet paper products (T-1 to T-6).

Table 8 Products selected for analyses

Product	Return mass	Colour decoration	Added colour decoration	Ecolabelled
Tissues				
P-1	Partly	Yes	Menthol	No
P-2	Partly		None	No
P-3	Partly		Balsam	No
P-4	No		None	Yes
P-5	No		Menthol	Yes
Toilet paper				
T-1	80%		None	Yes
T-2	No		None	Nej
T-3	No	Yes	None	Yes
T-4	No		None	Yes
T-5	No	Yes	None	No
T-6	Partly		None	No

*: Indistinctively identified

5.2 Analytical methods

5.2.1 Sample preparation

All paper was cut into minor pieces of approximately 3 x 3 mm.

5.3 Content analyses

5.3.1 GC/MS screening (PAH, PCB, bisphenol A, and other extractable organic compounds)

Approximately 2 g of the product is taken and extracted with dichloromethane added internal standards by means of Soxhlet extraction for 16 hours. A part sample of the extract is taken, analysed directly, and concentrated at combined gas chromatography and mass spectrometry (GC/MS), by scanning over a larger mass area. The content is calculated to relevant external standards (PAH –poly aromatic hydro carbons and PCB-poly chlorinated biphenyles) or internal standards (other extractable compounds).

The analyses are carried out as true double determination. The limit of detection is 1-10 mg/kg. Uncertainty is 10-15% RSD at quantification to external standards and uncertainty is stated to 50-100% RSD at quantification to internal standards.

5.3.2 Cadmium, cobalt, cupper, manganese, molybdenum, lead, tin, and zinc (ICP screening)

Approximately 10 g sample is calcined and the calcined residue is dissolved in nitric acid. The dissolved metals are determined accordingly on ICP-spectrophotometer (Inductively Coupled Plasma).

The analyses are carried out as true double determination. The limit of detection varies and is stated in the result section. Analytical uncertainty is 10% RSD.

5.3.3 Arsenic and selenium (ICP screening)

Approximately 0.2 g sample is opened with nitric acid and hydrogen peroxide in microwave oven by means of which the acid soluble metals are liberated. The dissolved metals are accordingly determined on ICP-spectrophotometer (Inductively Coupled Plasma).

The analyses are carried out as true double determination. The limit of detection varies and is stated in the result section. Analytical uncertainty is 10% RSD.

5.3.4 Acrylamide

A part sample is extracted with water that is derived with bromine to 2,3-dibromine propanoic amide that is extracted accordingly from the water phase. The extract is analysed on GC/ECD.

The analyses are carried out as true double determination. The limit of detection is 1 mg/kg. Determination uncertainty is 25% RSD.

5.3.5 Alcoholpolyethoxylates, octyl-, and nonylphenolethoxylates

A part sample is extracted with methanol and diluted 1:1 with aqueous ammonium acetate solution after which it is analysed at LC/MS with positive mode electro spray ionisation. The analysis includes alkyl phenol- and alcohol (C10 - C18) polyethoxylates with a chain length from 3 - approximately 15 ethoxy groups.

The analyses are carried out as true double determination. The limit of detection varies and is stated under the result section. Determination uncertainty is 15% RSD.

5.3.6 Colophony

A part sample of the Soxhlet extract is evaporated to dryness and re-dissolved in methanol and water (90:10) and analysed at combined liquid chromatography and mass spectrometry (LC/MS-DAD).

The analyses are carried out as true double determination. The limit of detection is 0.5 mg/kg. Determination uncertainty is 15-20% RSD.

5.3.7 Nitrosamines

The volatile N-nitrosamines are extracted at Soxhlet extraction and the extract is concentrated on kiesel gel. N-nitrosamine is determined on gas chromatography with chemi-luminescence detection and Thermal Energy Analyzer (TEA). Sub-supplier performs the analyses.

The analyses are carried out as true double determination. The limit of detection is 0.01 mg/kg.

5.3.8 EDTA and DTPA

The analysis of EDTA (ethylenediaminetetraacetic acid) and DTPA ([[(Carboxymethyl)imino]bis(ethylennitrilo)]-tetra-acetic acid) is performed by dissolving a part sample in mobile phase and analysing directly on ion chromatograph with anion bytter and conductivity detection (IC).

The analyses are carried out as true double determination. The limit of detection is 30 mg/kg. Uncertainty is 10-15%RSD.

5.4 Analytical results

5.4.1 GC/MS screening (extractable compounds)

The results for GC/MS screening are stated below. Two results indicate double determination. All identifications of the compounds are performed from the mass spectra by comparing with mass spectra in a data library. Spectra representing the best match are for each case considered at ”scientific judgement”. The components are included in a group designation with a total sum for the cases where identification is impossible. The limit of detection is 1-10 mg/kg.

The content of organic components in the extracts is generally low. Concentration of the extracts was necessary in order to identify the small concentrations of compounds in the extract with sufficiently certainty.

If possible, quantification of the determined components is performed from the analysis of the direct extract. For components exclusively determined in the analysis of the concentrated extract this extract was used for quantification. Uncertainty for these values is higher than the values calculated on the direct extract. Uncertainty is approximately 25% RSD. These values are noted with * in table 9.

Table 9. Analytical results for extractable compounds on all toilet paper products. The results are given in mg/kg. The limit of detection is given in the above mentioned text.

	Toilet paper											
Component	T-1		T-2		T-3		T-4		T-5		T-6	
Hydroxy biphenyl	-	-	-	-	-	-	5.4*	6.1*	1.7*	0.89*	-	-
9-Octadecenic acid methyl ester	26	33	-	-	18*	15*	-	-	-	-	-	-
9,12-Octadecadienic acid methyl ester	26*	29*	-	-	-	-	12*	17*	-	-	-	-
DEHA-diethyl hexyl adipate	-	-	-	-	-	-	-	-	14*	7.9*	-	-
Benzyl butyl phthalate	2.9*	6.5*	-	-	-	-	-	-	-	-	-	
Squalen	9.2	8.8	-	-	2.4	17	4.5	4.3	6.9*	9.8*	51*	27*
Bisphenol A	-	-	-	-	-	-	-	-	-	-	-	-
Glycerol tricaprylate	8.8	43	13	11	8.5	17	3.9	4.7	9.2	12	78*	87*
Isomer of glycerol tricaprylate	11	47	-	-	28	8.2	-	-	17	23	-	-
Stigmast-4-en-3-on	-	-	-	-	7.8*	5.0*	-	-	-	-	-	-
Unidentified alcanes, alcenes, alcoholes, ester, and cycloalcanes	-	-	13	10	-	-	5.6	3.7	-	-	-	-
Unidentified alcanes, alcenes, alcoholes, ester, and cycloalcanes	25	28	6.3*	4.3*	91*	85*	-	-	140*	330*	86*	120*
Unidentified phenyl compounds*	27*	29*	-	-	-	-	4.3*	3.2*	-	-	-	-
Unidentified*	13*	13*	10*	6.6*	86*	70*	5.4*	6.4*	5.2*	4.2*	0.74*	0.48*

-: means less than the limit of detection

*: quantified on concentrated extract

Table 9, continued. Analytical results for extractable compounds on all toilet paper products. The results are given in mg/kg. The limit of detection is given in the above mentioned text.

