Survey of chemicals in consumer products

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Survey of chemical compounds in textile fabrics

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Contents

| D | DANISH PREFACE | 5 |
|---|---|--|
| D | DANISH SUMMARY AND CONCLUSIONS | 7 |
| E | NGLISH PREFACE | 11 |
| E | NGLISH SUMMARY AND CONCLUSIONS | 13 |
| 1 | BACKGROUND | 17 |
| 2 | PURPOSE | 19 |
| 3 | SELECTION OF PRODUCTS | 21 |
| | 3.1 DESCRIPTION OF TEXTILE FABRICS3.2 COMMON CONSUMER HANDLING OF THE TEXTILE FABRICS3.3 OVERVIEW OF PURCHASED FABRICS FOR TESTING | 21 21 21 |
| 4 | SELECTION OF TESTS | 23 |
| | 4.1 Test programme 4.2 Selection of tests 4.3 Test methods 4.3.1 Test for selected organic compounds – testgroup A and D 4.3.2 Test for selected aromatic amines – testgroup C 4.3.3 Test for organic tin compounds – testgroup E 4.3.4 Test for heavy metals – testgroup G 4.3.5 Test for free formaldehyde 4.3.6 Test for extractable antimony (artificial saliva and perspiration) | 23 23 25 25 26 26 27 27 |
| 5 | RESULTS | 29 |
| | 5.1 SELECTED ORGANIC COMPOUNDS 5.2 AROMATIC AMINES 5.3 NONYL PHENOL ETHOXYLATES 5.4 SELECTED ORGANIC TIN COMPOUNDS 5.5 SELECTED HEAVY METALS 5.5.1 Extractable antimony (artificial saliva and perspiration) 5.6 FORMALDEHYDE 5.7 SCREENING | 29 30 31 31 32 34 34 35 |
| 6 | PRINCIPLES FOR HEALTH ASSESSMENT | 38 |
| | 6.1 Introduction6.2 Assessment scenarios6.3 Dermal exposure6.4 Oral intake6.5 Inhalation | 38 39 39 41 41 |
| 7 | EVALUATION OF ORGANIC SUBSTANCES | 44 |
| | 7.1 BIS(ETHYLHEXYL)-PHTHALATE (DEHP) 7.1.1 Identification 7.1.2 Health | 44 44 45 |

| | 7.1.3 Evaluation | 46 |
|---|--|---|
| | 7.2 4-CHLORANILINE | 48 |
| | 7.2.1 Identification | 48 |
| | 7.2.2 Health | 49 |
| | 7.2.3 Evaluation | 50 |
| | 7.3 FORMALDEHYDE | 51 |
| | 7.3.1 Identification | 51 |
| | 7.3.2 Health | 53 |
| | 7.3.3 Evaluation | 54 |
| | 7.4 NAPHTHALENE | 55 |
| | 7.4.1 Identification | 55 55 |
| | 7.4.2 Health | |
| | | 57 |
| | 7.4.3 Bioavailability | 58 |
| | 7.4.4 Evaluation | 58 |
| | 7.5 NICOTINE | 60 |
| | 7.5.1 Identification | 60 |
| | 7.5.2 Health | 61 |
| | 7.5.3 Evaluation | 62 |
| | 7.6 NONYLPHENOL / NONYLPHENOL ETHOXYLATE | 63 |
| | 7.6.1 Nonylphenol ethoxylate | 63 |
| | 7.6.2 Nonylphenol | 65 |
| | 7.6.3 Health | 66 |
| | 7.6.4 Evaluation | 67 |
| | 7.7 O-TOLUIDINE | 69 |
| | 7.7.1 Identification | 69 |
| | 7.7.2 Health | 70 |
| | 7.7.3 Evaluation | 71 |
| | 7.8 SUMMARY OF CONCLUSIONS | 72 |
| | | |
| 8 | | |
| 8 | EVALUATION OF METALS | 75 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY | 75 76 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification | 75 76 76 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health | 75 76 76 76 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation | 75 76 76 76 77 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC | 75 76 76 76 77 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification | 75 76 76 76 77 80 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health | 75 76 76 76 77 80 80 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation | 75 76 76 76 77 80 80 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM | 75 76 76 76 77 80 80 80 80 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation | 75 76 76 76 77 80 80 80 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health | 75 76 76 76 77 80 80 80 80 82 82 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification | 75 76 76 76 77 80 80 80 80 82 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health | 75 76 76 76 77 80 80 80 80 82 82 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation | 75 76 76 76 77 80 80 80 80 82 82 82 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM | 75 76 76 76 77 80 80 80 80 82 82 82 82 82 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification | 75 76 76 76 77 80 80 80 80 82 82 82 82 82 84 84 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation | 75 76 76 76 77 80 80 80 80 82 82 82 82 84 84 84 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation 8.5 CHROMIUM | 75 76 76 76 77 80 80 80 80 82 82 82 82 82 82 82 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation 8.5 CHROMIUM 8.5.1 Identification | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 82 84 84 84 85 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 82 86 86 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 82 82 86 86 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.4.3 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation 8.6 COBALT | 75 76 76 76 77 80 80 80 80 82 82 82 82 82 82 86 86 86 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.5.1 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation 8.6 COBALT 8.6.1 Identification | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 82 84 84 84 85 86 86 86 86 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.5.1 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation 8.6 COBALT 8.6.1 Identification 8.6.2 Health | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 84 84 84 85 86 86 86 86 89 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.5.1 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation 8.6 COBALT 8.6.1 Identification 8.6.2 Health 8.6.3 Evaluation | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 84 84 84 84 85 86 86 86 86 89 89 |
| 8 | EVALUATION OF METALS 8.1 ANTIMONY 8.1.1 Identification 8.1.2 Health 8.1.3 Evaluation 8.2 ARSENIC 8.2.1 Identification 8.2.2 Health 8.2.3 Evaluation 8.3 BARIUM 8.3.1 Identification 8.3.2 Health 8.3.3 Evaluation 8.4 CADMIUM 8.4.1 Identification 8.4.2 Health 8.5.1 Evaluation 8.5 CHROMIUM 8.5.1 Identification 8.5.2 Health 8.5.3 Evaluation 8.6 COBALT 8.6.1 Identification 8.6.2 Health | 75 76 76 76 76 77 80 80 80 80 82 82 82 82 82 84 84 84 85 86 86 86 86 89 |

| 8.7.2 Health | 91 |
|--|---|
| 8.7.3 Evaluation | 92 |
| 8.8 Lead | 93 |
| 8.8.1 Identification | 93 |
| 8.8.2 Health | 94 |
| 8.8.3 Evaluation | 94 |
| 8.9 Mercury | 95 |
| 8.9.1 Identification | 95 |
| 8.9.2 Health | 96 |
| 8.9.3 Evaluation | 97 |
| 8.10 NICKEL | 98 |
| 8.10.1 Identification | 98 |
| 8.10.2 Health | 99 |
| 8.10.3 Evaluation | 99 |
| 8.11 TIN | 100 |
| 8.11.1 Identification | 100 |
| 8.11.2 Health | 101 |
| 8.11.3 Evaluation | 101 |
| | 103 |
| 8.12 Summary | 102 |
| 8.12 SUMMARY 9 SCREENING | 102 101 |
| | |
| 9 SCREENING | 101 |
| 9 SCREENING 9.1 SPECIFIC COMPOUNDS | 101 101 |
| 9 SCREENING 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol | 101 101 101 |
| 9 SCREENING 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol | 101 101 <i>101</i> 102 |
| 9 SCREENING 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol | 101 101 101 102 103 |
| 9 SCREENING 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate | 101 101 101 102 103 103 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural | 101 101 101 102 103 103 104 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate | 101 101 101 102 103 103 104 104 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate 9.1.7 Squalene | 101 101 102 103 103 104 104 105 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate 9.1.7 Squalene 9.2 SUBSTANCE GROUPS 9.2.1 Hydrocarbons 9.2.2 Fatty acids | 101 101 102 103 103 104 104 105 105 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate 9.1.7 Squalene 9.2 SUBSTANCE GROUPS 9.2.1 Hydrocarbons 9.2.2 Fatty acids 9.2.3 Aliphatic alcohols | 101 101 101 102 103 103 104 104 105 105 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate 9.1.7 Squalene 9.2 SUBSTANCE GROUPS 9.2.1 Hydrocarbons 9.2.2 Fatty acids 9.2.3 Aliphatic alcohols 9.2.4 Aliphatic amides | 101 101 101 102 103 103 104 104 105 105 105 |
| 9.1 SPECIFIC COMPOUNDS 9.1.1 2,2'-oxybis ethanol 9.1.2 2-(2-butoxylethoxy)ethanol 9.1.3 Propylenglycol 9.1.4 Benzyl benzoate 9.1.5 5-hydroxyl-methylfurfural 9.1.6 bis(2-ethylhexyl)maleate 9.1.7 Squalene 9.2 SUBSTANCE GROUPS 9.2.1 Hydrocarbons 9.2.2 Fatty acids 9.2.3 Aliphatic alcohols | 101 101 102 103 103 104 104 105 105 106 106 |

Danish preface

Nærværende rapport sammenfatter resultaterne af projektet "Kortlægning af kemiske stoffer i tekstilmetervarer" (J. nr. M 7041-0542), som er foretaget for Miljøstyrelsen på baggrund af Miljøstyrelsens udbud af maj 2002.

Kortlægningen er en del af en særlig indsats for kortlægning af kemiske stoffer i forbrugerprodukter, bevilliget i finansloven.

Projektet er gennemført af Teknologisk Institut ved centrene Beklædning og Textil, Kemiteknik samt Miljø- og Affaldsteknik. Projektet har ikke haft en styregruppe tilknyttet; men underdirektør Aage K. Feddersen fra brancheforeningen Dansk Textil & Beklædning har været rådspurgt om projektafgræsningen (valg af tekstilmetervarer og analyseprogram). Brancheforeningen og forhandlere af indkøbte tekstilvarer har endvidere haft mulighed for at kommentere rapporten ved en høringsrunde.

Danish summary and conclusions

Der er i samråd med Miljøstyrelsen og brancheforeningen Dansk Textil & Beklædning udvalgt i alt 20 tekstilmetervarer, for hvilke der er foretaget analyser af indholdet af en række kemiske stoffer. Der er ved valget af produkter sigtet mod en så bred dækning af fibertyper og varetyper som muligt.

Tekstilmetervarerne er indkøbt i 6 forskellige forretninger i København og omegn.

De udvalgte tekstilvarer er analyseret specifikt for en række kemikalier:

- de organiske stoffer / stofgrupper nicotin, naphthalen, o-chlorphenol, C3-C4-alkylbenzener, tetrachlorethylen, nitrobenzen, DEHP (bis(2-ethylhexyl)phthalat) og formaldehyd
- 26 forskellige aromatiske aminer
- nonylphenolethoxylater
- organiske tinforbindelser
- tungmetallerne arsen, barium, cadmium, cobalt, chrom, kobber, kviksølv, nikkel, bly, antimon og tin

Analysebudgettet gav ikke mulighed for at analysere for alle stoffer for alle tekstilvarer. Ved fordelingen af analyser på de enkelte tekstilvarer er det tilstræbt, at få en så bred dækning af relevante analyser på fibertyper og varetyper som muligt.

Endvidere er der udført en kvalitativ screening for andre stoffer eller stofgrupper for 10 af de 20 tekstilvarer.

Der er desuden gennemført supplerende undersøgelser vedr. spyt- og svedekstraherbart antimon for 2 af tekstilmetervarerne indeholdende polyester og 4 beklædningstekstiler indeholdende 100% polyester. Beklædningstekstilerne er indkøbt i 3 forskellige forretninger i København og omegn.

Supplerende undersøgelser blev også gennemført for de tekstilmetervarer, hvor der blev fundet det største indhold af formaldehyd. Der blev foretaget en enkelt vask for at afklare, hvor meget indflydelse 1. gangs vask har på indholdet af formaldehyd.

Der er foretaget en sundhedsmæssig vurdering af de fundne kemiske stoffer med hensyn til potentielle risici ved indtagelse, ved indånding og ved hudpåvirkning. Vurderingerne er som udgangspunkt gennemført efter "worst case" princippet.

Blandt de organiske stoffer blev der i tekstilprøverne påvist nicotin, naphthalen, DEHP, formaldehyd, nonylphenolethoxylater samt 2 aromatiske aminer (4-chloroanlin og o-toluidin).

Aromatiske aminer blev fundet i 2 prøver i en mængde på omkring 3 gange detektionsgrænsen. De to aromatiske aminer er kræftfremkaldende, og tilstedeværelsen i selv små mængder må derfor anses som problematisk. De målte koncentrationer er dog væsentlig under de niveauer der i øjeblikket anses at udgøre en sundhedsmæssig risiko.

For de øvrige organiske stoffer anses der ikke at være nogen sundhedsmæssige risici i de fundne koncentrationer. For formaldehyd dog med den bemærkning at tilstedeværelsen af fri formaldehyd i ganske små koncentrationer kan være et problem for personer, der allerede er allergiske. De udførte vaskeforsøg viser, at der ved 1. gangs vask opnås en betydelig reduktion i den mængde af fri formaldehyd, der afgives fra tekstilerne.

Der blev påvist følgende tungmetaller i nogle af tekstilprøverne: Antimon, arsen, barium, bly, chrom, cobalt, kobber, nikkel og tin.

Generelt gælder det for flere af de ovenfor nævnte tungmetaller (arsen, chrom, kobber og tin), at de specielt er vurderet problematiske i det opstillede scenarie, der omfatter oral indtagelse. Det skal bemærkes, at der er anvendt et "worst case" scenarie, som omfatter en eksponering, hvor et barn putter tekstilet i munden og tygger på det. Det er forudsat, at alt kemisk stof optages i de % satser, der er anført under de enkelte metaller, dvs. en oral optagelse varierende fra 25-100%.

Optagelsen af et af metallerne (antimon) blev testet yderligere for at vurdere frigivelsen til spyt under en times ekstraktion med kunstigt spyt. Det blev fundet, at frigivelsen var meget lille (under detektionsgrænsen). Der er ikke foretaget lignende studier med de øvrige metaller. Med muligheden for en meget lav frigivelse fra tekstilet kan det derfor ikke udelukkes, at der ikke er et reelt sundhedsmæssigt problem.

Eksponeringsscenariet har da også netop været anvendt for at påvise, om der kunne være et problem, der burde undersøges nærmere, hvilket synes at være tilfældet for de nævnte metaller.

For arsen gælder det, at hvis man anvender de forudsætninger, som angivet ovenfor, kan det konkluderes, at der kan være sundhedsmæssige risici forbundet med oral indtagelse (tygning) af tekstiler med koncentrationer under detektionsgrænsen på 1 mg/kg. Det vil sige, at tygning af 20 gram tekstil om dagen giver en overskridelse af acceptabel daglig indtagelse. Giftigheden afhænger dog af den anvendte arsenforbindelse. Indånding og hudpåvirkning giver ingen sundhedsmæssige risici.

For chrom, som er fundet i to prøver, konkluderes det med hensyn til indtagelse, at såfremt chrom optræder i oxidationstrin VI, vil der være en betydelig sundhedsmæssig risiko. Hvis chrom optræder i oxidationstrin III, er der ingen nævneværdig risiko. Ved indånding og hudpåvirkning er der ingen sundhedsmæssige risici. Allergi eller overfølsomhedsreaktioner er dog ikke vurderet i forbindelse med hudpåvirkning.

For cobalt, som er fundet i 4 prøver, konkluderes det for indtagelse, at der er en betydelig sundhedsmæssig risiko for 2 af prøverne, og nogen risiko for de 2 andre. Ved indånding og hudpåvirkning er der ingen sundhedsmæssige risici.

Kobber er fundet i 10 prøver, og det konkluderes med hensyn til indtagelse og indånding, at der er sundhedsmæssig risiko for de 2 prøver med de højeste

koncentrationer, men ikke for de øvrige 8. Der er heller ingen sundhedsmæssig risiko i forbindelse med hudpåvirkning.