	Tissues									
	P-1		P-2		P-3		P-4		P-5	
Menthol	770	600	1.8*	0.96*	-	-	3.1*	2.7*	290	150
Menthenol (terpineol)	-	-	-	-	-	-	-	-	7.6*	4.4*
BHT (butylated hydro toluene)*	-	-	-	-	17	18	-	-	-	-
Phosphoric acid, dioctadecyl ester	-	-	-	-	26	24	-	-	-	-
Isopropyl myristate	22	20	-	-	37	33	2.6*	1.2*	-	-
Fatty acid ester	-	-	-	-	5.6	5.0	-	-	-	-
Isopropyl palmitate	-	-	-	-	2300	2000	7.1*	2.7*	-	-
DEHA (diethyl hexyl adipate)	16*	14*	-	-	-	-	-	-	-	-
Tetradecanoic acid	9.5*	6.4*	-	-	-	-	-	-	-	-
Sum of isomer of hexahydrohexamethyl-cyclopentabenzopyran (musk)	97*	85*	-	-	-	-	-	-	-	-
Squalen	4.1	1.7	3.9*	8.7*	-	-	33*	9.5*	2.9	4.4
Bisphenol A	-	-	-	-	-	-	-	-	-	-
Glycerol tricaprylate	5.9	5.6	11	9.2	-	-	30	14	13	14
Isomer of glycerol tricaprylate	-	-	11	11	-	-	-	-	16	16
Sitosterol	-	-	-	-	-	-	-	-	130*	79*
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	32	28	38	34	18000	19000	250	130	-	-
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	130*	110*	45*	37*	790*	920*	88*	49*	190*	120*
Unidentified	48*	30*	3.8	3.0	12	9	1.5*	1.1*	9.4*	13*

-: means less than the limit of detection
*: quantified on concentrated extract

Bisphenol A is not included as external standard; however, characteristic ion trace for Bisphenol A has been tested for all GC/MS chromatogrammes. The compound could not be detected in the samples. Compounds as aldehydes with few carbon atoms will not be detected at the analysis.

Except from menthol, diethylhexyladipat and benzyl butyl phthalate, all the chemical substances found in the analysis has its origin from the tree. Menthol is intentionally added to paper handkerchiefs with menthol and diethylhexyladipat and benzyl butyl phthalate can be added as softener in paper handkerchiefs with lotion/balsam. The concentration of the chemical substances that has its origin from the tree will vary with the type of tree, climate and geographical factors.

5.4.2 PCB and PAH

The following PCB's have been analysed: 2,4,4'-trichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, 2,3',4,4,5'-pentachlorobiphenyl, 2,2',3,4,5,5'-hexachlorobiphenyl, 2,2',4,4,5,5'-hexachlorobiphenyl, 2,2',3,4,4', and 5,5'-heptachlorobiphenyl. The limit of detection is 0.5 mg/kg for PCB and 0.2 mg/kg for PAH. Uncertainty is 15% RSD.

The following PAH's have been analysed: Acenaphten, Acenaphtylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysen, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, and Pyrene.

All selected tissue and toilet paper products have been analysed. No PCB's or PAH's have been detected in the analysed samples.

5.4.3 Metal analyses

Table 10 states the results for metal analyses. Metal analyses have been performed on the products produced of recycled paper, coloured paper, or that has a coloured decoration. Two results indicate double determination.

Table 10. Results for metal analyses on selected tissues. Results are given in mg/kg.

	Tissues						
Metal	P-1		P-2		P-3		Limit of detection
Cadmium	-	-	-	-	-	-	0.1
Cobalt	-	-	-	-	-	-	0.5
Cupper	57	59	0.60	0.62	1.7	1.5	0.5
Magnesium	230	180	320	260	170	130	0.1
Molybdenum	-	-	-	-	-	-	0.5
Lead	-	-	-	-	-	-	1.0
Antimony	-	-	-	-	-	-	1.0
Tin	-	-	-	-	-	-	1.0
Zinc	0.62	0.70	1.2	-	1.9	1.3	0.5
Arsenic	-	-	-	-	-	-	20
Selenium	-	-	-	-	-	-	20

-: means less than the limit of detection

Table 10 continued. Results for metal analyses on selected tissues. Results are given in mg/kg. The limit of detection is given in the above-mentioned table.

	Toilet paper									
Metal	T-1		T-2		T-3		T-5		T-6	
Cadmium	-	-	-	-	-	-	-	-	-	-
Cobalt	-	-	-	-	-	-	-	-	-	-
Cupper	1.4	1.4	0.64	0.67	0.68	0.75	7.2	7.1	0.78	1.3
Magnesium	150	140	290	240	720	620	260	200	300	240
Molybdenum	0.55	-	-	-	-	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-	-	-
Antimony	-	-	-	-	-	-	-	-	-	-
Tin	-	-	-	-	-	-	-	-	-	-
Zinc	14	12	-	-	-	-	0.52	0.54	2.1	3.9
Arsenic	-	-	-	-	-	-	-	-	-	-
Selenium	-	-	-	-	-	-	-	-	-	-

-: means less than the limit of detection

5.4.4 Nitrosamines

The following N-nitrosamines have been analysed: N-Nitrosodimethylamine, N-Nitrosomethylethylamine, N-Nitrosodiethylamine, N-Nitrosodipropylamine, N-Nitrosodibutylamine, N-Nitrosomorpholine, N-Nitrosopyrrolidine, N-Nitrosopiperidine, N-Nitrosodiisononylamine, and N-Nitrosodibenzylamine.

N-nitrosamines have been analysed on selected paper products (products produced from recycled paper with colour decoration or lacking information regarding paper pulp) (tissues P-1, P-2, and P-3). The limit of detection was 0.010 mg/kg. All analytical results are below the limit of detection i.e. N-nitrosamines have not been determined in any of the products.

5.4.5 Polyethoxylates

Table 11 provides the results of the analysis for alcoholethoxylates, octyl-, and nonyl phenol polyethoxylates. The analyses have been performed on selected products, i.e. products with no knowledge as to the paper pulp, recycled paper, or paper with colour content. Two results indicate double determination.

Table 11. Results of analyses for selected polyethoxylates on selected tissues. The results are given in mg/kg.

	Tissues						
	P-1		P-2		P-3		Limit of detection
Alcoholpolyethoxylate (APE)	170	160	-	-	-	-	20
Octylphenolpolyethoxylate (OPPE)	-	-	-	-	-	-	10
Nonylphenolpolyethoxylate (NPPE)	-	-	-	-	-	-	10

-: means less than the limit of detection

The results of the toilet paper products are below the limit of detection, e.g. there are no determined polyethoxylates in the toilet paper.

5.4.6 EDTA and DTPA

The results for the analysis for EDTA (ethylenediaminetetraacetic acid) and DTPA ([[(Carboxymethyl)imino]bis(ethylennitrilo)]-tetra- acetic acid) on selected paper products follow. The compounds are complex binding agents that theoretically can form part of the purification process for return fibres.

The products represent the paper goods with no knowledge as to the paper pulp, recycled paper, or paper with colour content.

As regards tissues P-1, P-2, and P-3 have been analysed – as to toilet paper T-1, T-2, T-3, T-5, and T-6 were analysed. The content is below the limit of detection of 30 mg/kg for all products, i.e. EDTA or DTPA have not been determined in either of the products.

5.4.7 Colophony

The results for colophony on all paper products are given in table 12. Two results indicate double determination. The limit of detection is 0.5 mg/kg.

Table 12. Results for analyses for colophony on all toilet paper products. The results are given in mg/kg. The limit of detection is given above.

	Toilet paper											
	T-1		T-2		T-3		T-4		T-5		T-6	
Colophony	-	-	-	-	1	1	-	-	-	-	-	-

-: means less than the limit of detection

Table 12 continued. Results for analyses for colophony on tissues. The results are given in mg/kg. The limit of detection is given above.

	Tissues									
	P-1		P-2		P-3		P-4		P-5	
Colophony	-	-	-	-	1	3	-	-	-	-

-: means less than the limit of detection

5.4.8 Acrylamide

All paper products have been analysed for acrylamide. All results are below the limit of detection of 1.0 mg/kg, i.e. acrylamide has not been identified in either of the samples.

5.4.9 Total outline of analytical results - tissues

	Tissues – chemical compound content mg/kg (average)				
	P-1	P-2	P-3	P-4	P-5
Screening for extractable compounds					
Menthol	690	1.4	-	2.9	220
Menthenol (terpineol)	-	-	-	-	6.0
BHT (butylated hydro toluene)*	-	-	18	-	-
Phosphoric acid, dioctadecyl ester	-	-	25	-	-
Isopropyl myristate	21	-	35	1.9	-
Fatty acid ester	-	-	5.3	-	-
Isopropylpalmitate	-	-	2200	4.9	-
DEHA (diethylhexyladipate)	15	-	-	-	-
Tetradecanoic acid	8.0	-	-	-	-
Sum of isomer of hexahydrohexamethyl-cyclopentabenzopyrane (moskus)	92	-	-	-	-
Squalene	2.9	6.3	-	21.5	3.7
Bisphenol A	-	-	-	-	-
Glycerol tricaprylate	5.8	10.1	-	22	14
Isomer of glycerol tricaprylate	-	11	-	-	16
Sitosterol	-	-	-	-	105
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	30	36	18500	190	-
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	120	41	855	69	155
Unidentified Metal	39	3.4	11	1.3	11.2
Cupper	58	0.61	1.6	Not analysed	Not analysed
Magnesium	205	0.6	1.6	Not analysed	Not analysed
Zinc	0.66	0.6	1.6	Not analysed	Not analysed
Alcohol polyethoxylate	165	-	-	Not analysed	Not analysed
Colophony	-	-	2	-	-

-: means less than the limit of detection
*: quantified on concentrated extract

5.4.10 Total outline of analytical results – toilet paper

	Toilet paper - chemical compound content mg/kg (average)					
	T-1	T-2	T-3	T-4	T-5	T-6
Sreening for extractable compounds						
Hydroxybiphenyl	-	-	-	5.8*	1.3*	-
9-Octadecenic acid methyl ester	30	-	17*	-	-	-
9,12-Octadecadienic acid methyl ester	28*	-	-	15*	-	-
DEHA-diethylhexyladipate	-	-	-	-	11	-
Benzyl butyl phthalate	4.7*	-	-	-	-	-
Squalene	9.0	-	9.7	4.4	8.4*	39*
Bisphenol A	-	-	-	-	-	-
Glycerol tricaprylate	26	12	12.8	4.3	10.6	83*
Isomer of glycerol tricaprylate	24	-	18	-	20	-
Stigmast-4-en-3-on	-	-	6.4*	-	-	-
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	-	12	-	4.7	-	-
Unidentified alcanes alcenes, alcoholes, ester, and cycloalcanes	27	5.3*	88*	-	235*	103*
Unidentified phenyl compounds	28*	-	-	3.8*	-	-
Unidentified	13*	8.3*	88*	5.9*	4.7*	0.6*
Metal						
Cupper	1.4	0.66	0.72	Not analysed	0.53	3.0
Magnesium	145	265	670	Not analysed	230	270
Molybdenum	0.3	-	-	Not analysed	-	-
Zinc	13	-	-	Not analysed	0.53	3.0
Colophony	-	-	1	-	-	-

-: means less than the limit of detection
*: quantified on concentrated extract

5.4.11 Summary of analytical results

The analyses of tissues and toilet paper generally show low levels of extractable organic compounds, i.e. compounds that can be liberated from the paper when in use. The compounds occur in highest concentrations are simple hydrocarbons. They occur in concentrations up to 19 g/kg for tissues and up to 330 mg/kg for toilet paper. A toilet roll weighs approximately 150 g, i.e. the content of the single analysed chemical compound is up to approximately 50 mg in one toilet roll. A packet of ten tissues weighs approximately 25 g, i.e. the content of the single analysed chemical compound compose up to approximately 0.5 mg in one packet of ten tissues.

Generally the concentration of extractable organic compounds is highest in toilet paper. Besides hydrocarbons odourants and compounds with softening effect are dominant in tissues. Almost all the chemical substances found in the analysis, with the exception of menthol and the softeners diethylhexyladipate and benzyl hexyl phthalate can be traced down to substances from the tree.

A large part of the other analysed organic compounds is not determined in either tissues or toilet paper. This applies to nitrosamines, PCB, PAH, and acrylamide.

The metals cupper and magnesium are determined in all samples with highest levels in products containing colour decorations. Furthermore, zinc in low concentrations has been determined in some of the products.

The analyses generally indicate relatively low concentrations of compounds that may be liberated at use. Furthermore, the analyses show that paper completely or partly based in return pulp does not contain more organic chemical compounds, metals, or other potentially hazardous compounds than paper based on new cellulose fibre. The major difference is evident between products with or without colour decoration, products with or without odourants, and products with or without softener/balsam.