Tin er fundet i en enkelt prøve, hvor det konkluderes, at der er sundhedsmæssig risiko ved indtagelse.

Hvad angår barium, bly og nikkel konkluderes det, at der ikke anses at være nogen sundhedsmæssige risici i de fundne koncentrationer.

Med hensyn til antimon konkluderes det på baggrund af de supplerende undersøgelser vedr. spyt- og svedekstraherbart antimon, at der ikke anses at være nogen sundhedsmæssige risici i de fundne koncentrationer.

Den kvalitative screening gav anledning til følgende konklusioner:

- der er påvist to glycoler, som er farlige ved indtagelse af det rene kemikalie
- der er påvist kortkædede hydrocarboner, som er sundhedsskadelige
- der er påvist alifatiske alkoholer, hvoraf nogle kan være meget giftige

Da der ikke er udført kvantitative analyser på disse stoffer og stofgrupper, kan der ikke siges noget mere konkret om sundshedsrisikoen for de aktuelle tekstilprøver.

English preface

This report presents the results of the project "Survey of chemicals compounds in textile fabrics" (J. no. M 7041-0542). The project has been carried out with support from the Danish Environmental Protection Agency (DEPA) and based on a tender from DEPA May 2002.

The survey is part of a special Danish government funded effort regarding survey of chemicals in consumer products.

The project has been carried out by the Danish Technological Institute – the sections Clothing and Textile, Chemical Technology and Environmental and Waste Technology. The project has not been followed by a Steering Committee, however deputy director Mr. Aage K. Feddersen from the Federation of Danish Textile and Clothing Industries has been consulted regarding the scope of the project (selection of textile fabrics and tests). Furthermore the Federation and suppliers of textile fabrics have commented on the results in connection with a hearing.

English summary and conclusions

In collaboration with the Danish Environmental Protection Agency and the Federation of Danish Textile and Clothing Industries 20 textile fabrics were selected. The fabrics were tested for a number of different chemical compounds. In the selection of the fabrics the aim was to cover as many different types of fibres and type of fabrics as possible.

The fabrics were purchased in 6 different shops in Copenhagen and environs.

The selected fabrics were analysed specifically for a number of compounds:

- the organic compounds nicotine, naphthalene, o-chlorophenole, C3-C4-alkylbezenes, tetrachlorethylene, nitrobenzene, DEHP (bis(2-ehylhexyle)phthalate) and formaldehyde
- 26 different aromatic amines
- nonyl phenol ethoxylates
- organic tin compounds
- the heavy metals arsenic, barium, cadmium, cobalt, chromium, copper, mercury, nickel, lead, antimony and tin.

The budget for analysis was not sufficient to test for all compounds in all fabrics. In the selection of tests for the specific fabrics the aim was to cover as many different relevant test on the type of fibres and fabrics as possible.

In addition a qualitative screening for other compounds or group of compounds was done for 10 of the 20 fabrics.

Furthermore supplementary studies concerning extractable antimony (artificial saliva and perspiration) were done for two of the fabric containing polyester and 4 apparel textiles containing 100% polyester. The apparel textiles were purchased in 3 different shops in Copenhagen and environs.

Supplementary studies were also done on the fabrics containing the highest concentration of free formaldehyde. The fabrics were washed once to determine the influence on the amount of free formaldehyde.

The potential effects on health of the detected chemical compounds have been evaluated with respect to oral exposure (putting the textile in the mouth), inhalation and dermal exposure (skin contact). The health assessments have been done according to the worst case principle.

Among the organic compounds nicotine, naphthalene, DEHP, formaldehyde, nonyl phenol ethoxylates and 2 aromatic amines (4-chloroanline and otoluidine) were found in the textiles.

Aromatic amines were found in two samples in amounts approximately 3 times the limit of detection. The two aromatic amines are carcinogenic, and the presence even in small amounts is problematic. However, the measured amounts are far below the levels currently regarded as representing a health risk.

Regarding the other detected organic compounds no health risk is expected at the measured concentrations. However regarding formaldehyde with the remark that the presence of free formaldehyde even in small amounts may be problematic for persons already allergic. The laundry trials show that after the 1. laundry the amount of free formaldehyde is significantly reduced.

The following heavy metals were found in the fabrics: Antimony, arsenic, barium, lead, chromium, cobalt, copper, nickel and tin.

In general, it was observed that for some of the above mentioned metals (arsenic, chromium, copper and tin) they may cause a health problem using the suggested scenario on oral intake. However, it should be noted that a "worst case" scenario has been used. The oral scenario consists of an exposure where a child puts the textile in the mount and chews/sucks on it. It is presumed that all chemical substance is absorbed at the percentages found for each metal, i.e varying from 25% to 100%.

The absorption of one metal (antimony) was tested further to assess the release to saliva during one-hour extraction in artificial saliva. It was observed that the release was insignificant, i.e. below the detection limit. No such studies have been performed for the remaining metals. At the possibility of a very low release of metals from the textile, it can not be excluded that the potential health problem is non-existing.

However, the purpose of the suggested exposure scenario was to detect areas of potential health problems to be studied further. This appears to be the situation for the mentioned metals.

For arsenic it is concluded using the presumptions mentioned above that oral intake of arsenic (by chewing) even at concentrations below the detection limit of 1mg/kg may cause concern. This means that chewing on 20 g textile per day may result in an exceeding of the acceptable daily intake. However, the toxicity depends on the specific compund. Inhalation of arsenic containing dust or skin contact to textiles are not considered as a health risk according to the scenario used.

Regarding chromium it is concluded that if the chromium consists of chromium(VI), there may be a health risk by oral intake for the two fabric with the highest concentration of total chromium. In case a significant part of the chromium is chromium(III) there will be no immediate health risk. Inhalation of chromium containing textile dust is not considered a health risk and the same applies to skin contact of textiles at the measured concentrations of chromium. No information has been recovered on the levels necessary to exclude possible allergy at skin contact. The level is individual and depending on sensitisation of the exposed person.

In 5 samples, cobalt was measured above the detection limit of 0.2 mg/kg, in two samples the cobalt concentration was approx. 40 mg/kg. A significant health risk regarding oral intake is expected for the samples containing cobalt concentrations above the detection limit. Regarding inhalation of textile dust no health risk is expected under the conditions used. The same applies to dermal absorption. However, a potential for allergy or sensitisation can not be excluded.

In two fabrics, relative high concentrations of copper were measured. For these two samples there may be a health risk by oral intake and inhalation while there was expected no health risks from the remaining textiles. Regarding dermal uptake by skin contact no health risk is expected at the measured concentrations.

Of the four analysed samples only one contained concentration above the detection limit. The measured concentration of tin in the sample may cause a health risk by oral intake. Oral intake by the remaining textiles, inhalation and skin contacts by all samples is not considered to present any health risk to consumers at the measured concentrations.

Regarding barium, lead and nickel no health risk is expected at the measured concentrations.

Concerning antimony a variety of concentrations up to 200 mg/kg were measured in textiles consisting of or containing PET. Because of the results from the first estimates a further refinement was decided. The study on migration of antimony in artificial perspiration showed that up to 10% of antimony was able to migrate from the textile into the liquid. In migration studies using artificial saliva, antimony did not migrate from the textile to an extent where it resulted in concentrations above the detection level of 0.5 mg/kg textile. Therefore no health problems are expected from the textiles at the measured concentrations. It is therefore concluded that there is no immediate health risks expected in relation to the measured concentrations of antimony.

The following conclusions can be drawn from the qualitative screening:

- Two glycol's harmful if swallowed were identified (for the pure chemical).
- Several short-chained hydrocarbons were identified. Short-chained hydrocarbons are considered health hazardous.
- Several aliphatic alcohol's were identified, some may be toxic.

Because no quantitative analysis were performed for these compounds and group of compounds a more detailed evaluation could not be done.

1 Background

Increasing focus has been put on the chemicals the consumers are exposed to in everyday life. Chemical compounds with undesirable effect have been found in several studies in common products on the consumer marked. DEPA has therefore initiated a survey of chemicals in consumer products – including a survey of chemicals in textile fabrics.

DTI has extensive experience working with the industry, knowledge about textile products, testing for chemical compounds in textiles as well as environmental and health assessment of chemical compounds.

<u>DTI Clothing and Textile</u> has been involved in several environmental projects focussed on the clothing and textile industry in the last 10 years (including the project "Chemicals in textiles"). Furthermore DTI Clothing and Textile has tested and certified numerous different textile products according to the private textile label Oeko-Tex Standard 100.

<u>DTI Chemical Technology</u> is accredited by DANAK to test soil, water and several materials for many different organic compounds and heavy metals. In addition DTI Chemical Technology carries out all relevant Oeko-Tex Standard 100 tests.

<u>DTI Environmental and Waste Technology</u> was involved in the development of the Danish UPH - screeningsystem. However experience has demonstrated that this kind of screening is very rough and the applicability limited in risk assessments.

Continuously DTI Environmental and Waste Technology is working with environmental and health assessment of chemical compounds partly in connection with the working environment and partly in connection with risk assessment for DEPA.

2 Purpose

- To test selected textiles for selected chemical compounds.
- To assess whether the detected compounds in the detected amounts are hazardous to human health.

3 Selection of products

3.1 DESCRIPTION OF TEXTILE FABRICS

Table 3.1 presents an overview of the type of textile products covered by the project and a description of the products – including the type of fibres.

TABLE 3.1 TYPE OF TEXTILE FABRICS COVERED BY THE PROJECT

| Fabrics for | Description |
|--------------------------|--|
| Clothing | Very large group. Primarily cotton, wool, viscose (and modal), polyester and nylon. To a certain extent also acrylics. Furthermore also silk, acetate and polypropylene (silk, acetate and polypropylene (among other things in linning). For linning primarily polyester, but viscose, nylon and acetate are also relevant. Shrink resist treatments are widely used in connection with natural fibres and regenerated fibres (e.g. viscose). |
| Curtains | Primarily cotton and polyester and blends. To a lesser extent acrylics, viscose, wool and polychloride (PVC-special fibre). |
| Table cloths | Primarily 100% cotton. To a lesser extent blends with polyester, acrylics and flax. Fabrics that have been treated with chemicals in order to make the product seem smooth and easy to maintain are very common. Shrink resist treatments are also widely used. |
| Upholstery | Making up is rarely done by the consumer in connection with coverings for |
| (furniture) and cushions | furniture. In case wool, cotton and blends with polyester are used. Making up is more common in connection with cushions. In case coverings are primarily made of cotton and blends with polyester. |
| Dinner napkins | Rarely done by the consumer. Primarily cotton and blends with polyester. |
| Bed linen and bedspreads | Rarely done by the consumer. In case primarily cotton and to a lesser extent blends with polyester. |

3.2 COMMON CONSUMER HANDLING OF THE TEXTILE FABRICS

In general making up is done more or less in the same manner by the consumer independent of the type of fabrics. Typically the consumer will do the cutting and sewing by themselves. Ironing and pressing before use are also common however not in connection with fabric made of synthetic fibre like polyester and nylon.

In most cases the finish product is not washed before use. In general washing trials are therefore estimated not to be relevant because the aim is to evaluate the health aspect in connection with common consumer handling of the fabrics. In addition by omitting washing trials before testing a "worst case" scenario is obtained.

However a few washing trials where done in order to determine, how much free formaldehyde is washed out during the first laundry.

3.3 Overview of purchased fabrics for testing

Table 3.2 presents an overview of purchased fabrics. In the column "Used for" the information given by the assistants in the stores are listed.

TABLE 3.2 OVERVIEW OF PURCHASED FABRICS FOR TESTING

| | PURCHASED FABRICS FOR TESTING | |
|------------------------------------|---|---|
| Sample no. | Description | Used for |
| A) Nylon, flowers | 100 % nylon, knitted, printed, flower design / red (several shades) / brown / black | Apparel (i.a. blouses) |
| B) 100 % cotton, yellow | 100 % cotton, woven, printed, flowers / leaves | Bed linen / cushions / |
| (children) | design, yellow (primarily) / red (several shades) / blue (several shades) / green (several shades) / orange / brown | clothing (i.a. trousers / shirts) for CHILDREN |
| C) Acrylic / nylon | 85 % acrylic / 15% nylon, knitted, printed, flower / dotted design, red / green / brown / black | Apparel (i.a. trousers. / blouses / shirts / skirts) |
| D) 100% cotton (blue) | 100% cotton, woven, dyied, dark blue | Cloths |
| E) Cotton/PET brown | 60 % cotton / 40% polyester, woven, brown | Curtains / upholstery |
| F) 100% PET (colorful) | 100 % polyester, woven, printed, Asiatic design, red / blue/ yellow / grey/ brown | Apparel (i.a dresses, skirts) |
| G) 100 % cotton (animal motive) | 100 % cotton, woven, printed, animal design, red (several shades) / yellow / brown / green / white / black | Bed linen / cushions / apparel (i.a. shirts, dresses, shirts) for CHILDREN |
| H) 100 % PET (white) | 100% PET, woven, white (bleached) | Curtains |
| I) 100 % cotton (flowers) | 100% cotton, woven, printed, flower design, red (several shades) / purple / green / light and dark beige. | Curtains |
| J) 100% flax | 100% flax, woven, printed, red w. small white patterns | Apparel (i.a. dresses) |
| K) Pet/wool | 55% polyester / 45 % wool, woven, light green | Apparel (i.a. trousers) |
| L) 100% viscose | 100 % viscose, woven, printed, leopard / giraffe design, brown / black | Apparel (i.a. blouses and skirts) |
| M) 100% wool | 100% wool, woven, printed, check pattern, green / black / white. | Apparel (i.a. skirts, jackets, trousers) |
| N) 100 % cotton (Versace) | 100% cotton, woven, printed, black and white stripes/ yellow (Versace logo) | Apparel (i.a. jackets, trousers) |
| O) 100 % cotton (bear) | 100% cotton, knitted, printed, bear design, grey / black / white | Apparel (i.a. blouses) for children |
| P) 100 % wool (furniture) | 100% wool, woven, brown | Upholstery |
| Q) 100 % cotton (oilcloth) | 100 % cotton w. wax (easy to maintain) | Cloths |
| R) Cotton/pet (napkins) | 67% cotton / 33% polyester, flower design woven, white / green / red | Dinner napkins |
| S) 100% pet (cloth) | 100% polyester, knitted, dyied, blue | Cloths |
| T) 100% pet (cushion) | 100 % polyester, woven, printed, green / white pattern | Cushions |

In the selection of the fabrics the aim was to cover as many different types of fibres and type of fabrics as possible.

The fabrics were purchased in 6 different shops in Copenhagen and environs.

Table 3.3 presents an overview of purchased finished products for supplementary studies regarding extractable antimony (artificial saliva and perspiration). The apparel textiles were purchased in 3 different shops in Copenhagen and environs.

TABLE 3.3 OVERVIEW OF PURCHASED FINISHED PRODUCTS

| Sample no. | Description | Used for |
|-----------------------|---|--------------------|
| U) 100 % PET | 100 % polyester, trousers, woven, black | Apparel for men |
| (trousers) | | |
| V) 100 % PET (blouse) | 100 % polyester, blouse, knitted, black / brown / white | Apparel for ladies |
| | pattern | |
| X) 100 % PET | 100 % polyester, underwear - shirt, knitted, black | Apparel for men |
| (underwear) | | |
| Y) 100 % PET (fleece) | 100 % polyester, fleece jacket, knitted, black | Apparel for |
| | | children |

4 Selection of tests

4.1 TEST PROGRAMME

In the initial phase of the project the following test were considered (the different chemical compounds were pooled in 7 groups, A-G)

A – Determination of the content of selected organic compounds in the textiles The compounds:

Nicotine, naphthalene, o-chlorophenol, C3-C4-alkylbenzenes, tetrachloroethylene, nitrobenzene and DEHP.

B – Determination of the content of toluenediisocyanate (TDI) in the textiles

C – Determination of the content of aromatic amines in the textiles

Detection of 26 known compounds including all 20 amines in the German law "Neufassung der bedarfsgegenständeverordnung" of 23. December 1997".

D – Determination of the content of nonyl phenol ethoxylates in the textiles

E – Determination of the content of organic tin-compounds in the textiles

Selected organic compounds: e.g. mono-, di-, tri- and tetrabutyltin.

F – Determination of the content of selected brominated flame retardants in the textiles

Selected brominated flame retardants: e.g. OBDP, 4-BDPE, 4,4-DBBP, PBDPE, HBBP, HBCD, TBBPA.

G – Determination of the content of heavy metals in the textiles

The heavy metals:

Arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb) and tin (Sn).

4.2 SELECTION OF TESTS

The budget for analysis was not sufficient to test for all compounds in all fabrics.

It was decided not to test for brominated flame retardants (testgroup F). It is very unlikely to find these compounds. The probability is strongest in connection with fabric for furniture. Furthermore the test is very expensive, because development of a proper test is necessary.

It was decided to focus on heavy metals (testgroup G), aromatic amines (testgroup C) and selected organic compounds (testgroup A). 15, 10 and 10 fabrics were tested for these compounds respectively.

Toluenediisocyanate (TDI) - testgroup B – was estimated primarily to be relevant in connection with the use of foam made of polyurethane. Some fabrics for furniture are fitted with a foambacking. It was decided not to test for TDI.

Four fabrics were tested for nonyl phenol ethoxylates (NPEO), testgroup D. NPEO is primarily used as detergents, but can also be used in printing pastes.

Organic tin compounds (test group E) are primarily relevant in connection with foam, but also in connection with fabrics made of natural fibres. In the latter case the compounds are used as biocides. Four fabrics were tested.

Furthermore it was decided to test 10 fabrics for the content of free formaldehyde. Formaldehyde can liberate from many different fabrics in different amounts. The highest levels can be seen in connection with "shrink resist" treatments and printed fabrics. The samples with the highest amounts of free formaldehyde (L, M and Q) were washed once to determine the influence on the amount of free formaldehyde.

Normally on would expect that some of the free formaldehyde is removed during washing.

In table 4.1 the final selection of tests can be seen.

TABLE 4.1 OVERVIEW OF FINAL TEST PROGRAMME

| Sample no. | Test group | | | | | |
|------------------------------------|------------|---|---|---|---|--------------|
| • | Α | С | D | E | G | Formaldehyde |
| A) Nylon, flowers | | Х | | | | |
| B) 100 % cotton, yellow (children) | Х | Х | Х | Х | Х | Х |
| C) Acrylic / nylon | | | | | Х | X |
| D) 100% cotton (blue) | | | | | Х | |
| E) Cotton/PET brown | Х | | | | | |
| F) 100% PET (colorful) | | | | | Х | Х |
| G) 100 % cotton (animal motive) | Χ | Х | Х | Х | Х | Х |
| H) 100 % PET (white) | | | | | Х | |
| I) 100 % cotton (flowers) | Χ | Х | | | Х | |
| J) 100% flax | Х | Х | | Χ | Χ | Х |
| K) Pet/wool | | Х | | | | |
| L) 100% viscose | Χ | Х | | | Х | Х |
| M) 100% wool | Χ | Х | | | Х | Х |
| N) 100 % cotton (Versace) | | | | | Х | Х |
| O) 100 % cotton (bear) | Χ | Х | Χ | Х | Х | Х |
| P) 100 % wool (furniture) | | | | | Х | |
| Q) 100 % cotton (oilcloth) | Х | | Χ | | Χ | Х |
| R) Cotton/pet (napkins) | | | | | Х | |
| S) 100% pet (cloth) | | Х | | | | |
| T) 100% pet (cushion) | Х | | | | | |

In the selection of tests for the specific fabrics the aim was to cover as many different relevant test on the type of fibres and fabrics as possible.

In addition a qualitative screening for other compounds or group of compounds was done for the 10 fabric in test group A.

Furthermore supplementary studies concerning extractable antimony (artificial saliva and perspiration) were done for two of the fabric containing polyester and 4 apparel textiles containing 100% polyester, according to table 4.2

TABLE 4.2 OVERVIEW OF TEST PROGRAMME

| Sample no. | Extractable antimony (artificial | Extractable antimony (artificial |
|-------------------------|----------------------------------|----------------------------------|
| | salvia) | perspiration) |
| F) 100% PET (colorfull) | X | X |
| R) Cotton/pet | X | |
| (napkins) | | |
| U) 100 % PET | | X |
| (trousers) | | |
| V) 100 % PET (blouse) | | X |
| X) 100 % PET | X | X |
| (underwear) | | |
| Y) 100 % PET (fleece) | X | X |

The four apparel textiles (sample no. U, V, X and Y) were also tested for the content of total antimony (as sample no. F and R).

4.3 TEST METHODS

In the following chapter the methodology used in the testing is described in details.

4.3.1 Test for selected organic compounds - testgroup A and D

A weighted amount of sample material (approx. 5 g) was soxhlet-extracted with tert-butyl methyl ether (MTBE) added with deuteriummarked internal standards for 8 hours. The extract was concentrated using Kuderna Danish.

The extract was tested for selected organic compounds by capillary gas chromatography combined with mass spectrometry (GC-MS-SIM-mode). The content of selected compounds was determined with the use of external standards.

Furthermore the extract was screened for other compounds or group of compounds by scanning in the mass-range 29-450 amu (GC-MS-SCAN-mode).

Detected compounds were identified by comparing the mass-specter with the mass-specters in the NIST-library.

Sample preparation in duplicate was done.

4.3.2 Test for selected aromatic amines - testgroup C

A weighted amount of sample material (approx. 1 g) added with deuteriummarked internal standards was extracted with a citrate buffer followed by preconcentration on a SPE-column and eluted with tert-butyl methyl ether (MTBE).

The eluate was tested for selected aromatic amines by capillary gas chromatography combined with mass spectrometry (GC-MS-SIM-mode).

The content of selected compounds was determined with the use of external standards.

Sample preparation in duplicate was done.

4.3.3 Test for organic tin compounds – testgroup E

A weighted amount of sample material (approx. 2.5 g), added with internal standard, was extracted with a acetic acid/acetate –buffer in methanol. The extract was derivatized with sodium tetraethylborate, preconcentrated on SPE-column and eluted with isooctane.

The eluate was tested for selected organic tin compounds by capillary gas chromatography combined with mass spectrometry (GC-MS-SIM-mode). The content of selected compounds was determined with the use of external standards.

Standards and blanks were prepared in the same manner.

Sample preparation in duplicate was done.

4.3.4 Test for heavy metals – testgroup G

0.5 g of sample was prepared with nitric acid in a PFA autoclave by microwave induced heating. Sample preparation in duplicate was done. Blanks were prepared in the same manner.

The sample solutions were tested for As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb and Sn by flow injection inductively coupled plasma mass spectrometry (FI ICP-MS) with internal standards.

The quantification was done with the use of external standards. Before and after the samples 2 control samples traceable to NIST were tested, for current control of the calibration. Mixing standards containing the elements were prepared from a 100 mg/l Perkin-Elmer mixing standard. Separate standards of mercury Hg were prepared accordingly from a 10 mg/l Perkin-Elmer Hg stock solution. Standards and control samples are traceable to NIST.

A Perkin-Elmer Sciex Elan 5000 ICP-Masse Spectrometer linked to a Perkin-Elmer FIAS 400 with an AS-90 autosampler was used.

4.3.4.1 Test for barium

The sample solutions were tested for Ba by inductively coupled plasma atomic emission spectrometry (ICP-AES)

The quantification was done with the use of external standards. Standards were prepared from a 1000 μ g/ml PE stock solution. Standards and control samples are traceable to NIST.

A Perkin-Elmer Optima 3300 dv plasma emission spectrometer was used.

4.3.4.2 Test for total tin

A weighted sample (approx. 0.5 g) was incinerated in an oven. The ignition residue was extracted with hydrochloric acid.

The solution was tested for Sn by flow injection inductively coupled plasma mass spectrometry (FI ICP-MS) with internal standards as described above. Sample preparation in duplicate was done. Blanks were prepared in the same manner.

4.3.5 Test for free formaldehyde

The content of free formaldehyde was measured according to EN ISO 14184.

4.3.6 Test for extractable antimony (artificial saliva and perspiration)

Furthermore supplementary studies concerning extractable antimony (artificial saliva and perspiration) were done for two of the fabric containing polyester and 4 apparel textiles containing 100% polyester, according to table 4.2.

The following method is estimated by the Danish Technological Institute, Clothing and Textile to be suitable to measure extractable antimony (artificial saliva and perspiration):

The following artificial salvia solution was used for the extraction:

| NaCl | 4.5 g/l |
|---------------------------------|----------|
| KCl | 0.3 g/l |
| Na ₂ SO ₄ | 0.3 g/l |
| NH ₄ Cl | 0.4 g/l |
| Lactic acid | 3.0 g/l |
| Carbamide | 0.2 g/l |

The following artificial perspiration solution was used for the extraction:

| l-Histidine-monohydrochloride-1-hydrate | 0.5 g/l |
|---|----------|
| NaCl | 5.0 g/l |
| NaH,PO ₄ · H,O | 1.95 g/l |
| pH adjustment with 0.1 M NaOH to pH 5.5 | |

2 g of samples (approx. 5x5 mm) was extracted with 100 ml solution at 40 °C for 1 hour.

Sample preparation in duplicate was done. Blanks were prepared in the same manner.

The solutions were tested for Sb by flow injection inductively coupled plasma mass spectrometry (FI ICP-MS) with internal standards as described above.

The quantification was done with the use of external standards. Before and after the samples 1 control sample was tested, for current control of the calibration.

Mixing standards containing Sb were prepared from a 100 mg/l Perkin-Elmer mixing standard by dilution with artificial solution. Standards and control samples are traceable to NIST.

A Perkin-Elmer Sciex Elan 5000 ICP-Masse Spectrometer linked to a Perkin-Elmer FIAS 400 with a AS-90 autosampler was used.

5 Results

5.1 SELECTED ORGANIC COMPOUNDS

The following compounds are included in testgroup A:

TABLE 5.1 SELECTED ORGANIC COMPOUNDS

| Compound | CAS-no. | Limit of detection (mg/kg) |
|------------------------------------|----------|----------------------------|
| Acridine | 260-97-6 | 0.02 |
| Σ C9H12 (C3 alkylbenzenes) | | 0.6 |
| Σ C10H14 (C4 alkylbenzenes) | | 0.6 |
| DEHP (bis(2-ethylhexyl)phthalate) | 117-81-7 | 0.7 |
| Naphthalene | 91-20-3 | 0.01 |
| Nicotine | 59-26-7 | 0.02 |
| Nitrobenzene | 98-95-3 | 0.05 |
| o-Chloorphenol | 95-57-8 | 0.02 |
| Tetrachloroethylene | 127-18-4 | 0.005 |

The results were:

TABLE 5.2 TEST RESULTS FOR SELECTED ORGANIC COMPOUNDS

| Sample no. | Results (mg | Results (mg/kg) | |
|------------------------------------|-------------|-----------------|-------------|
| | Nicotine | DEHP | Naphthalene |
| B) 100 % cotton, yellow (children) | 0.22 / 0.11 | 8.6 / 6.7 | - |
| E) Cotton/PET brown | 0.20 / 0.02 | 4.0 / 1.8 | - |
| G) 100 % cotton (animal motive) | 0.25 / 0.14 | 3.9 / 3.2 | - |
| I) 100 % cotton (flowers) | 0.16 / 0.11 | 2.6 / 6.9 | - |
| J) 100% flax | 0.14 / 0.08 | 6.2 / 1.5 | 0.12 / 0.08 |
| L) 100% viscose | - | 3.7 / 1.0 | 2.4 / 3.8 |
| M) 100% wool | 0.09 / 0.13 | 3.5 / 4.7 | 0.47 / 0.68 |
| O) 100 % cotton (bear) | 0.05 / 0.03 | 3.3 / 1.8 | 0.06 / 0.04 |
| Q) 100 % cotton (oilcloth) | 0.11 / 0.13 | 3.6 / 2.8 | 0.15 / 0.16 |
| T) 100% pet (cushion) | 0.19 / 0.16 | 1.7 / 2.6 | - |

[&]quot;-" means below the limit of detection (l.o.d.). Determinations in duplicate are listen with the symbol "/" between the two values.

DEHP (bis(2-ethylhexyl)phthalate) was detected in all 10 tested samples. Nicotine was detected in 9 out of 10 sample, naphthalene was found in 5 out of 10 samples. The other organic compounds were not detected in levels above the l.o.d.

The health assessments of the results are presented in chapter 7.1 (DEHP), 7.4 (naphthalene) and 7.5 (nicotine).

5.2 AROMATIC AMINES

The following compounds are included in testgroup C (aromatic amines):

TABLE 5.3 AROMATIC AMINES

| TABLE 5.3 AROMATIC AMINES | | |
|--|----------|----------------|
| Compounds | CAS-no. | L.o.d. (mg/kg) |
| 4-Aminobiphenyle | 92-67-1 | 0.5 |
| Benzidine | 92-87-5 | 0.5 |
| 4-Chloro-o-toluidine | 95-69-2 | 0.5 |
| 2-Naphthylamine | 91-59-8 | 0.5 |
| o-Aminoazotoluene | 97-56-3 | 0.5 |
| 2-Amino-4-nitrotoluene | 99-55-8 | 0.5 |
| 4-Chloroaniline | 106-47-8 | 0.5 |
| 2,4-Diaminoanisole | 615-05-4 | 1 |
| 4,4¹-Diaminodiphenyelmethane | 101-77-9 | 0.5 |
| 3,3¹- Dichlorobenzidine | 91-94-1 | 0.5 |
| 3,3¹- Dimethoxybenzidine | 119-90-4 | 0.5 |
| 3,3¹- Dimethylbenzidine | 119-93-7 | 0.5 |
| 3,3¹- Dimethyle-4,4¹-diaminodiphenylemethane | 838-88-0 | 0.5 |
| p-Cresidine | 120-71-8 | 0.5 |
| 4,4¹-Methylene-bis-(2-chloroaniline) | 101-14-4 | 0.5 |
| 4,4-Oxydianiline (4,4¹-Diaminodiphenylether) | 101-80-4 | 0.5 |
| 4,4-Thiodianiline (4,4¹-Diaminodiphenylesulfide) | 139-65-1 | 0.5 |
| o-Toluidine | 95-53-4 | 0.3 |
| 2,4-Toluendiamine (2,4-Diaminotoluene) | 95-80-7 | 1 |
| 2,4,5-Trimethylaniline | 137-17-7 | 0.5 |
| o-Anisidine | 90-04-0 | 0.5 |
| 2,4-Xylidine | 95-68-1 | 0.5 |
| 2,6-Xylidine | 87-62-7 | 0.5 |
| Acridine | 260-97-6 | 0.3 |
| 2,6-Dichloro-4-nitroaniline | 99-30-9 | 0.5 |
| 2-Chloro-4-nitroaniline | 121-87-9 | 0.5 |
| | | |

The results were:

TABLE 5.4 TEST RESULTS FOR AROMATIC AMINES

| Sample no. | Results (mg/kg) |
|------------------------------------|--------------------------------------|
| | |
| A) Nylon, flowers | - |
| B) 100 % cotton, yellow (children) | - |
| G) 100 % cotton (animal motive) | - |
| I) 100 % cotton (flowers) | - |
| J) 100% flax | - |
| K) Pet/wool | • |
| L) 100% viscose | - |
| M) 100% wool | o-Toluidine: 0.82 \pm 3.4 $\%$ |
| O) 100 % cotton (bear) | 4-Chloroaniline: 1.22 \pm 3.4 $\%$ |
| S) 100% pet (cloth) | - |

[&]quot;-" means below the l.o.d.