6 Selected substances and data searching

Based on analysis of the constituents, the Danish EPA has selected the following substances for assessments of their effects on health:

- hydroxybiphenyl
- isopropyl myristate
- isopropyl palmitate
- 9-octadecenoic methyl ester
- 9,12-octadecadienoic acid methyl ester
- menthenol
- menthol
- sitosterol
- stigmast-4-en-3-one
- squalene

Some of these substances show structural similarities, and therefore it is assumed that their impact on health will be comparable. This applies to the following group of substances:

- isopropyl myristate
- isopropyl palmitate
- 9-octadecenoic methyl ester
- 9,12-octadecadienoic acid methyl ester

and the two substances - menthenol and menthol. Finally, sitosterol and stigmast-4-en-3-one are comparable.

Data searches were made in the following Internet-based databases for identification of physical-chemical data and health-impacting properties:

1. Chembank
2. Chemfinder
3. Ullmann
4. ECB
5. HSDB
6. IRIS
7. CCRIS
8. GENETOX
9. IUCLID
10. PHYSPROP
11. Web of Science
12. NTP

Table 13 presents a review of the results of the data search. The survey shows whether the 11 databases contain data on the individual substances.

In addition, we investigated whether the substance is contained on the Danish EPA's list of chemicals for the regulation of the cosmetics industry or on the Positive List for foodstuffs.

Table 13 Survey of the results of the data search. The database and data source numbers refer to the above numbers
+ indicates data found. - indicates no data found.

Substance	CAS No.	1	2	3	4	5	6	7	8	9	10	11	12
Hydroxybiphenyl	90-43-7	+	+	+	+	+	-	+	-	+	+	+	+
Isopropyl myristate	110-27-0	+	+	-	+	+	-	-	-	+	+	+	-
Isopropyl palmitate	142-91-6	+	-	-	+	+	-	-	-	+	+	+	-
9-octadecenoic methyl ester	2462-84-2/112-62-9	+	+	-	+	+	-	+	-	-	+	+	-
9,12-octadecadienoic acid methyl ester	112-63-0	+	+	-	+	+	-	-	-	-	+	+	-
Menthenol	98-55-5	+	+	+	+	+	-	+	-	-	+	+	-
Menthol/Cyclohexanol	89-78-1	+	+	-	+	+	-	+	+	-	+	+	+
Stigmast-4-en-3-one	1058-61-3	-	-	-	-	-	-	-	-	-	-	-	-
Sitosterol	83-47-6/83-46-5	-	-	-	+	-	-	+	-	-	+	+	-
Squalene	111-02-4/7683-64-9	+	+	+	+	-	-	+	-	-	+	+	-

Data for the individual CAS numbers are divided into individual toxicological parameters as illustrated in table 14.

Table 14. Identified human toxicological data divided up by the investigated CAS numbers

Toxicological parameter	Substance									
	Hydroxy-biphenyl	Isopropyl myristate	Isopropyl palmitate	9-octa-decenoic acid methyl ester	9,12-octadecadie-noic acid methyl ester	Men-thenol	Menthol/ Cyclohe-xanol	Stigmast-4-en-3-one	Sito-sterol	Squa-lene
Acute toxicity										
Inhalation	-	+	-	-	+	-	+	+	-	-
Ingestion	+	+	+	-	+	+	+	+	-	+
Skin contact	+	+	+	-	+	-	-	+	-	-
Irritation and corrosiveness	-	-	+	+	+	+	+	+	-	-
Subacute/chro-nic toxicity										
Allergy and hypersensitivity	+	+	-	-	+	-	+	+	-	-
Organ effects	+	+	-	-	+	-	+	+	-	-
Mutagenicity	+	+	-	-	-	+	+	-	-	-
Carcinogenic	+	+	-	+	-	-	+	+	-	-
Reproductive toxicity	+	+	-	-	-	-	+	-	-	-

7 Toxicological profile of selected substances

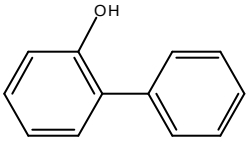
The following profiles of the selected substances' impact on health have been drawn up based on the data available in the databases mentioned in section 6 above.

When the assessment of consumers' health is made, the assessment is a worst case assessment. This is because the assessment is made with the concentration of the chemical substances in the products and not with the concentration of the migrated amount of chemical substances.

7.1 Toxicological profile of hydroxybiphenyl

7.1.1 Identification and physical-chemical properties

Identification

Chemical name	hydroxybiphenyl
EINECS name	biphenyl-2-ol
CAS no.	90-43-7
Molecular formula	$C_{12}H_{10}O$
Structural formula	

Applications

This substance is often used as a biocide for e.g. fruit and vegetables to prevent the growth of mould fungi on the surface during storage. It has been approved in many countries for the treatment of citrus fruits (12). It is also used in washing up liquids, vegetable wax and for paper to be used with foodstuffs (16). The substance is probably used as a slimicide in the production of paper articles or it can be found in the products as it can have its origin from the lignin in trees.

Synonyms

Many synonyms are used for hydroxybiphenyl, of which a number have been selected here (12):

- 1,1'-biphenyl-2-ol
- 2-hydroxybiphenyl
- biphenylol
- dowicide 1
- hydroxdiphenyl
- hydroxy-2-phenylbenzene

- OPP
- orthohydroxydipbenyl
- orthoxenol
- o-xonal
- phenylphenol
- preventol O extra
- remol TRF
- torsite
- tumescal OPE
- xenol

Regulation

EU classification	Irritant (eyes, respiratory passages and skin)
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	max 0.2% expressed as phenol
Foodstuffs (the positive list, 2000)	Entered on the positive list (antioxidants and preservatives)
Foodstuffs (the flavour list, 2002)	not on the list

The substance is on the EU list of hazardous substances under the classification Xi; R36/37/38. The substance must be labelled with N; R50 (dangerous for the environment/very toxic to aquatic organisms).

Physical/chemical properties

The physical-chemical properties of hydroxybiphenyl are shown in table 15.

Table 15. Physical-chemical properties of hydroxybiphenyl.

Physical/chemical properties	Data	Reference
Physical form	solid substance	5
Molecular weight (g/mol)	170.2104	2
Melting point (ºC)	57	2
Boiling point (ºC)	282	2
Vapour pressure (Pa)	0.2666	10
Specific weight (kg/L)	1.213	2
Log Kow	3.09	10
Water-solubility (mg/L)	38	5

7.1.2 Toxicological properties

Acute toxicity

Inhalation	The substance can cause eye irritations (15).
Ingestion	Upon ingestion the toxicity of the substance is assessed as low (13). Animal tests on mice indicated a fatal dose of 2 g/kg (11). A fatal human dose of 10 g has been observed in 2 cases (15). The WHO has established limits for acceptable daily ingestion at 0.2 mg/kg (13). Acceptable concentrations on fruit and vegetables

	have been set at 10-25 ppm/10-25 mg/kg (15).
Skin contact	Tests on rabbits and mice with a 5% solution have shown that the substance can cause skin and eye irritations upon contact (22).
Irritation and corrosiveness	No data
Subacute/chronic toxicity	
Allergy and hyper-sensitivity	The substance is not believed to cause skin hypersensitivity (11).
Organs	The substance can cause effects to the cornea upon exposure to a 5 % solution in sesame oil or a 1 % aqueous solution (15).
Mutagenicity	Individual animal tests on rats and mice have shown signs of mutagenicity following injection with 300-500 mg/kg per day (11, 22). Tests on human white blood corpuscles have shown dose response (11).
Carcinogenic	The substance has not been evaluated for its carcinogenic properties due to a lack of data (group) in IARC (WHO's cancer research institute, the International Agency for Research on Cancer)(15).
Reproductive toxicity	Tests on mice, rats and rabbits have not shown reproductive toxicity at daily doses of up to 600 mg/kg. (13, 15).