Only 2 out of 10 samples contained levels above the l.o.d., o-toluidine in sample M and 4-chloroaniline in sample O.

The health assessments of the results are presented in chapter 7.2 (4-chloroaniline) and 7.7 (o-toluidine).

5.3 Nonyl Phenol Ethoxylates

For testgroup D nonyl phenols (NP) testing was done with a l.o.d. of 0.1 mg/kg. For nonyl phenole mono/diethoxylate (NP1 + NP2) with a l.o.d. of 3 mg/kg.

The results were:

TABLE 5.5 TEST RESULTS FOR NONYL PHENOL ETHOXYLATES

| Sample no. | Results (mg/kg) | | |
|------------------------------------|-----------------------|---|------------------------------|
| | Nonyl phenols (NP) | Nonyl phenol mono / diethoxylate (NP1+ NP2) | Sum of NP, NP1 and NP2 |
| B) 100 % cotton, yellow (children) | 0.5 ± 22 % | 5.0 ± 2.5 % | 5.5 |
| G) 100 % cotton (animal motive) | 1.8 ± 1.5 % | 16 ± 2.5 % | 17.8 |
| O) 100 % cotton (bear) | - | - | - |
| Q) 100 % cotton (oilcloth) | 6.4 ± 24.5 % | 20 ± 5.6 % | 26.4 |

[&]quot;-" means below the l.o.d.

In 3 out of 4 tested samples nonyl phenol ethoxylates were found in levels above the l.o.d.

The health assessments of the results are presented in chapter 7.6.

5.4 SELECTED ORGANIC TIN COMPOUNDS

In sample G - 100% cotton (animal motive)— tin was found in levels above the l.o.d. Additional testing was done in order to determine the type of organic tin. The results were:

Monobutyltin (MBT): $7.2 \mu g/g$ Dibutyltin (DBT): $9.7 \mu g/g$.

The health assessments of the results are presented in chapter 8.11.

5.5 SELECTED HEAVY METALS

The following heavy metals are included in testgroup G:

TABLE 5.6 SELECTED HEAVY METALS

| TABLE 5.6 SELEC | CTED HEAVY META |
|------------------|-----------------|
| Heavy metal | L.o.d. (mg/kg) |
| Arsenic (As) | 1 |
| Barium (Ba) | 0.3 |
| Cadmium (Cd) | 0.05 |
| Cobalt (Co) | 0.2 |
| Chromium (Cr) | 0.2 |
| Copper (Cu) | 1 |
| Mercury (Hg) | 0.05 |
| Nickel (Ni) | 1 |
| Lead (Pb) | 0.5 |
| Antimony (Sb) | 0.5 |
| Tin (Sn) | 0.05 |
| | |

The results were (all in mg/kg):

TABLE 5.7 TEST RESULTS FOR SELECTED HEAVY METALS

| Sample no. | As | Ва | Cd | Со | Cr | Cu |
|-----------------------|----------|-----------|----|---------|------------|---------|
| B) 100 % cotton, | - | 1.2±0.09 | - | 2.2 | 7.4 | 25±3.2 |
| yellow (children) | | - | | 0.45 | 4.7 | |
| C) Acrylic / nylon | - | 0.76±0.02 | - | - | 0.31±0.02 | - |
| D) 100% cotton (blue) | - | 0.67±0.05 | - | - | 0.24±0.02 | 680 |
| F) 100% PET | - | 1.6±0.1 | - | 21±0.34 | 0.40±0.03 | - |
| (colourful) | | | | | | |
| G) 100 % cotton | - | 2.3±0.2 | - | - | 0.69±0.06 | - |
| (animal motive) | | | | | | 1.5 |
| H) 100 % PET (white) | - | 0.85 | - | - | - | - |
| | | 1.2 | | | | |
| I) 100 % cotton | - | 2.8 | - | - | 0.20 | - |
| (flowers) | | 0.7 | | | - | |
| J) 100% flax | - | 1.0±0.09 | - | - | 0.20±0.007 | 20±0.32 |
| L) 100% viscose | 1.0±0.15 | - | - | 43±0.56 | - | - |
| M) 100% wool | - | 9.9±0.2 | - | 5.6 | - | 5.0 |
| | | | | | | ±0.007 |
| N) 100 % cotton | - | 1.1±0.02 | - | 48 | 64 | 1.6 |
| (Versace) | | | | 32 | 44 | 1.1 |
| O) 100 % cotton | - | 1.1±0.09 | - | - | 0.51±0.03 | 5.3 |
| (bear) | | | | | | ±0.02 |
| P) 100 % wool | - | 0.66 | - | - | 65.2±0.9 | 4.9 |
| (furniture) | | 0.44 | | | | ±0.33 |
| Q) 100 % cotton | - | 0.95±0.05 | - | - | 0.50 | 260±17 |
| (oilcloth) | | | | | 1.7 | |
| R) Cotton/pet | - | 2.0±0.4 | - | - | 0.20±0.003 | 11±0.92 |
| (napkins) | | | | | | |

TABLE 5.7 (CONTINUED) TESTRESULTS FOR SELECTED HEAVY METALS

| Sample no. | Hg | Ni | Pb | Sb | Sn |
|------------------------------------|----|-----|------------|-----------|-----------------|
| B) 100 % cotton, yellow (children) | - | - | - | - | - |
| C) Acrylic / nylon | - | 1.1 | - | - | not measured |
| D) 100% cotton (blue) | - | - | - | - | not measured |
| F) 100% PET (colorful) | - | - | 1.2 1.6 | 110±8.7 | not measured |
| G) 100 % cotton (animal motive) | - | - | - | - | 4.9±0.3 |
| H) 100 % PET (white) | - | • | - | 200±15 | not measured |
| I) 100 % cotton (flowers) | - | - | - | o.63 - | not measured |
| J) 100% flax | - | - | - | - | - |
| L) 100% viscose | - | - | - | - | not measured |
| M) 100% wool | - | - | 0.73±0.054 | - | not measured |
| N) 100 % cotton (Versace) | - | - | - | - | not measured |
| O) 100 % cotton (bear) | - | - | 0.51±0.009 | - | - |
| P) 100 % wool (furniture) | - | - | 0.63±0.004 | - | not measured |
| Q) 100 % cotton (oilcloth) | - | - | - | - | not measured |
| R) Cotton/pet (napkins) | - | | - | 35±4.5 | not measured |

[&]quot;-" means below the l.o.d. The number after \pm states the statistical standard deviation. If the standard deviation is higher than 20% of the average of the determination in duplicate both results are listed. Standard deviation of this magnitude are probably a result of inhomogeneity in the textile sample.

Cadmium and mercury were not found in levels above the l.o.d. in any of the 15 samples. Barium was detected in 14 samples. Chromium was found in 12, copper in 10, cobalt in 5 and antimony and lead in 4 samples. Arsenic, nickel and tin were only detected in 1 sample.

The health assessments of the results are presented in chapter 8.

5.5.1 Extractable antimony (artificial saliva and perspiration)

Supplementary testing concerning extractable antimony (artificial saliva and perspiration) were done for two of the fabric containing polyester and 4 apparel textiles containing 100% polyester. The results are presented in table 5.8. The results for the content of total antimony are listed for comparison.

The l.o.d. for extractable antimony – artificial salvia and perspiration - are 0.5 mg/kg and 1.0 mg/kg respectively

The results were (all in mg/kg):

TABLE 5.8 TESTRESULTS FOR TOTAL ANTIMONY COMPARED WITH EXTRACTABLE ANTIMONY (ARTIFICIAL SALVIA AND PERSPIRATION)

| Sample no. | Total antimony | Extractable antimony | Extractable antimony |
|-------------------------|----------------|-----------------------|---------------------------|
| ' | ' | (artificial salvia) ´ | (artificial perspiration) |
| F) 100% PET (colorfull) | 110±8.7 | - | - |
| R) Cotton/pet | 35±4.5 | - | not measured |
| (napkins) | | | |
| U) 100 % PET | 8,3 | not measured | - |
| (trousers) | 13 | | |
| V) 100 % PET (blouse) | 35 | not measured | 3.5±0,1 |
| | 48 | | |
| X) 100 % PET | 7.0±0.5 | - | - |
| (underwear) | | | |
| Y) 100 % PET (fleece) | 27±1.6 | - | - |

[&]quot;-" means below the l.o.d. The number after \pm states the statistical standard deviation. If the standard deviation is higher than 20% of the average of the determination in duplicate both results are listed. Standard deviation of this magnitude are probably a result of inhomogeneity in the textile sample.

The table shows that in only one sample extractable antimony in detectable level was found. The amount is only 10% of the total antimony in the sample.

The health assessments of the results are presented in chapter 8.1.

5.6 FORMALDEHYDE

The amount of free formaldehyde was determined according to the test method EN ISO 14184. According to the test method levels below 20 ppm (20 mg/kg) shall be reported as "not detectable". The method is used in the European ecolabel. The limit values in the eoclabel is max 30 ppm for products with skin contact and 300 ppm for all other products.

The results were:

TABLE 5.9 TEST RESULTS FOR FORMALDEHYDE

| Sample no. | Formaldehyde according to EN ISO 14184 (mg/kg = ppm) | Formaldehyde after 1. laundry (mg/kg = ppm) |
|------------------------------------|---|--|
| B) 100 % cotton, yellow (children) | - | not measured |
| C) Acrylic / nylon | - | not measured |
| F) 100% PET (colorful) | - | not measured |
| G) 100 % cotton (animal motive) | - | not measured |
| J) 100% flax | - | not measured |
| L) 100% viscose | 43 | - |
| M) 100% wool | 35 | 21 |
| N) 100 % cotton (Versace) | - | not measured |
| O) 100 % cotton (bear) | - | not measured |
| Q) 100 % cotton (oilcloth) | 82 | - |

[&]quot;-" means below the l.o.d.

Only in 3 samples levels above 20 ppm were found. For these three samples testing were repeated after 1st laundry according to the following:

- Sample L: Normal household programme, 40°C, normal dosing of liquid chlorine and liquid colour detergent.
- Sample M: Wool programme, 40°C, normal dosing of liquid detergent for wool.
- Sample Q: Normal household programme, 40°C, normal dosing of liquid chlorine and liquid color detergent.

After this treatment only sample M contained free formaldehyde above the l.o.d. of 20 ppm.

The health assessments of the results are presented in chapter 7.3.

5.7 SCREENING

Table 5.10 presents the results of the qualitative screening for other compounds or group of compounds for the 10 fabrics in test group A.

Table 5.10 Other compounds or group of compounds found in the screening of testgroup A fabrics $\underline{\ }$

| Sample | Detected compounds |
|------------------------|---|
| B) 100% cotton, yellow | Phthalate*, fatty acids, $C_xH_y(C_{8-20})$, $C_xH_y(C_{20-40})$, 2-2`-oxybis ethanol, |
| (children) | squalene, aliphatic alcohols, aliphatic amide |
| E) Cotton/PET brown | fatty acids, aliphatic amide |
| G) 100% (animal | fatty acids, 2-2`-oxybis ethanol |
| motive) | |
| I) 100% cotton | fatty acids, $C_xH_y(C_{8-20})$, $C_xH_y(C_{20-40})$,), 2-2`-oxybis ethanol, propylene |
| (flowers) | glycol, aliphatic amide |
| J) 100% flax | bis (2-ethylhexyl) maleate, 2-2`-oxybis ethanol, squalene |
| L) 100% viscose | Phthalate*, 5-hydroxy-methyl-furfural |
| M) 100% wool | fatty acids, C_xH_y (C_{20-40}), 2-2`-oxybis ethanol, 2-(2-butoxy-ethoxy)ethanol |
| O) 100% cotton (bear) | fatty acids, $C_x H_y (C_{20-40})$ |
| Q) 100% cotton | C_xH_y (C_{20-40}), bis (2-ethylhexyl) maleate, benzylbenzoate, 2-2`-oxybis |
| (oilcloth) | ethanol |
| T) 100% PET (cushion) | fatty acids, $C_xH_y(C_{20-40})$ |

^{*:} presumed to be DEHP

The health assessments of the results are presented in chapter 9.

6 Principles for health assessment

6.1 Introduction

In the studied textiles, several chemical compounds have been observed that may relate to the manufacture of fibres or from the processing of the finished textiles. The potential effects on health of these chemical compounds have been examined. For the health assessment, a series of scenarios have been developed to establish the potential risk to the consumer.

Of the organic compounds analysed for, the following compounds were detected in the textile samples:

- DEHP
- 4-Chloroaniline
- Formaldehyde
- Naphthalene
- Nicotine
- Nonylphenol, nonylphenol mono- and diethoxylate
- o-Toluidine

Metals were also analysed for and the following observed:

- Antimony
- Arsenic
- Barium
- Cadmium
- Chromium
- Cobalt
- Copper
- Lead
- Mercury
- Nickel
- Tin

A screening was performed at a later stage. Several compounds were identified but not quantified.

In the following sections, the selected compounds have been discussed. The discussion takes its background in data from the project "Chemicals in textiles" (Larsen *et al.* 2000) which is supplemented with further data. Then an evaluation of the significance of the measured concentrations using the scenarios is described below.

The assessment follows the EU principles of risk assessment for chemical substances described in the TGD (1996, 2002). In the TGD, among other the exposure of consumers is included. A few data and information is based on the American "Exposure handbook" (US-EPA 1997), which contain extensive data on American consumers.

6.2 ASSESSMENT SCENARIOS

The textile fabrics focused on in the study are often further worked up by the consumers to e.g. curtains, table cloths, clothes, bed linen and bed blankets.

The exposure of the consumer therefore varies according to the end-use of the textile. It has been chosen to start the evaluation by the exposure scenarios where the exposure is considered the highest. This means uses with close bodily contact such as clothes and bed linen. The direct exposure from e.g. curtains, table cloths and blankets is estimated to be lower and more of another character like inhalation of volatile compounds or compounds adsorbed to dust fibres.

The duration of the contact exposure is considered too short to involve a significant migration of chemical compounds to the skin from household textiles such as towels being wet or via sweat.

The exposure to children is considered increased if they e.g. place the textile in the mouth and sucks or chews on it.

Scenarios have been developed regarding:

- Dermal exposure (skin contact)
- Oral exposure (putting textile in the mouth)
- Inhalation

6.3 DERMAL EXPOSURE

Before percutaneous exposure the chemical compound has to migrate from the textile to the skin. When the compound has reached the skin the compound may be absorbed percutaneous to the blood stream and then distributed throughout the body.

The uptake after contact may be from "free" chemical compounds or from degradation products in the textile. The degradation of the compounds may take place in the textile, via bacteria/enzymes on the skin or in the gastrointestinal-tract after absorption.

The exposure can be expressed in the equation (TGD 1996) which is modified to the exposure scenario:

$$U_{derm} = \frac{Q_{prod} \times Fc_{prod} \times F_{AREA,derm} \times N_{event}}{BW}$$

| is the potential uptake of the compound | mg/kg bw/day |
|--|---|
| is the amount of textile | kg |
| is the fraction of compound in the textile | mg/kg |
| is the fraction of exposed skin | |
| Number of exposure events | per day |
| Bodyweight (bw) | kg |
| | is the amount of textile is the fraction of compound in the textile is the fraction of exposed skin Number of exposure events |

For the assessment of dermal exposure, a full coverage of the body except head, hands and feet is used.

The total area of the body has been measured to be depending on age, etc. The total body area has been set to 18500 cm² with an uncovered area of 2940 cm² (16%) for a man of 180 cm height and 70 kg weight (Hayes 1991). For European standard (TGD 1996) is used American measurements (US EPA 1989, 1997) which measures the total body area to 19400 cm² for men and 16900 cm² for women and a total average of 18150 cm² of which head, neck and feet are 2981 cm² (16%).

In the study, a surface area for an adult of 15000 cm² is used, corresponding to approx. 85% coverage of the body with textile. Using 333 g/m² the clothing of an adult person thus weights a total of 500 g. This may be a little on the upper edge according to the expert of the Danish Technological Institute (Laursen SE, *pers. comm.* 2002) but is used as a "reasonable worst case".