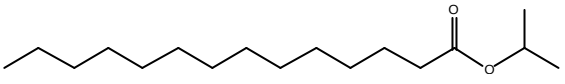
7.1.3 Conclusion

The substance can cause skin and eye irritations upon contact. Long-term exposure to the substance can cause chronic eye effects. There is insufficient data to assess the carcinogenic properties of the substance.

Hydroxybiphenyl was found in two toilet paper products in concentrations of 0.9 to 6.1 mg/kg. This is below the acceptable level for fruit and vegetables. The level is also below the permitted limit under the Cosmetics executive order. The level corresponds to approx. 0.13 to 0.9 mg per roll of toilet paper.

7.2 Toxicological profile for isopropyl myristate

7.2.1 Identification and physical-chemical properties

Identification	
Chemical name	Isopropyl myristate
EINECS name	Isopropyl myristate
CAS no.	110-27-0
Molecular formula	$C_{17}H_{34}O_2$
Structural formula	

Applications
Isopropyl myristate is used, for example, in cosmetics products, washing powders and cleaning materials, lubricants and medical goods. The substance is on the list of food aromas. The substance may be used in cleaning processes on recycled fibres for paper manufacture.

Synonyms
Below is a list of synonyms for isopropyl myristate (12):

- Tetradecanoic acid 1-methylethyl ester
- Estergel

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	Dangerous for the environment (N;R51/53)
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	entered on the list

On the Danish EPA's guideline list for self-classification of hazardous substances, isopropyl myristate is assessed as dangerous for the environment/toxic to aquatic organisms, may cause long term effects in the aquatic environment (N;R51/53).

Physical/chemical properties
The physical-chemical properties of isopropyl myristate are shown in table 16.

Table 16. Physical-chemical properties of isopropyl myristate.

Physical/chemical properties	Data	Reference
Physical form	liquid	5
Molecular weight (g/mol)	270.4544	2
Melting point (ºC)	3	10
Boiling point (ºC)	192.6	10
Vapour pressure (Pa)	0.01247	10
Specific weight (kg/L)	0.85	5
Log Kow	7.17	10
Water-solubility (mg/L)	0.0135	10

7.2.2 Toxicological properties

Acute toxicity

Inhalation	The substance can cause eye irritations (information on quantities not available) (19).
Ingestion	The substance shows low acute toxicity upon ingestion. LD50 values for rats and mice are > 10 and 50 g/kg bw, respectively (11). NOAEL is 1 g/kg/day in the case of rats.
Skin contact	The substance can cause skin and eye irritations

	upon contact assessed based on tests on mice and rabbits using the pure substance, 1- 5 g/kg (11, 19).
Irritation and corrosiveness	No data
Subacute/chronic toxicity	
Allergy and hyper-sensitivity	Tests on guinea pigs do not indicate skin hypersensitivity (11, 15, 19).
Organs	Daily exposure to skin contact with the substance in doses of approx. 5 g/kg/day (rabbits) show that effect is caused to the skin and that the substance can be absorbed through the skin with the consequent organ effects. Animal tests on rats exposed to repeated ingestion of high doses (10 %) indicate risks of organ effects to liver, kidneys and spleen (19). Lower doses showed no sign of such injuries.
Mutagenicity	Tests for mutagenicity showed no signs of this (11).
Carcinogenic	Animal tests on mice by exposing their skin to the substance dissolved in acetone solution showed no signs of skin cancer.
Reproductive toxicity	One investigation has been reported and there were no signs of reproductive toxicity (11).

7.2.3 Conclusion

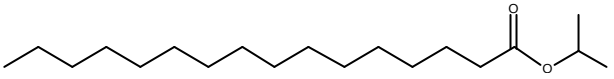
The substance may cause skin and eye irritation upon contact with quantities of 1- 5 g/kg. The available data shows that the substance can cause effects to skin and organs upon long-term skin contact. The substance shows no signs of sensitisation, mutagenicity, cancer or reproductive toxicity.

Isopropyl myristate is found in concentrations of between 1.2 and 37 mg/kg in 3 paper handkerchief products. The level corresponds to approx. 0.03 to 0.9 mg per packet of paper handkerchiefs.

7.3 Toxicological profile of isopropyl palmitate

7.3.1 Identification and physical-chemical properties

Identification

Chemical name	isopropyl palmitate
EINECS name	isopropyl palmitate
CAS no.	142-91-6
Molecular formula	$C_{19}H_{38}O_2$
Structural formula	

Applications

Isopropyl palmitate is used as a softener and emulsifier in cosmetics and hygiene products (19). The substance is also used in the chemical and metallurgical industries (19). The substance is contained as a balsam in paper handkerchiefs.

Synonyms
Selected synonyms for isopropyl palmitate are listed below:

- 1–methylethyl Hexadecanoate
- apicerol 2/014081
- bentone Gel LOI
- crodamol IPP
- deltyl
- deltyl Prime
- emcol IP
- emerest 2316
- estol 1517
- exceparl IPP
- hexadecanoic acid, isopropyl ester
- hexadecanoic acid, 1-methylethyl ester
- isopalm
- isopropyl hexadecanoate
- isopropyl Palmitate
- isopropylan
- lanalene
- lexol
- propal
- ritalan
- stepan D 70
- unimate IPP
- witconol 2316

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	entered on the list

Physical/chemical properties
The physical-chemical properties of isopropyl palmitate are shown in table 17.

Table 17. Physical-chemical properties of isopropyl palmitate.

Physical/chemical properties		Reference
Physical form	liquid	2
Molecular weight (g/mol)	298.51	10
Melting point (ºC)	13.5	10
Boiling point (ºC)	160	10

Vapour pressure (Pa)	0.0075	10
Specific weight (kg/L)	0.85	10
Log Kow	8.16	10
Water-solubility (mg/L)	0.00135	10

7.3.2 Toxicological properties

Acute toxicity

Inhalation	No data
Ingestion	LD50 for rats established at 5 g/kg (11)
Skin contact	Animal tests on mice and rabbits show effects at 5g/kg (19).
Irritation and corrosiveness	Animal tests on rabbits show minor skin and eye irritations when exposed to the substance; concentrations not available (11, 19)

Subacute/chronic toxicity

Allergy and hyper-sensitivity	No data
Organs	No data
Mutagenicity	No data
Carcinogenic	No data
Reproductive toxicity	No data

The substance may be compared with the substances 9-octadecenoic acid methyl ester (CAS no. 2462-84-2 and 112-62-9) – see section 7.4.