The surface area for a child is set to 8800 cm², which correspond to a child at the age of 3 to 6 years. This is a high value since a child weighing 10 kg which is the recommended weight of a child in TGD (1996) is more likely to be close to 1 year of age and having a surface area of approx. 6700 cm² (US-EPA 1997). The area of the large side is used in the study relating to the "reasonable worst case". Using textile coverage of 85% of the surface area results in an exposed body surface area of 7500 cm² for a child. Thus, the weight of the textiles worn close to the body of a child is set to 250 g.

Dermal absorption

After exposure to the skin the chemical compound has to pass the skin before actual absorption is taking place. Only a few data of percutaneous absorption of the studied compounds have been found. The dermal absorption is therefore estimated.

Depending on the exposure and/or the compounds' lipophilicity the dermal penetration is assumed to be insignificant for very lipophilic compounds with an octanol/water distribution coefficient log Kow less than –1 or more than 5 (OECD 1993).

Dermal penetration is considered very small for compounds with a log Kow less than -1 (i.e. very hydrophilic) and for compounds with a molecular weight above 700 (Vermeire *et al.* 1993). According to a Dutch model the dermal absorption is estimated to 10% for compounds with a molecular weight above 500 g/mol and a log Kow <-1 or >4 (De Heer 1999). The latter values are also included in the TGD (1996).

In standard assessments when no information is available a typical dermal absorption of 100% is used (TGD 1996, 2002). In the report this has been performed with all organic compounds. If information on absorption was available the information has been used in refining of the estimates. It has been performed by multiplying the dermal potential uptake (U_{derm}) with the absorption factor (F_{abs}):

$$A_{derm} = U_{derm} \times F_{abs}$$

The absorption of metals presumed very small. For zinc the dermal absorption is 2% in liquid zinc compounds and in solids assumed 0.2% in the

EU risk assessment draft 2002. For chromium slow penetration rates of ⁵¹Cr has been observed: 0.07% in 3 hours and 0.18% in 50 hours (Fairhurst and Minty 1989). Approximately the same relation is used in the scenarios for dermal absorption of metals but modified to 0.1% for all metals.

Summary of used parameters in the standard scenarios

The weight of an adult is set to 70 kg. The weight of textiles covering 85% of the body is set to 500 g. The weight of a child is set to 10 kg and the weight of textiles to 250 g. Further is used a scenario of a T-shirt weighing 160 g and a child as the exposed consumer.

6.4 ORALINTAKE

Oral exposure may take place when a child puts the textile into the mouth and is sucking or chewing on it. By oral exposure the absorption takes place by uptake over the epithelium in the mouth cavity or in the gastrointestinal-tract.

Residues on hands which later may come in contact with food or by other routes directly or indirectly gets into the mouth and orally ingested is considered insignificant in this study.

The oral intake is estimated according to the equation (OECD 1993, TGD 1996):

$$I_{oral} = \frac{V_{oral} \times C_{oral} \times F_{orl} \times N_{event}}{BW}$$

where:

 I_{oral} Intake of the compound mg/kg bw/day V_{prod} Weight of product placed in mouth kg or g C_{oral} Concentration of compound in the product mg/kg or μ g/g

Number of events per day

In this study presumed 1 /day

Body weight kg

Fraction absorbed (bioavailable part)

As scenario is chosen a child sucking/chewing on textile equivalent to 20×20 cm = 400 cm² weighting 20 g. A slightly higher density of textile than used in the body covering is chosen (500 g/m²). The child is assumed the use the textile found by hand which may well be of a heavier quality than the textile worn in close body contact. It is also presumed that a child potentially will put more lightweight textile than heavier textile into the mouth.

6.5 INHALATION

Exposure to consumers from compounds by inhalation may happen from the inhalation of dust from fibres containing the chemical compound or as dust to which the compound is adsorbed. Finally for volatile compounds a direct exposure for evaporated chemical compounds may take place.

The duration of the exposure can theoretically be from the purchase to the disposal of the textile.

The exposure by inhalation is expressed as the concentration of the compound in the inhalation air zone and presented as the average concentration over a reference period, e.g. 8 hours for the working

environment. For the consumer, the reference period may be from 16 to 24 hours in the home.

To estimate the exposure by inhalation, it is necessary to know the inhalation rate, the volume of the room and the release rate of the compound to the room or the concentration in the room.

The inhalation rate of an average adult is set to 20 m³/day corresponding to 0.83 m³/hour (standard in TGD 1996).

The concentration in closed room is presumed to be higher than by outdoor use of textiles. For the estimation of the concentration in the room is used an equation for volatile compounds and airborne particles. It is assumed that the compound is released instantly to the room and is distributed homogeneously in the room. The size of the standard room is set to 20 m² and the height to 2.5 metres, i.e. the room volume is 50 m³. Concerning bedrooms the value is estimated to be too high and the standard bedroom volume is therefore set to 20 m³.

For estimation of the theoretical maximum achievable concentration of the compound in air is used the Ideal Gas Law, slightly modified (TGD 1996):

$$C_{air,\text{max}} = C_{tex} \times \frac{MW}{22.4} \times \frac{273}{TEMP_a} \times \frac{P_a}{101325} \quad (mg/m^3)$$

| where | | |
|------------------------------|---|-----------------------------|
| $C_{air, max}$ | Maximum achievable concentration in air | mg/m ³ |
| $C_{\scriptscriptstyle tex}$ | Concentration of compound in textile | mg/kg |
| MW | Molecular weight | g/mol |
| 22.4 | The volume occupied by 1 mol of any compound in the gaseous | 1 |
| | state at 0°C and 1 atm | |
| 273 | Temperature 0°C in degrees Kelvin | ${}^{\mathrm{o}}\mathrm{K}$ |
| $TEMP_{_a}$ | Actual temperature in degrees Kelvin | ${}^{\mathrm{o}}\mathrm{K}$ |
| $P_{_a}$ | Actual pressure in Pascal | Pa |
| 101325 | Standard normal atmospheric pressure in Pascal | Pa |

The same equation is used in the EASE model developed for the working environment (TGD 1996). Because the temperature for vapour pressure of the compounds are expressed at room temperature for the studied compounds the temperature correction factor is excluded.

The concentration in inhaled air is the estimated according to the equation:

$$C_{inh} = \frac{Q_{prod} \times C_{air,max}}{V_{room}} \quad (mg/m^3)$$

where C_{inh} Concentration in inhaled air mg/m³ Q_{prod} Quantity of textile used in the room kg Maximum achievable air concentration in the room mg/m³ V_{max} Volume of the room m³ Used: 20

The amount of inhaled compound is then:

| | $I_{inh} = \frac{resp + contact}{resp}$ | $\langle N_{event} (mg)$ | /kgBW/day) |
|------------------|--|----------------------------|-----------------------------|
| | BW | | |
| where | | | |
| I _{inh} | Amount of inhaled compound | mg | mg/kg bw/d |
| F_{resp} | Inhalable or respirable fraction of compound | | (if unknown: 1 (i.e. 100%)) |
| C_{inh} | Concentration in inhaled air | mg/m³ | |
| Q_{inh} | Inhalation rate of adult | m³/hour | (adult: 0.8 m³/h, 20 m³/d) |
| $T_{contact}$ | Duration of exposure | hours | |
| N_{event} | Number of events | per day | |
| BW | Body weight | kg | used: |

adult: 70 kg child: 10 kg

 $F_{\text{norm}} \times C_{\text{ind}} \times O_{\text{ind}} \times T_{\text{normal}}$

As room scenario the room volume is set to 20 m³ and in the room is presumed to be 30 m² of textiles equivalent to 10 kg. The amount of textiles includes bed linen, curtains, clothes, etc. all with an exposure potential to the consumer of inhalable compounds.

For the organic compounds it is assumed that the maximum inhalable concentration is reached immediately and homogeneously dispersed in the room. No ventilation is included in the scenario.

For volatile metals (mercury) it is assumed that the total amount evaporates. For non-volatile compounds it is assumed that dust from textiles are inhalable and that this fraction at maximum is 0.01%.

7 Evaluation of organic substances

7.1 BIS(ETHYLHEXYL)-PHTHALATE (DEHP)

7.1.1 Identification

Name DEHP

IUPAC name Bis(2-ethylhexyl) phthalate

CAS no. 117-81-7 EINECS no. 204-211-0 Molecular formula $C_{24} H_{38} O_4$ Molecular structure

CH₃
CH₃
CH₃

Molecular weight 390.6 g/mol

Synonyms di(2-ethylhexyl)-phthalate (DEHP)

Phthalic acid di(ethylhexyl) ester

1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl)

ester

The melting point is -55°C. The boiling point is 233°C. The vapour pressure is 3.4×10⁻⁵ Pa at 20°C. The low vapour pressure indicates that DEHP does not evaporate in its pure state. However, DEHP has been measured in indoor air indicating that DEHP evaporates from the products containing DEHP. The temperature is crucial. For instance, the vapour pressure increases 320 times from 20°C to 70°C measured in a car (BUA 1986).

Several values of water solubility varying between 0.003 to 1.3 mg/l have been recovered from literature references. Because DEHP in water easily forms stable colloidal dispersions that increase the amount of DEHP in the water phase, a colloidal water solubility of 0.34 mg/l (ECETOC 1985) and a non-colloidal water solubility of 0.003 mg/l is recommended. The formation of colloids is significant for the interpretation of studies in aqueous medium while the non-colloidal water solubility is relevant for long-term distribution in the environment.

The log Kow values varies between 4.8 and 9.6. Most values are presumably underestimated due to the readiness to form colloidal dispersion. The log Kow is set to 7.45 based on a study by De Bruijn *et al.* (1989).

The adsorption to organic carbon, given as the adsorption coefficient log Koc, is measured to vary between 4.8 and 5.9 and average 5.3. The high log Koc indicate that DEHP is strongly adsorbed to organic material such as dust.

7.1.1.1 Classification

DEHP is classified, EU index no. 607-317-00-9 (Miljøministeriet 2002): Rep2;R60-61 Reprotoxic. May impair fertility. Also may cause harm to the unborn child

7.1.1.2 Source

DEHP is used in the formulation of polymers as softener. DEHP is not chemically bound to the polymers, i.e. DEHP may be released during the use of material containing DEHP. DEHP is not degraded in the material as long as the molecule remains in the material. Release of DEHP is therefore possible as long as the material is in use. The release from the material is assumed to depend on surface area and not the content of DEHP.

7.1.1.3 Chemical analyses

A summary of the measured concentrations of DEHP in textiles (cf. section 5) is presented in table 7.1.

Table 7.1 Analyses results from double determination of DEHP in textile (MG/KG)

| Sampl | Textile | DEHP_1 | DEHP_2 | Average |
|-------|--------------------------------|--------|--------|---------|
| е | | mg/kg | mg/kg | mg/kg |
| В | 100% cotton, yellow (children) | 8.6 | 6.7 | 7.7 |
| E | Cotton/PET, brown | 4.0 | 1.8 | 2.9 |
| G | 100% cotton, animal motive | 3.9 | 3.2 | 3.6 |
| I | 100% cotton, flowers | 2.6 | 6.9 | 4.8 |
| J | 100% flax | 6.2 | 1.5 | 3.9 |
| L | 100% viscose | 3.7 | 1.0 | 2.4 |
| М | 100% wool | 3.5 | 4.7 | 4.1 |
| 0 | 100% cotton (bear) | 3.3 | 1.8 | 2.6 |
| Q | 100% cotton (oilcloth) | 3.6 | 2.8 | 3.2 |
| Т | 100% PET (pillow) | 1.7 | 2.6 | 2.2 |

7.1.2 Health

Softeners are usually not chemically bound in polymers. Therefore, a potential exposure of the consumer of the product by oral or dermal route may take place. Inhalation is also possible. However indoor air may contain DEHP from other sources as well and the contribution of DEHP from textiles to the total DEHP load is unknown.

7.1.2.1 *Intake*

Evaluations of the uptake of DEHP from the gastrointestinal tract is based on measurements of the excretion in urine after administration of ¹⁴C-labelled DEHP. The results of the studies indicate that absorption from the gastrointestinal tract happens very fast after oral administration. Oral intake of minor amounts of DEHP does not result in the exposure to intact DEHP since hydrolysis of DEHP happens quickly in the intestine. To humans the absorption is approx. 50% of dose up to 200 mg/kg bw (Rhodes *et al.* 1983). Thus, a bioavailability of 50% is considered acceptable in this context for adult persons.

No data were found on children, The absorption may depend on physiological, biochemical or genetically age-dependent differences between adults and children. Thus, 100% absorption is found reasonable to presume for children.

The acute toxicity to mammals is for rats LD_{50} >20000 mg/kg and for mice LD_{50} >9860 mg/kg.

7.1.2.2 Dermal absorption

Dermal absorption studies have been performed as *in vitro* and *in vivo* studies where DEHP was placed directly on the skin. The absorption rate depends on the concentration of the substance in contact with the skin surface and the absorption rate. Several studies have been performed on the bioavailability of ¹⁴C-DEHP applied to skin from urinal and faecal recoveries, residues on exposed in adsorption into the body. Based on exposure duration, time for excretion and applied dose a realistic value for *in vivo* dermal absorption has been estimated to 20% for rats and guinea pigs varying from 6.5% (rats, Elsis *et al.* 1989), 9% (rats, Melnick *et al.* 1987) and 26% (guinea pigs, Ng *et al.* 1992).

The results from Scott *et al.* (1989) and Barber *et al.* (1992) indicates that rat skin is four times more permeable than human skin. Using a correction factor of 4 from rat to human skin, a dermal absorption of 5% for potential human absorption is derived. A bioavailability of 5% is therefore used in the calculations of exposure to DEHP in textiles.

Dermal toxicity in rabbits is determined to be >20000 mg/kg (LD₅₀).

7.1.2.3 Chronic effects

Several studies on long-term effects of DEHP have been performed. In chronic studies, the lowest dose with observed effects (NOAEL is the highest dose with no observable adverse effects) using DEHP in the feed was 3.7 mg/kg bw. The value was based on effects on testicles in a 13-week study (Poon *et al.* 1997).

DEHP is a weak irritant to the skin but allergy has not been registered.

7.1.2.4 Bioavailability

The bioavailability by oral or dermal exposure has been estimated from toxico-kinetic studies (cf. above) to the results (table 7.2) which are used in the calculations.

TABLE 7.2 BIOAVAILABILITY AT EXPOSURE OF DEHP (KEMI 2000)

| Exposure route | Exposed | Human systemic bioavailability |
|----------------|----------|--------------------------------|
| Oral | Adults | 50% |
| | Children | 100% |
| Dermal | Adults | 5% |
| | Children | 5% |

7.1.3 Evaluation

7.1.3.1 Dermal exposure

Using a dermal absorption of 5% the maximum dermal absorption ($A_{\mbox{\tiny derm}}$) is 0.01 mg/kg bw/day. It should be noted that it is presumed that all chemical substance is absorbed in 1 day, which is unrealistic. However, for a tiered evaluation, it is considered acceptable.

Calculation example (textile B in table 7.5):

Assuming 100% absorption:

Adult exposure: $7.7 \times 0.5 / 70 = 0.055$ mg/kg bw

Child exposure: $7.7 \times 0.25/10 = 0.195$ mg/kg bw

T-shirt, child exposure: $7.7 \times 0.16 / 10 = 0.123$ mg/kg bw

Assuming 5% absorption:

Adult absorption (A_{derm} , adult): $0.055 \times 0.05 = 0.00275$ mg/kg bw Child absorption (A_{derm} , child): $0.195 \times 0.05 = 0.0096$ mg/kg bw

TABLE 7.3 DERMAL ABSORPTION OF DEHP

| Te | extile | Average | 0.5 kg textile | Adult | Child | Tshirt | A _{derm} . adult | A _{derm} . child |
|----|-----------------------------------|---------|-------------------|----------|----------|----------|---------------------------|---------------------------|
| | | mg/kg | mg | mg/kg/bw | mg/kg bw | mg/kg bw | mg/kg bw | mg/kg bw |
| В | 100% cotton, yellow (children) | 7.7 | 3.85 | 0.0550 | 0.1925 | 0.123 | 0.0028 | 0.0096 |
| Ε | Cotton/PET, brown | 2.9 | 1.45 | 0.0207 | 0.0725 | 0.046 | 0.0010 | 0.0036 |
| G | 100% cotton, animal motive | 3.6 | 1.8 | 0.0257 | 0.0900 | 0.057 | 0.0013 | 0.0045 |
| Π | 100% cotton, flowers | 4.8 | 2.4 | 0.0304 | 0.1200 | 0.076 | 0.0017 | 0.0060 |
| J | 100% flax | 3.9 | 1.95 | 0.0279 | 0.0975 | 0.062 | 0.0014 | 0.0049 |
| L | 100% viscose | 2.4 | 1.2 | 0.0171 | 0.0600 | 0.038 | 0.0009 | 0.0030 |
| М | 100% wool | 4.1 | 2.05 | 0.0293 | 0.1025 | 0.065 | 0.0015 | 0.0051 |
| 0 | 100% cotton (bear) | 2.6 | 1.3 | 0.0186 | 0.0650 | 0.041 | 0.0009 | 0.0033 |
| Q | 100% cotton (oilcloth) | 3.2 | 1.6 | 0.0229 | 0.0800 | 0.051 | 0.0011 | 0.0040 |
| Т | 100% PET (pillow) | 2.2 | 1.1 | 0.0157 | 0.0550 | 0.035 | 0.0008 | 0.0028 |
| М | aximum* | 8.6 | 4.3 | 0.0614 | 0.2150 | 0.137 | 0.0031 | 0.0108 |

^{*:} maximum concentration measured in the selected textiles

A chronic NOAEL 3.7 mg/kg bw/day was observed as the lowest value from several chronic studies. In the estimations on dermal absorption, to the lowest chronic NOAEL 3.7 mg/kg bw/day a margin of safety of more than 300 was observed. This is considered sufficient and no further refinements in estimations are performed. Therefore, DEHP in the tested textiles is not considered to represent any health risks at the measured concentrations.

7.1.3.2 Oral and inhalation exposure

By oral exposure is presumed a child sucking/chewing on textile equivalent to 400 cm² or 20 gram. The body weight of the child is set to 10 kg and bioavailability of DEHP to 100%. Based on these assumptions, the amount of substance taken up by the body is estimated, cf. equation in section 6.4, example and results in table below.

Calculation example of oral intake by child:

$$I_{oral, child} = 20 \text{ (g)} \times 7.7 \text{ (}\mu\text{g/g)} \times 1 \text{ (}100\%\text{)} \text{ / }10 \text{ (kg)} = 15.4 \text{ }\mu\text{g/kg} \text{ bw per event}$$

By inhalation it is presumed that the substance evaporates to the maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is $20~\text{m}^3$ and that inhalation by an adult person takes place 24 hours in the room (Inhalation: $\mu g/kg$ bw/day).

Based on these assumptions, the amount of substance taken up by the body by inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[7.7 \times 390.6/22.4 \times (3.4 \times 10^{-5})/101325] \times 10/20 = 2.25 \times 10^{-8}$ mg/m³

Inhalation = $2.25 \times 10^{-8} \times 20/70 = 6.44 \times 10^{-9} \text{ mg/kg bw/day} = 6.44 \times 10^{-6} \text{ µg/kg bw/day}$

TABLE 7.4 INTAKE OF DEHP BY CHILD (ORAL BY CHEWING ON TEXTILE) AND INHALATION BY ADULT

| | Textile | Average* | Oral, child | 'n | Inhalation |
|---|-----------------------------------|------------------|-------------|------------|------------|
| | | | | Inhalation | |
| | | mg/kg textile | μg/kg bw | μg/m³ | μg/kg bw |
| В | 100% cotton, yellow (children) | 7.7 | 15.4 | 2.25E-05 | 6.44E-06 |
| E | Cotton/PET, brown | 2.9 | 5.8 | 8.48E-06 | 2.42E-06 |
| G | 100% cotton, animal motive | 3.6 | 7.2 | 1.05E-05 | 3.01E-06 |
| I | 100% cotton, flowers | 4.8 | 9.6 | 1.40E-05 | 4.01E-06 |
| J | 100% flax | 3.9 | 7.8 | 1.14E-05 | 3.26E-06 |
| L | 100% viscose | 2.4 | 4.8 | 7.02E-06 | 2.01E-06 |
| М | 100% wool | 4.1 | 8.2 | 1.20E-05 | 3.43E-06 |
| 0 | 100% cotton (bear) | 2.6 | 5.2 | 7.61E-06 | 2.17E-06 |
| Q | 100% cotton (oilcloth) | 3.2 | 6.4 | 9.36E-06 | 2.67E-06 |
| Т | 100% PET (pillow) | 2.2 | 4.4 | 6.44E-06 | 1.84E-06 |

^{*:} Cf. table 7.1

The lowest value found in several chronic studies was a NOAEL of 3.7 mg/kg bw/day. Based on this value there is still a margin of safety of more than 200 (oral child) which may be considered sufficient. All estimated values on inhalation in table 7.5 are far below the NOAEL 3.7 mg/kg bw. A further refinement of the estimates was not considered necessary.

7.1.3.3 Summary conclusion

From the above results on DEHP in textiles, it is concluded that neither by oral, inhalation or dermal contact any health risk is expected from exposure of DEHP at the measured concentrations in textiles. However, it should be noted that the compound is on the list of undesirable substances due to its reprotoxic effects (MST 2000).

7.2 4-CHLORANILINE

7.2.1 Identification

 $CI - \sqrt{} NH_2$

Molecular weight 127.58

Synonyms *p*-Chloroaniline

1-Amino-4-chlorobenzene

The melting point is 72.5°C. The boiling point is 232°C at 1 atm pressure. The vapour pressure is 3.33 Pa at 25°C. The water solubility is 3900 mg/l. The octanol/water distribution coefficient log Kow is 1.83.

7.2.1.1 Classification

4-Chloraniline is classified under EU index no. 612-137-00-9 (Miljøministeriet 2002):

Carc2;R45 Carcinogenic. May cause cancer

T;R23/24/25 R43 Toxic. Toxic by inhalation, in contact with skin and if

swallowed. May cause sensitisation by skin contact

N;R50/53 Dangerous for the environment. Very toxic to aquatic

organisms; may cause long-term adverse effects in the

aquatic environment.

7.2.1.2 Source

4-Chloroaniline is used in the manufacture of colorants, pesticides and pharmaceuticals.

7.2.1.3 Chemical analyses

4-Chloroaniline has only been found in sample O (100% cotton, bear) in a concentration of 1.22 mg/kg \pm 3.4%. In no other sample, concentrations were found above the detection limit of 0.5 mg/kg.

7.2.2 Health

4-Chloranilin is acute toxic to humans and classified carcinogenic (cf. above).

Acute toxicity data:

| Acute oral, rat | LD_{50} | 310 mg/kg | Lewis and Sweet 1984 |
|----------------------|------------------|-----------|----------------------|
| Acute oral, mouse | LD ₅₀ | 100 mg/kg | Lewis and Sweet 1984 |
| Acute dermal, rat | $LD_{50}^{'}$ | 340 mg/kg | Lewis and Sweet 1984 |
| Acute dermal, cat | LDso | 239 mg/kg | Lewis and Sweet 1984 |
| Acute dermal, rabbit | LD ₅₀ | 360 mg/kg | Lewis and Sweet 1984 |

From the data mentioned above the acute oral toxicity LD_{50} is about 100 to 300 mg/kg which is relatively low.

Data for acute dermal toxicity ${\rm LD}_{\rm 50}$ is about 200 to 400 mg/kg which is also relatively low.

Of inhalation results was found that humans exposed to 44 mg/m³ for 1 minute developed severe toxic effects (Verschueren 1996).

4-Chloroaniline is considered carcinogenic (Miljøministeriet 2002). Therefore, no threshold limit value is set.

However if the presence of 4-chloroaniline (and other carcinogenic arylamines) is from degradation of azocolourants, a Directive on restriction of use of azocolourants include 4-chloroaniline. The directive states that the release of 4-chloroaniline should not exceed detectable concentrations, i.e. above 30 ppm in the finished textile articles or in the dyed parts thereof which may come into direct and prolonged contact with the human skin or oral cavity (EC 2002).

7.2.3 Evaluation

7.2.3.1 Dermal exposure

Dermal exposure and uptake of 4.chloroaniline is estimated for the textile in which it was observed and for a concentration corresponding to the detection limit. Because the dermal absorption is unknown 100% absorption is used.

Calculation (textile O in table 5.4):

Adult exposure: $1.22 \times 0.5 / 70 = 0.0087$ mg/kg bw Child exposure: $1.22 \times 0.25/10 = 0.0305$ mg/kg bw

T-shirt, child exposure: $1.22 \times 0.16 / 10 = 0.0195$ mg/kg bw

TABLE 7.5 DERMAL ABSORPTION OF 4-CHLORANILIN

| Sampl | Textile | Chloroaniline | 0.5 kg textile | Adult | Child | Tshirt |
|-------|--------------------|---------------|----------------|----------|--------|----------|
| е | | | | | | |
| | | mg/kg | mg | mg/kg/bw | mg/kg | mg/kg bw |
| | | | | | bw | |
| 0 | 100% cotton (bear) | 1.22 | 0.61 | 0.0087 | 0.0305 | 0.0195 |
| | Detection Limit | 0.5 | 0.25 | 0.0036 | 0.0125 | 0.0080 |

4-Chloraniline is measured in one sample above the detection limit. No dermal values for comparison are available. In general, any contact with the substance should be avoided, as it is carcinogenic.

7.2.3.2 Intake and inhalation

By oral exposure and potential uptake it is presumed that a child sucks or chews on a piece of textile equivalent to 400 cm² or 20 gram. The child body weight is set to 10 kg and the bioavailability 100%. Based on this, the amount of substance taken up is estimated.

Calculation example of oral intake by child:

$$I_{oral, child} = 20 \text{ (g)} \times 7.7 \text{ (}\mu\text{g/g)} \times 1 \text{ (}100\%\text{)} / 10 \text{ (kg)} = 2.44 \text{ }\mu\text{g/kg} \text{ bw per event}$$

By inhalation it is presumed that the substance evaporates to the maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m^3 , and that inhalation by an adult person takes place 24 hours in the room (Inhalation: $\mu g/kg \ bw/dag$).

Calculation example of inhalation by adult:

C inhalation = $[1.22 \times 127.58/22.4 \times (3.33)/101325] \times 10/20 = 1.14 \times 10^{-4} \text{ mg/m}^3$ Inhalation = $1.14 \times 10^{-4} \times 20/70 = 3.3 \times 10^{-5} \text{ mg/kg bw/day} = 3.3 \times 10^{-2} \text{ µg/kg bw/day}$

Table 7.6 Oral intake by child and inhalation by adult of chloroaniline

| Sampl | Textile | Chloroaniline | Oral, child | C Inhalation | Inhalation |
|-------|--------------------|---------------|-------------|--------------|------------|
| e | | | | | |
| | | mg/kg | mg/kg bw | μg/m³ | μg/kg bw |
| 0 | 100% cotton (bear) | 1.22 | 0.00244 | 0.114 | 0.033 |
| | Detection limit | 0.5 | 0.00100 | 0.047 | 0.013 |

Like for skin contact it is not possible to perform an assessment since the substance is carcinogenic and no threshold limit values has been set.

7.2.3.3 Conclusion

4-Chloroaniline was discovered above the detection limit in only one sample. It is not possible to evaluate its health risks at dermal contact, oral uptake or inhalation. The substance is classified carcinogenic and any contact with the substance should be avoided even at low concentrations.

However, relating to the directive on azocolourants (EC 2002) the one detected concentration in the textile sample O was far below 30 mg/kg and thus no health problems may be expected at the measured concentration and the current knowledge.

7.3 FORMALDEHYDE

7.3.1 Identification

Name Formaldehyde CAS no. 50-00-0 EINECS no. 200-001-8 Molecular formula CH_2O Molecular CH_2O CH_2 structure

Molecular weight 30.03 g/mol

Synonyms Formalin (formaldehyde in 37% solution)

Methaldehyde Methylene oxide Oxymethylene

Formaldehyde is a gas at room temperature. The melting point is -92°C. The boiling point is -19°C.

The water solubility is high. The information vary which may be because formaldehyde in water hydrates to methylene glycol (forms polymers). The most realistic level is between 400,000 mg/l (at 20° C) and 550,000 mg/l because polymers are formed at $\geq 55\%$ solutions (the solution becomes opalescent, IPCS 2002).

The vapour pressure is high: 518000 Pa at 25°C (Boublik *et al.* 1984) in its pure form (gas). In the calculations is used the vapour pressure for a 37% solution which is 202.6 Pa at 20°C. The octanol/water distribution coefficient is low with a measured log Kow 0.35. The adsorption coefficient is low with a log Koc 0.70 to 1.57.

The odour threshold is 0.5-1 ppm (0.02-1 mg/m³) in air and 0.8-102 mg/l in water for most people. Air concentrations associated with sensory irritation is generally above 0.3 to 0.5 ppm (0.3 to 0.6 mg/m³) (IPCS 1989, 2002).

7.3.1.1 Classification

Formaldehyde is classified under EU index no. 605-001-00-5 (Miljøministeriet 2002):

Carc3;R40 R43 Possible risks of irreversible effects. May cause

sensitisation by skin contact

T;R23/24/25 Toxic. Toxic by inhalation, in contact with skin or if

swallowed.

C;R34 Corrosive. Cause burns

It is noted that concentrations 1-5% is classified Carc3; R40 R43 and concentrations 0.2 to 1% classified R43.

7.3.1.2 Source

Formaldehyde is used in several products and processes. Only the most relevant to this project is mentioned.

Formaldehyde is added to several consumer products as preservative to prevent microbial destruction of the product.

Formaldehyde releasing formulations are used in the textile industry during manufacturing, especially in crease impregnation, e.g. production of crease-resistant and easy-care textiles but also as flame-retardant and other functional after-treatments. Formaldehyde releasing cross-binding substances may be used in textile printing. From such textiles formaldehyde may be released to air. In 1970-80, the average concentrations of formaldehyde in air of textile factories were measured to 0.2-2 ppm (0.24-2.4 mg/m³). At later measurements lower concentrations were found following lower content of formaldehyde in textiles (IPCS 2002).

Formalin is contained in several colorants, either in the manufacture or as preservative.

Crease-resistant preservatives that release formaldehyde have been used in viscose, cotton and cotton/polyester textiles since 1920. Hatch and Maibach (1995) has mentioned 9 resins, which release different amounts of formaldehyde.

A previously very used resin like urea-formaldehyde, UF-resins, are less used today the previously (Priha 1995). Also other formaldehyde releasing substances like cross-linking agents, which form cross-linking between the molecular structures in textile fibres, are substituted by formaldehyde-free substances. Information from USA exists, which state that the average concentration of free formaldehyde in textiles, is 100-200 mg/kg textile (Scheman *et al.* 1998). In Denmark, the normal concentration of formaldehyde is below 100 mg/kg textile and only rarely above 100 mg/kg (Larsen *et al.* 2000).

7.3.1.3 Chemical analyses

Formaldehyde is observed in three analysed textile samples at concentrations above 20 ppm, varying between 21 and 82 mg/kg textile, cf. table 7.7. After a first laundry, formaldehyde was only detected in one of the three textiles.