7.3.3 Conclusion

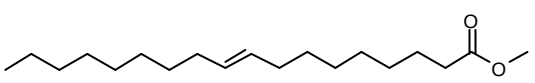
Only small amounts of data were found on the toxic effects. The data found indicate minor skin and eye irritation.

Isopropyl palmitate is found in 2 paper handkerchief products in concentrations of between 2.7 and 2300 mg/kg. The level corresponds to approx. 0.07 to 60 mg per packet of paper handkerchiefs. Presumably there is no risk at these concentrations.

7.4 Toxicological profile of 9-octadecenoic acid methyl ester

7.4.1 Identification and physical-chemical properties

Identification

Chemical name	9-octadecenoic methyl ester
EINECS name	methyl 9-octadecenoate
CAS no.	112-62-9 and 2462-84-2
Molecular formula	$C_{19}H_{36}O_2$
Structural formula	

Applications

The substance is used in the production of washing powder and cleaning materials as a surfactant, an emulsifier in cosmetics, a softener in printing, an additive to rubber and wax (15). The substance may be used as a softener in paper manufacture or form part of the cleaning process on recycled fibres.

Synonyms
The following synonyms are used for 9-octadecenoic acid methyl ester:

- methyl 9-octadecenoate
- methyl cis-9-octadecenoate
- methyl oleate
- 9-octadecenoic acid (Z)-, methyl ester
- oleic acid methyl ester

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	Dangerous for the environment (N;R51/53)
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	entered on the list

On the Danish EPA's guideline list for self-classification the substance is assessed as dangerous for the environment; toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (N;R51/53).

Physical/chemical properties
The physical-chemical properties of 9-octadecenoic acid methyl ester are shown in table 18.

Table 18. Physical-chemical properties of 9- octadecenoic acid methyl ester.

Physical/chemical properties	Data	Reference
Physical form	liquid	2
Molecular weight (g/mol)	296.49	2
Melting point (ºC)	-19.9	2
Boiling point (ºC)	218.5	2
Vapour pressure (Pa)	0.00084	10
Specific weight (kg/L)	0.87	2
Log Kow	7.45	10
Water-solubility (mg/L)	0.00184	10

7.4.2 Toxicological properties

Acute toxicity

Inhalation	No data
Ingestion	No data
Skin contact	No data
Irritation and corrosiveness	No data

Subacute/chronic toxicity

Allergy and hyper-sensitivity	No data
Organs	No data
Mutagenicity	No data
Carcinogenic	A single study reports skin cancer when tests were made on mice with the pure substance; concentration not available (17)
Reproductive toxicity	No data

7.4.3 Conclusion

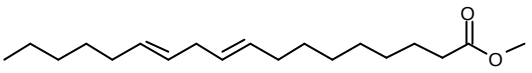
Only small amounts of data were found on the toxic effects. One study showed skin cancer when tested on mice. The possibility that the substance is carcinogenic cannot be excluded.

9-octadecenoic acid methyl ester was found in two toilet paper products in concentrations of between 15 and 33 mg/kg. The level corresponds to approx. 2.3 to 5 mg per roll of toilet paper.

7.5 Toxicological profile of 9,12-octadecadienoic acid methyl ester

7.5.1 Identification and physical-chemical properties

Identification

Chemical name	9,12-octadecadienoic acid methyl ester
EINECS name	methyl linoleate
CAS no.	112-63-0
Molecular formula	$C_{19}H_{34}O_2$
Structural formula	

Applications

The substance is used in the production of acetone, phenol and as a catalyst in polymerisation (15). The substance is thought to be used as an auxiliary substance with binding agents in paper manufacture.

Synonyms

The list below shows selected synonyms for 9,12-octadecadienoic acid methyl ester (12):

- Linoleic acid, methyl ester
- Methyl cis,cis-9,12-octadecadienoate
- Methyl 9-cis,12-cis-octadecadienoate
- Methyl linolate
- Methyl octadecadienoate
- Methyl octadecadienoate
- cis-9,cis-12-octadecadienoic acid methyl ester
- Cumen hydroperoxid

Regulation

EU classification	Not classified
Danish EPA guideline list for self-classification	Dangerous for the environment (N;R51/53)
Cosmetics executive order	Not regulated
Foodstuffs (the positive list, 2000)	Not on the positive list
Foodstuffs (the flavour list, 2002)	Entered on the list

On the Danish EPA's guideline list for self-classification of hazardous substances, 9,12-octadecadienoic acid methyl ester is assessed as dangerous for the environment; toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (N;R51/53).

Physical/chemical properties

The physical-chemical properties of 9,12-octadecadienoic acid methyl ester are shown in table 19.

Table 19. Physical-chemical properties of 9,12-octadecadienoic acid methyl ester.

Physical/chemical properties	Data	Reference
Physical form	Liquid	10
Molecular weight (g/mol)	294.47	11
Melting point (ºC)	-35	10
Boiling point (ºC)	215	10
Vapour pressure (Pa)	0.00049	10
Specific weight (kg/L)	0.888	11
Log Kow	6.82	10
Water-solubility (mg/L)	0.00288	10

7.5.2 Toxicological properties

Acute toxicity

Inhalation	The substance is moderately toxic upon inhalation (>10 % solution) (15).
Ingestion	The substance is moderately toxic upon ingestion (15). Ingestion (human) in concentrations of 3% has resulted in vomiting and gastritis. Human ingestion in concentrations of more than 35 % has led to serious injuries and death.
Skin contact	Hydrogen peroxide solutions in concentrations of 3 % and over are generally considered to be capable of causing skin and eye irritation. (15) There is no specific information on concentrations of this substance.
Irritation and corrosiveness	Exposure to concentrations of 10% and above can result in corrosion of skin and the respiratory passages.

Subacute/chronic toxicity

Allergy and hyper-	The substance can cause hypersensitivity upon

sensitivity	direct contact (15).
Organs	The substance can give rise to chronic effects upon contact with eyes or skin (15).
Mutagenicity	No data
Carcinogenic	No data
Reproductive toxicity	No data

7.5.3 Conclusion

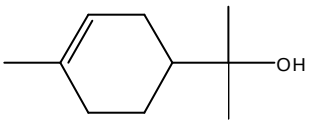
Only small amounts of data were found on the toxic effects of the substance. It can give rise to skin and eye irritations in concentrations of approx. 10 % and corrosion at higher concentrations. Moreover, the substance can result in hypersensitivity and permanent injuries upon repeated contact.

9,12-octadecadienoic acid methyl ester was found in two toilet paper products in concentrations between 12 and 29 mg/kg, which is considerably less than 10%. The level corresponds to approx. 1.8 to 4.4 mg per roll of toilet paper.