TABLE 7.7 ANALYSES RESULTS OF FORMALDEHYDE

| Sample no. | Formaldehyde according | |
|------------------------------------|------------------------|-----------------------|
| | to | laundry (mg/kg = ppm) |
| | EN ISO 14184 | |
| | (mg/kg = ppm) | |
| B) 100 % cotton, yellow (children) | - | not measured |
| C) Acrylic / nylon | - | not measured |
| F) 100% PET (colourful) | - | not measured |
| G) 100 % cotton (animal motive) | - | not measured |
| J) 100% flax | - | not measured |
| L) 100% viscose | 43 | - |
| M) 100% wool | 35 | 21 |
| N) 100 % cotton (Versace) | - | not measured |
| O) 100 % cotton (bear) | - | not measured |
| Q) 100 % cotton (oilcloth) | 82 | - |

^{*} Analysed after EN ISO 14184. The test method is selected partly because it is recommended in the EU eco-labelling of textiles, where the requirement is max. 30 ppm for products in skin contact and 300 ppm for others. And partly because it is an ISO test. Note that the test method prescribes that concentrations below 20 ppm shall be reported as "not detectable".

7.3.2 Health

Formaldehyde is toxic to humans and the compound suspected to be carcinogenic. In epidemiological studies on humans exposed to formaldehyde in the working environment, no causal relation between formaldehyde exposure and nasal-or lung tumours could be observed. Based on the data of formaldehyde's mode of action, formaldehyde is probably not carcinogenic to humans at low exposures especially at exposure conditions that do not induce cytotoxic effects (IPCS 1989).

Formaldehyde is eye and skin irritant (IPCS 1989.

7.3.2.1 Acute toxicity

Several data on acute toxicity exist. Of these are mentioned:

| Acute oral, rat | LD _{so} | 600 mg/kg | IUCLID 2002 |
|-------------------------|------------------------|---------------------|-------------------|
| Acute oral, mouse | LD ₅₀ | 42 mg/kg | IUCLID 2002/RTECS |
| Acute dermal, rabbit | LD ₅₀ | 270 mg/kg | IPCS 1989 |
| Acute inhalation, rat | LC ₅₀ , 4 h | 578 mg/m³ (480 ppm) | IPCS 1989 |
| Acute inhalation, mouse | LC ₅₀ , 4 h | 497 mg/m³ (412 ppm) | |

From the mentioned values it is noted that the acute oral toxicity is relatively high. The lowest acute oral toxicity determined as LD_{50} is 42 mg/kg.

The acute dermal toxicity is in a single study determined to be 2-300 mg/kg indicating that the compound is health hazardous by skin contact.

Relating to acute inhalation toxicity the mentioned values of LC_{50} below 1 mg/l (4 h), which is a low value, indicate that the compound is toxic by inhalation.

7.3.2.2 Long-term effects

Several long-term and chronic studies exist. The results are thoroughly discussed in several references, e.g. IPCS (1989 and 2002).

A two-year study with repeated oral administration to rats via drinking water gave the highest concentration without permanent adverse effects (NOAEC) of 260 mg/l, corresponding to 15 and 21 mg/kg bodyweight for male and female rats, respectively.

A test for dermal contact of 26 weeks showed skin irritation at the highest dose without permanent effects (NOAEC) at 0.1% solutions and a systemic effect NOAEC at 1% solution, which was the highest concentration tested.

Inhalation between 3 days to 2 years showed a NOAEC of 1.2 mg/m³ (1 ppm) with lesions of the nasal epithelium in rats.

Formaldehyde is known for its ability to cause sensitisation (allergy). Especially is formaldehyde recognised as being allergenic via skin contact and respiratory system (Thomsen 1990).

Formaldehyde is suspected to be carcinogenic by inhalation in animal studies.

7.3.3 Evaluation

In previous analyses of textiles the formaldehyde concentration were significantly higher than current analyses (IPCS 2002). The reduced concentrations are achieved by active efforts from industry, authorities and interest groups.

The concentrations in the sampled textiles are below 100 mg/kg. Seven out of 10 are below the 20 mg/kg which qualify the EU ecolabel "non-detectable". However formaldehyde is known as an airway allergen and a contact allergen (Thomsen 1990). The concentration at long-term exposures that may lead to sensitisation or allergy is unknown. The presence of formaldehyde may pose a problem to persons already allergic. Allergic persons are expected to react to even very small concentrations. No studies on the subject were available.

7.3.3.1 Dermal absorption

Dermal exposure to formaldehyde is calculated the same way as the previous compounds. 100% absorption is assumed.

Calculation example:

Adult exposure: $43 \times 0.5 / 70 = 0.307$ mg/kg bw Child exposure: $43 \times 0.25/10 = 1.075$ mg/kg bw

T-shirt, child exposure: $43 \times 0.16 / 10 = 0.688$ mg/kg bw

TABLE 7.8 DERMAL UPTAKE OF FORMALDEHYDE

| Textile | | Formaldehyde | 0.5 kg textile | Adult | Child | Tshirt |
|---------|------------------------|--------------|-------------------|----------|----------|----------|
| | | mg/kg | mg | mg/kg bw | mg/kg bw | mg/kg bw |
| L | 100% viscose | 43 | 21.5 | 0.3071 | 1.0750 | 0.688 |
| М | 100% wool | 35 | 17.5 | 0.2500 | 0.8750 | 0.560 |
| Q | 100% cotton (oilcloth) | 82 | 41 | 0.5857 | 2.0500 | 1.312 |

The highest estimated absorption is 2 mg/kg bw. This is approx. 100 times less than the acute toxic value that indicates the compound to be toxic by dermal contact. However, the use of oilcloth for clothing purposes is considered very limited.

7.3.3.2 Oral intake and inhalation

By oral exposure is presumed a child sucking/chewing on textile equivalent to 400 cm² or 20 g. The body weight of the child is set to 10 kg and the bioavailability of formaldehyde to 100%. Based on these assumptions, the

amount of substance taken up by the body is estimated, cf. equation in section 6.4, example and results in table below.

Calculation example of oral intake by child:

 $I_{oral, child} = 20 \text{ (g)} \times 43 \text{ (µg/g)} \times 1 \text{ (100\%)} / 10 \text{ (kg)} = 86 \text{ µg/kg bw per event}$

By inhalation it is presumed the vapour pressure is comparable to a 37% formaldehyde solution and that the substance evaporates to the maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m^3 , and that inhalation by an adult person takes place 24 hours in the room (Inhalation: $\mu g/kg \text{ bw/day}$).

Based on these assumptions, the amount of substance taken up by the body via inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[43\times30.03/22.4\times202.6/101325] \times 10/20 = 0.0576 \text{ mg/m}^3$ Inhalation = $0.0576\times20/70 = 0.0164 \text{ mg/kg bw/day}$

TABLE 7.9 ORAL INTAKE AND INHALATION OF FORMALDEHYDE

| Textile | | Formaldehyde | Oral, child | C Inhalation | Inhalation | |
|---------|------------------------|--------------|-------------|--------------|------------|--|
| | | mg/kg | mg/kg bw | mg/m³ | mg/kg bw | |
| L | 100% viscose | 43 | 0.086 | 0.0576 | 0.0164 | |
| М | 100% wool | 35 | 0.070 | 0.0469 | 0.0134 | |
| Q | 100% cotton (oilcloth) | 82 | 0.164 | 0.1099 | 0.0314 | |

From the table it is observed that the highest estimated oral intake was 0.16 mg/kg. This is approx. 100 times lower than the chronic NOAEL of 15 mg/kg bw. Therefore, no health risk from oral intake during sucking on the sampled textiles is expected.

On inhalation the inhalation concentrations are below the threshold limit value of 0.4 mg/ m³ (AT 2002), below the two year inhalation NOAEC of 1.2 mg/m³ and below the level of sensory irritation of 0.3 mg/m³ for all textiles.

7.3.3.3 Conclusion

Formaldehyde is under suspicion of being carcinogenic by inhalation. However, the values estimated for dermal, oral and inhalation are considered acceptable in relation to the scenarios because the estimated values are below the found chronic study values. It is noted that 3 of the textile samples (L, M and Q) exceed the ecolabel criteria of 30 ppm in the textile.

7.4 NAPHTHALENE

7.4.1 Identification

Name Naphthalene CAS no. 91-20-3 EINECS no. 202-049-5 Molecular formula $C_{10}H_{8}$

Molecular structure

Molecular weight

128.18 g/mol Synonyms Naphthalin

Naphthene

The melting point is 80.2°C. The boiling point is 218°C. The vapour pressure is 10.5 Pa at 25°C. The water solubility is 31 mg/l at 25°C. The distribution coefficient n-octanol/water log Kow is 3.4. The distribution coefficient log Koc is estimated to 3.26.

7.4.1.1 Classification

Naphthalene is classified under EU index no. 601-052-00-2:

Possible risks of irreversible effects Carc3;R40* Xn; R22 Harmful. Harmful if swallowed

Dangerous for the environment. Very toxic to aquatic N;R50/53

organisms, may cause long-term adverse effects in the

aquatic environment

*: Added at 29th ATP (2002) and therefore not yet included in the List of Dangerous Substances (Miljøministeriet 2002).

7.4.1.2 Source

Naphthalene is used mostly in the production of other chemical substances. The major part is used in the manufacture of phthalic acid anhydride. Naphthalene is also used in the production of colorants via the intermediates naphthol and naphthalene sulphonic acid. The colorants are usually azocolorants.

Naphthalene in the production of naphthalene sulphonic acids is also used for other purposes. A minor amount is used in the manufacture of mothballs, for specific effects in the film industry (pyrotechnics), creosote and tar paints and in the manufacture of pesticides, etc.

7.4.1.3 Chemical analyses

The concentration measured in the textile samples is presented in the table below.

TABLE 7.10 SUMMARY OF ANALYTICAL DOUBLE DETERMINATION OF NAPHTHALENE IN TEXTILES (MG/KG)

| Sampl | Textile | Naph_1 | Naph_2 | Average |
|-------|--------------------------------|--------|--------|---------|
| e | | | | |
| | | mg/kg | mg/kg | mg/kg |
| В | 100% cotton, yellow (children) | - | - | - |
| E | Cotton/PET, brown | - | - | - |
| G | 100% cotton, animal motive | - | - | - |
| I | 100% cotton, flowers | - | - | - |
| J | 100% flax | 0.12 | 0.08 | 0.10 |
| L | 100% viscose | 2.4 | 3.8 | 3.1 |
| М | 100% wool | 0.47 | 0.68 | 0.58 |
| 0 | 100% cotton (bear) | 0.06 | 0.04 | 0.05 |
| Q | 100% cotton (oilcloth) | 0.15 | 0.16 | 0.16 |
| T | 100% PET (pillow) | - | - | - |

^{-:} below detection limit of 0.01 mg/kg

Naphthalene was measured above the detection limit 0.01 mg/kg in 5 of the samples.

7.4.2 Health

Naphthalene can be taken up via all exposure routes (inhalation, percutaneous and oral).

7.4.2.1 Acute toxicity

Based on several reported incidences of acute poisoning with acute systemic effects after oral intake of naphthalene, e.g. as mothballs, haemolytic anaemia is considered the major problem to humans (Gosselin *et al.* 1984). From the data, no limit for effects (NOAEL) could be established. Therefore, any significant exposure at the mg/kg bw level is considered to be of concern.

Exposure to children from textiles stored for prolonged periods with naphthalene containing mothballs also gives cause of concern. Documented evidence exists for the development of serious haemolytic anaemia after such an exposure even if there were no quantitative information on levels or duration of the exposure.

Considering local effects on the respiratory system after repeated exposure at inhalation and carcinogenic effects there is reason of concern wherever there is possibilities of repeated exposure by inhalation of naphthalene. The use of mothballs is therefore not recommended. Other data indicate a significant toxicity of naphthalene after oral administration.

7.4.2.2 Oral intake

Acute oral toxicity to rats is determined to 2300 mg/kg (LD_{50}). The lowest oral dose with lethal effects was 1500 mg/kg for females and 2000 mg/kg for males (Gaines 1969).

For mouse the acute oral toxicity LD_{50} was 533 mg/kg for males and 710 mg/kg for females (Shopp *et al.* 1984).

At repeated oral exposure the highest dose where no adverse effects were observed (NOAEL) 133 mg/kg for systemic toxicity in a 90 days mouse study.

Naphthalene has previously been used as anthelmintic and vermicide (Reynolds 1982). The dose is unknown but probably at the level 0.1-0.5 g, three times a day, corresponding to approx. 4-20 mg/kg bw/day (ACGIH 1991).

Several incidents of oral intake of mothballs are described of which the majority included children. In all cases haemolytic anaemia was diagnosticised. However, a dose-response concentration could not be deducted. One mothball weighs 0.5-2 g and contains of 97-100% naphthalene, whether they swallowed or just sucked on is unknown.

7.4.2.3 Dermal contact

Few references were found on acute lethal effects following dermal contact. In a study by Gaines (1969) 40 rats were exposed to dermal contact at 2500 mg/kg without any mortalities.

Another study on dermal contact included repeated applications for 6 hours per day, 5 days a week for 13 weeks (90 days) at up to 1000 mg/kg bw/day. The highest level without adverse effects (NOAEL) was 1000 mg/kg for systemic effects even though mild skin irritation could be observed (Bushy Run 1986).

Based on a rat study that indicates that naphthalene may be carcinogenic has caused an amendment to the classification "Carc. cat3" (29 ATP 2002).

7.4.3 Bioavailability

The absorbed naphthalene is excreted quickly in the urine. Rats administered single dosages of ¹⁴C-labelled naphthalene excreted 75.6% of the radioactivity within 24 hours and after 72 hours, 83% was excreted via urine, 6% via faeces, 4% remained in the body. The remaining part was unaccounted for (Bakke *et al.* 1985).

7.4.3.1 Inhalation

Based on a 28 days inhalation study on rats where local respiratory effects (destruction of nasal epithelia tissue) a lowest level for long-term effects (LOAEL) was determined to 5 mg/m³ (IUCLID 1993).

7.4.3.2 Dermal

No data on dermal absorption were found but the high lipophilicity of naphthalene indicates that dermal absorption is a likely exposure route.

In an unpublished study, 500 mg naphthalene was applied to the skin of rabbits for 4 hours. In half the animals (3) erythremes were visible after 30 minutes to 6 days of exposure (IUCLID).

The available data present no possibility to determine a highest level of no lasting effects (NOAEL) on account of haemolytic anaemia. Therefore any exposure in the level mg/kg body weight are considered of concern. Thus, the risk of exposure to children from textiles stored for prolonged periods together with naphthalene mothballs is considered to be of concern. Documented evidence exists on the development of serious haemolytic anaemia from such exposures even if the duration and amount of exposure is unknown.

Referring to the carcinogenic effect no conclusions from the limited data on man can be made. The carcinogenic potential of naphthalene is well-examined in animal studies. In a 2-year inhalation study on rats an increased incidence of respiratory epithelial adenomas and olfactory epitelial neuroblastomas were observed even at the lowest exposure of 10 ppm (50 mg/m³) which is considered the result of chronic tissue irritation.

7.4.4 Evaluation

7.4.4.1 Dermal absorption

Dermal exposure and absorption of naphthalene is estimated from the measured average concentrations and the maximum concentration. The absorption is assumed 100%.

Calculation example (textile B in table):

Adult exposure: $0.1 \times 0.5 / 70 = 0.0007$ mg/kg bw Child exposure: $0.1 \times 0.25/10 = 0.0025$ mg/kg bw T-shirt, child exposure: $0.1 \times 0.16 / 10 = 0.0016$ mg/kg bw

TABLE 7.11 ABSORPTION AFTER DERMAL EXPOSURE TO NAPHTHALENE

| Textile | | Average | 0.5 kg textile | Adult | Child | Tshirt |
|---------|------------------------|---------|-------------------|----------|----------|-------------|
| | | mg/kg | mg | mg/kg/bw | mg/kg bw | mg/kg bw |
| J | 100% flax | 0.1 | 0.05 | 0.0007 | 0.0025 | 0.0016 |
| L | 100% viscose | 3.1 | 1.55 | 0.0221 | 0.0775 | 0.0496 |
| М | 100% wool | 0.58 | 0.29 | 0.0041 | 0.0145 | 0.0093 |
| 0 | 100% cotton (bear) | 0.05 | 0.025 | 0.0004 | 0.0013 | 0.0008 |
| Q | 100% cotton (oilcloth) | 0.16 | 0.08 | 0.0011 | 0.0040 | 0.0026 |
| | Maximum | 3.8 | 1.9 | 0.0271 | 0.0950 | 0.0608 |

None of the estimated concentrations exceeds 1 mg/kg bw/day even at 100% absorption.