7.6 Toxicological profile of menthenol

7.6.1 Identification and physical-chemical properties

Identification

Chemical name	Menthenol
EINECS name	p-menth-1-en-8-ol
CAS no.	98-55-5
Molecular formula	$C_{10}H_{18}O$
Structural formula	

Applications

The substance is used as a fragrance in perfumes and as an additive in food. It occurs naturally in, for example, nectarines, and grape and cranberry juice, where 13 % is a-terpinol (11, 13, 15). It is believed that the substance is used as an aromatic together with menthol in paper handkerchiefs.

Synonyms

A numbers of synonyms are used for menthenol (12). of which a number have been selected here (12):

- alpha,alpha,4-trimethyl-3-cyclohexene-1-methanol
- p-menth-1-en-8-ol
- 1-p-menthen-8-ol
- 1-methyl-4-isopropyl-1-cyclohexen-8-ol
- 2-(4-methyl-3-cyclohexenyl)-2-propanol
- DL a-terpineol

Regulation

EU classification	Not classified

Danish EPA guideline list for self-classification	Not assessed
Cosmetics executive order	Not regulated
Foodstuffs (the positive list, 2000)	Not on the positive list
Foodstuffs (the flavour list, 2002)	entered on the list

Physical/chemical properties

The physical-chemical properties of menthenol are shown in table 20.

Table 20. Physical-chemical properties of menthenol

Physical/chemical properties	Data	Reference
Physical form	liquid	2
Molecular weight (g/mol)	154.25	10
Melting point (ºC)	34.5	2
Boiling point (ºC)	218	2
Vapour pressure (Pa)	5.64	10
Specific weight (kg/L)	0.93	2
Log Kow	2.98	10
Water-solubility (mg/L)	710	10

7.6.2 Toxicological properties

Acute toxicity

Inhalation	No data
Ingestion	LD50 for rats established at 2 -7 g/kg (11). Ingestion is assessed to cause the same effects as pine oil, i.e. effects on the central nervous system and gastritis (11, 15).
Skin contact	No data
Irritation and corrosiveness	The substance is comparable to pine oil which causes irritation to the eyes and mucous membranes (especially respiratory passages) in concentrations above 2 % (13, 15).

Subacute/chronic toxicity

Allergy and hyper-sensitivity	No data
Organs	No data
Mutagenicity	A single Ames test shows dose related effects on mice; other tests were negative (11)
Carcinogenic	No data
Reproductive toxicity	No data

7.6.3 Conclusion

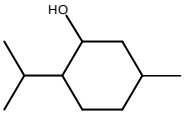
Only small amounts of data were found on the toxic effects of the substance. The substance is assessed as having the same effects as pine oil, which are irritation of the mucous membranes and eyes, and it effects the central nervous system and may cause gastritis.

Menthenol is found in one paper handkerchief product in concentrations between 4.4 and 7.6 mg/kg. The level corresponds to approx. 0.11 to 0.2 mg per packet of paper handkerchiefs.

7.7 Toxicological profile of menthol

7.7.1 Identification and physical-chemical properties

Identification

Chemical name	Menthol
EINECS name	Menthol
CAS no.	89-78-1
Molecular formula	$C_{10}H_{20}O$
Structural formula	

Applications

The substance is used as an aromatic in such products as tooth paste (0.5 %), mouth wash, cigarettes, cosmetics and chewing gum (11, 22). The substance is used to give aroma to paper handkerchiefs.

Synonyms

Selected synonyms for menthol are listed below:

- cyclohexanol, 2-isopropyl-5-methyl
- cyclohexanol, 5-methyl-2-(1-methylethyl)
- cyclohexanol, 5- methyl -2-(1- methylethyl)-, (1alpha,2beta,5alpha)
- headache-crystals
- hexahydrothymol
- p-menthan-3-ol
- 3-p-menthanol
- menthol, cis-1,3,trans-1,4
- (+-)-menthol
- 5-methyl -2-(1-methylethyl)cyclohexanol
- peppermint-camphor-
- racementhol

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	entered on the list

Physical/chemical properties

The physical-chemical properties of menthol are shown in table 21.

Table 21. Physical-chemical properties of menthol

Physical/chemical properties	Data	Reference
Physical form	solid substance	5

Molecular weight (g/mol)	156.27	10
Melting point (ºC)	35	10
Boiling point (ºC)	212	10
Vapour pressure (Pa)	14.67	10
Specific weight (kg/L)	0.89	2
Log Kow	3.4	10
Water-solubility (mg/L)	456	10

7.7.2 Toxicological properties

Acute toxicity

Inhalation	Reports indicate that exposure through inhalation (from menthol cigarettes) can give rise to mental irritation and irritation of the mucous membranes in people (11, 15).
Ingestion	LD50 for rats established at 3 -10 g/kg (11). The fatal human dose has been calculated at 50-500 mg/kg (15).
Skin contact	No data
Irritation and corrosiveness	Eye irritations upon direct contact with the substance when carried on the fingers and mild human skin irritations (11).

Subacute/chronic toxicity

Allergy and hyper-sensitivity	A report tells of incidences with cases where children have been treated with menthol (up to 2%) when they have had a cold. This gave allergic reations (11). Hypersensitivity in human beings has been reported to products containing menthol (including cigarettes)(15)
Organs	Chronic eye injuries have been confirmed in accidents where tooth paste has come into contact with the eyes, approx. 0,5 % (11).
Mutagenicity	Tests have shown no effects (30).
Carcinogenic	Animal tests have not shown effects (11, 17, 18, 22).
Reproductive toxicity	No data

7.7.3 Conclusion

Direct contact with the substance may have harmful effects on the skin and respiratory passages. Exposure to products containing menthol in concentrations of approx. 0.5 % has led to chronic eye effects. The substance causes skin irritations. Hypersensitivity has been reported.

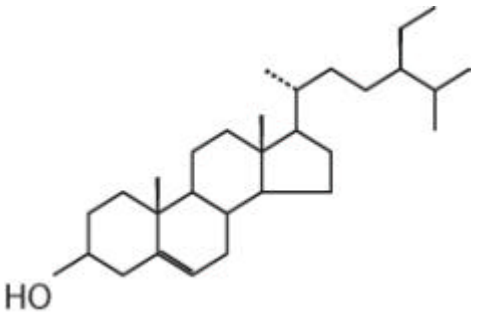
Menthol is found in 4 paper handkerchief products in concentrations of between 2.7 and 770 mg/kg, which correspond to a maximum of approx. 0.08 %. The level corresponds to approx. 0.07 to 19 mg per packet of paper handkerchiefs. This concentration is not expected to cause any problems as the concentration of menthol in the paper handkerchiefs is relatively low

compared to the concentration that can cause allergic reactions or other damages.

7.8 Toxicological profile of sitosterol

7.8.1 Identification and physical-chemical properties

Identification

Chemical name	Sitosterol
EINECS name	(3beta,24S)-stigmast-5-en-3-ol
CAS no.	83-47-6 and 83-46-5
Molecular formula	$C_{29}H_{50}O$
Structural formula	

Applications

Stigmasterols are plant sterols found in cocoa butter and soybeans. They are important raw materials in the industrial production of synthetic hormones(21). The substance is also used in the treatment of cancer (11). The substance may be used in paper goods as a softener (balsam) in the form of cocoa oil or soybean oil.

Synonyms

Selected synonyms for sitosterol are listed below:

- angelicin (steroid)
- azuprostat
- cinchol
- cupreol
- alpha-dihydrofucosterol
- delta 5-Stigmasten-3-beta-ol
- beta-sitosterin
- sobatum

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	not on the list

Physical/chemical properties

The physical-chemical properties of sitosterol are shown in table 22.

Table 22. Physical-chemical properties of sitosterol. (- no data was found)

Physical/chemical properties	Data	Reference
Physical form	-	
Molecular weight (g/mol)	414.72	10
Melting point (ºC)	147	10
Boiling point (ºC)	-	
Vapour pressure (Pa)	-	
Specific weight (kg/L)	-	
Log Kow	-	
Water-solubility (mg/L)	-	

7.8.2 Toxicological properties

Acute toxicity

Inhalation	Animal tests do not show effects (17).
Ingestion	Animal tests show no effects upon ingestion of 5 mg/kg and up to 25 g/kg (24).
Skin contact	Animal tests do not show effects (24).
Irritation and corrosiveness	Animal tests do not show effects (24).

Subacute/chronic toxicity

Allergy and hyper-sensitivity	Tests have shown no effects (23, 24).
Organs	Tests have shown no effects (23, 24).
Mutagenicity	No data
Cancer	Used as an anti-cancer drug (24).
Reproductive toxicity	No data

7.8.3 Conclusion

Toxic effects were not encountered among the available data. However, there is no data on mutagenicity or reproductive toxicity.

Sitosterol is found in one paper handkerchief product in concentrations of between 4.4 and 7.6 mg/kg. The level corresponds to approx. 0.1 to 0.2 mg per packet of paper handkerchiefs.

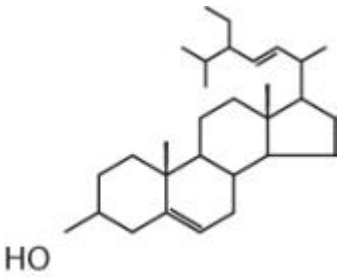
7.9 Toxicological profile for stigmast-4-en-3-one

7.9.1 Identification and physical-chemical properties

Identification

Chemical name	stigmast-4-en-3-one
EINECS name	not registered in EINECS
CAS no.	1058-61-3
Molecular formula	not known

Structural formula



Applications
Stigmasterols are plant sterols found in cocoa butter and soybeans. They are important raw materials in the industrial production of synthetic hormones (21). The substance may be used as a softener in paper articles or occur as a contaminant possibly in combination with other auxiliary substances.

Synonyms
No synonyms were found for stigmast-4-en-3-one.

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	not on the list

Physical/chemical properties
No data was found on the physical-chemical properties of this substance.

7.9.2 Toxicological properties

No data was found for stigmast-4-en-3-one.

7.9.3 Conclusion

The substance is assessed as comparable to other sterols (see section 7.8). No data has been found for sterols that indicates toxic effects. However, there is no data concerning mutagenicity and reproductive toxicity.

Stigmast-4-en-3-one is found in one toilet paper product in concentrations of 5 to 7.8 mg/kg. The level corresponds to approx. 0.8 to 1.2 mg per roll of toilet paper.

7.10 Toxicological profile of squalene

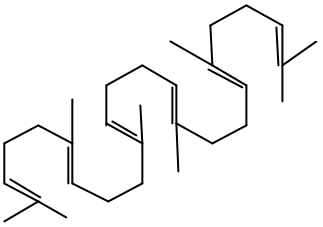
7.10.1 Identification and physical-chemical properties

Identification

Chemical name	Squalene
EINECS name	2,6,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexaene
CAS no.	111-02-4
Molecular	$C_{30}H_{50}$

formula

Structural formula



Applications

The substance is used in biochemical and pharmaceutical research and production of medicinal goods, organic dyes, rubber, aromatics and surfactants. It occurs naturally in shark oil and human sebum. The substance is used as an alternative medicine. Triterpene squalene (CAS no. 7683-64-9) occurs in concentrations of up to 0.5 % in olive oil. At present, the substance may occur as a contaminant in other raw materials used in paper goods or it can be added as a surfactant in paper manufacturing cleaning processes.

Synonyms

The following synonyms are used for squalene (12):

- 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene
- hexamethyltetracosahexaene
- spinacene
- trans-spinacene
- (E,E,E,E)-squalene
- all-trans-squalene
- trans-squalene
- supraene

Regulation

EU classification	not classified
Danish EPA guideline list for self-classification	not assessed
Cosmetics executive order	not regulated
Foodstuffs (the positive list, 2000)	not on the positive list
Foodstuffs (the flavour list, 2002)	not on the list
List of alternative medicines approved for sale	not on the list

Physical/chemical properties

The physical-chemical properties of squalene are shown in table 23.

Table 23. Physical-chemical properties of squalene (- no data was found)

Physical/chemical properties		Reference
Physical form	liquid	2
Molecular weight (g/mol)	410.725	2

Melting point (ºC)	-75	2
Boiling point (ºC)	285	2
Vapour pressure (Pa)	-	
Specific weight (kg/L)	0.858	2
Log Kow	14.12	10
Water-solubility (mg/L)	-	

7.10.2 Toxicological properties

Acute toxicity

Inhalation	No data
Ingestion	LD50 for rats established at 5 g/kg (22)
Skin contact	No data
Irritation and corrosiveness	No data

Subacute/chronic toxicity

Allergy and hyper-sensitivity	No data
Organs	No data
Mutagenicity	No data
Cancer	No data
Reproductive toxicity	No data

Squalene is one of the triterpenes, also denominated steroids. This same group includes hormones such as testosterone, cortisone, cholesterin, oestradiol and progesterone (29). The molecular form of these substances varies but they have structural similarities.

7.10.3 Conclusion

Data concerning the toxic effects of this substance is extremely sparse. The substance is assessed as producing hormone-like effects, as it is a steroid and it has structural similarities to hormones.

The substance is found in 5 toilet paper products and 4 paper handkerchief products. Concentrations of between 2.4 and 51 mg/kg in toilet paper and between 1.7 and 33 mg/kg in paper handkerchiefs have been found. The level corresponds to approx. 0.4 to 7.7 mg per roll of toilet paper, and to approx. 0.01 to 0.8 mg per packet of paper handkerchiefs.

8 Literature

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