The highest concentration of naphthalene was measured in viscose. It might be a cause of concern of the textile is stored with mothballs of naphthalene. However, the probability is considered low for Danish consumers and the conclusion is that there is no reason for immediate concern.

7.4.4.2 Oral intake and inhalation

By oral exposure is presumed a child sucking/chewing on textile equivalent to 400 cm² or 20 g. The body weight of the child is set to 10 kg and the bioavailability 100%. Based on these assumptions, the amount of substance taken up by the body is estimated, cf. equation in section 6.4, example and results in table below.

Calculation example of oral intake by child:

$$I_{oral, child} = 20 \text{ (g)} \times 0.1 \text{ (µg/g)} \times 1 \text{ (100\%)} / 10 \text{ (kg)} = 2 \text{ µg/kg bw per event}$$

By inhalation it is presumed that the substance evaporates to its maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m^3 , and that inhalation by an adult person takes place 24 hours in the room (Inhalation: $\mu g/kg$ bw/day).

Based on these assumptions, the amount of substance taken up by the body via inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[0.1 \times 128.18/22.4 \times 10.5/101325] \times 10/20 = 2.96 \times 10^{-5} \text{ mg/m}^3$ Inhalation = $2.96 \times 10^{-5} \times 20/70 = 8.47 \times 10^{-6} \text{ mg/kg bw/day}$

TABLE 7.12 ORAL INTAKE AND INHALATION OF NAPHTHALENE

| Textile | e | Oral,child | C inhalation | Inhalation |
|---------|------------------------|------------|--------------|------------|
| | | mg/kg bw | μg/m³ | μg/kg bw |
| J | 100% flax | 0,0002 | 0,030 | 0,008 |
| L | 100% viscose | 0,0062 | 0,919 | 0,263 |
| М | 100% wool | 0,0012 | 0,172 | 0,049 |
| 0 | 100% cotton (bear) | 0,0001 | 0,015 | 0,004 |
| Q | 100% cotton (oilcloth) | 0,0003 | 0,047 | 0,014 |
| | Maximum | 0,0076 | 1,127 | 0,322 |

From the results is observed that none of the amounts taken in by oral exposure or inhalation will exceed absorption at the mg/kg level. Therefore no health risk is implied for textiles at the measured concentrations.

7.4.4.3 Conclusion

Naphthalene implies no health risks to the consumer by dermal contact, oral intake or inhalation at the concentrations measured in the selected textiles.

7.5 NICOTINE

7.5.1 Identification

Name Nicotine

IUPAC name (S)-3-(1-methylpyrrolidin-2-yl)-pyridin

CAS no. 54-11-5 S-isomer 22083-74-5 RS-isomers

75202-10-7 unknown stereoisomer

EINECS no. 200-193-3 Molecular formula $C_{10} H_{14} N_2$ Molecular structure $C_{10} H_{3} N_2$

Molecular weight 162.22 g/mol

Synonyms 3-(1-methyl-2-pyrrolidinyl)-pyridin

1-methyl-2-(3-pyridyl)-pyrrolidine

Nikotin

The melting point is -80°C. The boiling point is 246°C and the vapour pressure is 5.65 Pa at 25°C. The octanol/water distribution coefficient log Kow is 0.93 at 25°C. The substance is miscible with water (Tomlin 1997).

7.5.1.1 Classification

Nicotine is classified under EU index no. 614-001-00-4 (Miljøministeriet 2002):

T;R25 Toxic. Toxic if swallowed

Tx;R27 Very toxic. Very toxic in contact with skin

N;R51/53 Dangerous for the environment. Toxic to aquatic organisms,

may cause long-term adverse effects in the aquatic environment

7.5.1.2 Source

The source of the observed nicotine is unknown. Extract of nicotine from tobacco plants has a historical use as insecticide in crops but has been substituted by technical nicotine and nicotine sulphate. The extract consisted mostly of the S-isomer where the technical nicotine is a racemic mixture of R and S isomers (Tomlin 1997). The chemical analysis does not disclose whether the nicotine is of natural or technical origin. A possible contamination of the samples from cigarette smoking could not be eliminated.

Besides being used as insecticide nicotine is also used as pest fumigant.

7.5.1.3 Chemical analyses

In the chemical analysis nicotine was searched for specifically using a nicotine standard. Nicotine was found in all samples except one. A summary of the measured concentrations is presented in the table below.

Table 7.13 Summary of measured nicotine double determinations. Results are given in

MG/KG TEXTILE

| Textile | | Nicotin1 | Nicotin2 | Average |
|---------|--------------------------------|----------|----------|---------|
| | | mg/kg | mg/kg | mg/kg |
| В | 100% cotton, yellow (children) | 0.22 | 0.11 | 0.17 |
| E | Cotton/PET, brown | 0.2 | 0.02 | 0.11 |
| G | 100% cotton, animal motive | 0.25 | 0.14 | 0.20 |
| I | 100% cotton, flowers | 0.16 | 0.11 | 0.14 |
| J | 100% flax | 0.14 | 0.08 | 0.11 |
| L | 100% viscose | - | - | - |
| М | 100% wool | 0.09 | 0.13 | 0.11 |
| 0 | 100% cotton (bear) | 0.05 | 0.03 | 0.04 |
| Q | 100% cotton (oilcloth) | 0.11 | 0.13 | 0.12 |
| Т | 100% PET (pillow) | 0.19 | 0.16 | 0.18 |

^{-:} below detection limit 0,02 mg/kg

The measured concentrations are within a narrow range except two samples. This could indicate a contamination of the samples. Residues from potential pesticide would cause a larger variation in concentrations, and because other pesticides may have been substituting the use of nicotine.

The use of nicotine as pesticide is probably only relevant in the Far East. However, it should be noted that tobacco growing often takes place at the same locations as cotton growing

7.5.2 Health

7.5.2.1 Oral intake

A likely lethal oral dose to human is probably less than 5 mg/kg for a person weighing 70 kg (Gosselin *et al.* 1984). It is assumed that oral intake of 40-60 mg nicotine is lethal to human (US-EPA 1987).

In animal studies, LD_{50} acute oral, rat is 50-60 mg/kg (Klaassen *et al* 1995). Of other data is mentioned:

| LD ₅₀ oral, rat | 188 mg/kg | Hayes and Laws 1991 |
|------------------------------|-----------|----------------------|
| LD ₅₀ oral, mouse | 24 mg/kg | Hayes and Laws 1991. |

7.5.2.2 Dermal absorption

Nicotine is absorbed easily percutaneously and is considered toxic at skin contact. Lethal oral dose to human is given as 40-60 mg (Hardman *et al.*1996). To rabbits, a dermal acute toxicity (LD_{50}) of 140 mg/kg (Lewis 1996) is found. On dermal toxicity, an acute percutaneous LD_{50} of 50 mg/kg to rabbits has been found. By direct intravenous administration LD_{50} to rats was determined to 1 mg/kg (Gossel and Brinker 1994).

7.5.2.3 Inhalation

Nicotine is easily absorbed from the respiratory tract, mucous membranes in mouth and via skin (Hardman *et al.* 1996). Nicotine and it metabolites are excreted quickly via the kidneys (Hardman *et al.* 1996).

7.5.2.4 Threshold limit values

TLV-TWA: 0.5 mg/m³ (Clansky 1990) note: penetrates skin AT-TLV: 0.5 mg/m³ (AT 2002) note: H (penetrates skin)

7.5.3 Evaluation

7.5.3.1 Dermal absorption

The table below summarises the estimated absorption concentrations resulting from dermal exposure of the measured concentrations in textile samples. Dermal absorption is assumed 100%.

Calculation example (textile 1 in table):

Adult absorption: $0.17 \times 0.5 / 70 \times 1 = 0.0012$ mg/kg bw Child absorption: $0.17 \times 0.25/10 \times 1 = 0.0043$ mg/kg bw

T-shirt, child absorption: $0.17 \times 0.16 / 10 \times 1 = 0.0027$ mg/kg bw

TABLE 7.14 ABSORPTION BY DERMAL CONTACT TO NICOTINE

| Textile | Average | 0.5 kg tøj | Adult | Child | Tshirt |
|-----------------------------------|---------------|------------|----------|----------|----------|
| | mg/kg textile | mg | mg/kg bw | mg/kg bw | mg/kg bw |
| 100% cotton, yellow (children) | 0.17 | 0.085 | 0.0012 | 0.0043 | 0.0027 |
| Cotton/PET, brown | 0.11 | 0.055 | 0.0008 | 0.0028 | 0.0018 |
| 100% cotton, animal motive | 0.20 | 0.1 | 0.0014 | 0.0050 | 0.0032 |
| 100% cotton, flowers | 0.14 | 0.07 | 0.0010 | 0.0035 | 0.0022 |
| 100% flax | 0.11 | 0.055 | 0.0008 | 0.0028 | 0.0018 |
| 100% wool | 0.11 | 0.055 | 0.0008 | 0.0028 | 0.0018 |
| 100% cotton (bear) | 0.04 | 0.02 | 0.0003 | 0.0010 | 0.0006 |
| 100% cotton (oilcloth) | 0.12 | 0.06 | 0.0009 | 0.0030 | 0.0019 |
| 100% PET (pillow) | 0.18 | 0.09 | 0.0013 | 0.0045 | 0.0029 |
| Maximum | 0.25 | 0.125 | 0.0018 | 0.0063 | 0.0040 |

The evaluation is based on dermal effects observed above 1 mg/kg and the exposure assuming 100% absorption at maximum is 6 µg/kg bw.

The conclusion is that nicotine did not give reason to expect health risks at the concentrations measured in textile.

7.5.3.2 Oral intake and inhalation

By oral exposure is presumed a child sucking/chewing on textile equivalent to 400 cm² or 20 g. The body weight of the child is set to 10 kg and the bioavailability 100%. Based on these assumptions, the amount of substance taken up by the body is estimated, cf. equation in section 6.4, example and results in table below.

Calculation example of oral intake by child:

$$I_{oral child} = 20 \text{ (g)} \times 0.17 \text{ (µg/g)} \times 1 \text{ (100\%)} / 10 \text{ (kg)} = 0.34 \text{ µg/kg bw per event}$$

By inhalation it is presumed that the substance evaporates to its maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m³, and that inhalation by an adult person takes place 24 hours in the room (Inhalation: µg/kg bw/day).

Based on these assumptions, the amount of substance taken up by the body via inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[0.17 \times 162.22/22.4 \times 5.65/101325] \ 10/\ 20 = 3.4 \times 10^{-5} \ \text{mg/m}^3$ Inhalation = $3.4 \times 10^{-5} \times 20/70 = 9.8 \times 10^{-6} \ \text{mg/kg bw/day}$

TABLE 7.15 ORAL INTAKE AND INHALATION OF NICOTINE

| Tex | tile | Nicotine | Oral, child | C Inhalation | Inhalation |
|-----|--------------------------------|------------------|-------------|--------------|------------|
| | | mg/kg textile | μg/kg bw | μg/m³ | μg/kg bw |
| В | 100% cotton, yellow (children) | 0.17 | 0.340 | 0.034 | 0.010 |
| Ε | Cotton/PET, brown | 0.11 | 0.220 | 0.022 | 0.006 |
| G | 100% cotton, animal motive | 0.2 | 0.400 | 0.040 | 0.012 |
| I | 100% cotton, flowers | 0.14 | 0.280 | 0.028 | 0.008 |
| J | 100% flax | 0.11 | 0.220 | 0.022 | 0.006 |
| М | 100% wool | 0.11 | 0.220 | 0.022 | 0.006 |
| 0 | 100% cotton (bear) | 0.04 | 0.080 | 0.008 | 0.002 |
| Q | 100% cotton (oilcloth) | 0.12 | 0.240 | 0.024 | 0.007 |
| Т | 100% PET (pillow) | 0.18 | 0.360 | 0.036 | 0.010 |
| | Maximum | 0.25 | 0.500 | 0.050 | 0.014 |

As observed from the estimated results the oral intake is far below 1 mg/kg: all values estimated to < 1µg/kg bw. The threshold limit value for the working environment is 0.5 mg/m 3 (AT 2002) The estimated concentrations in the consumer scenarios are at maximum 0,05 µg/m 3 . Thus, a margin of safety of approx. 10,000 to the threshold limit value in the working environment is considered sufficient.

7.5.3.3 Conclusion

It is concluded that the measured concentrations in textile gave no reason to expect health risks by contact to skin, oral intake or by inhalation.

7.6 Nonylphenol / nonylphenol ethoxylate

Nonylphenol and nonylphenol ethoxylates have been measured in textiles of cotton. Nonylphenol is not used directly but is considered to be a degradation product from the use of nonylphenol ethoxylate, which is used in textile processes.

7.6.1 Nonylphenol ethoxylate

7.6.1.1 Identification

Name Nonylphenol ethoxylate (NPE)

CAS no. 9016-45-9 Nonylphenol ethoxylate (EO >1)

Molecular formula $C_{15} H_{24} O (C_2 H_4 O) n$

Structure formula $C_9H_{19}-(C_6H_4)-(OC_2H_4)-OH$

Molecular weight $220 + n \times 44$ n: number of ethyloxide units

Synonyms Nonylphenol polyoxyethylene ether

Nonylphenol polyethylene glycol Nonylphenol polyethylene glycolether

Of detected substances is mentioned nonylphenol mono- and diethoxylate. CAS, numbers are presented below:

| No. EO | CAS no.: | Chemical name |
|--------|------------|---|
| 1 | 104-35-8 | 2-(p-nonylphenoxy)-ethanol, blanding af nonyl isomere |
| 1 | 27986-36-2 | 2-(nonylphenoxy)-ethanol |
| 2 | 20427-84-3 | 2-(2-(4-nonylphenoxy) ethoxy-ethanol |
| 2 | 27176-93-8 | 2-(2-(nonylphenoxy)-ethoxy-ethanol |

The melting point vary with the chain length of the ethyleneoxide between – 6°C (EO 7) and 67°C (EO 40). The vapour pressure is given as <10 Pa (EO 9). The water solubility is >1000 mg/l for NPE EO9 at 20°C but vary with the branching of the alkyl part of the molecule and is directly proportional to the number of ethyleneoxide units.

7.6.1.2 Classification

Nonylphenol ethoxylates are not classified.

7.6.1.3 Source

Nonylphenol ethoxylate (NPE) is manufactured by reacting nonylphenol with ethylene oxide. Nonylphenol ethoxylate is a non-ionisk tenside (surfactant) and is used among other in textile processing.

NPE is degraded from the long ethylene oxide chains by splitting of the ethylene oxide (EO) units until only the short-chained NPEs are left, typically mono- and diethylene oxide. The degradation rate decreases with increasing EO-chain length and branching.

Alkyl phenol ethoxylates is used in the textile industry for washing and scouring of raw cotton. The cotton is rinsed thoroughly after the treatment but residues of NPEO may remain in small amounts. NPEO derived surfactants may also be used for other purposes than washing of cotton. In later treatments of the textile, NPEO may be included as emulgator and dispersion agent. All mentioned uses may be the explanation of the recovered residues.

7.6.1.4 Health

In toxico-kinetic studies with administration of 14 C-labelled NPE (EO9), 70% was recovered in faeces and 20 % in the urine. Based on a number of 90-day studies in rats and dogs, LOAEL (lowest dose with observable adverse effects) was determined to 40 mg/kg bw/day (Nielsen *et al.* 1999). NPEO is determined to have an acute oral toxicity LD $_{50}$ of 1310 mg/kg in rats. By percutaneous absorption the acute toxicity in rabbits LD $_{50}$ is determined to 2120 mg/kg (RTECS 1999).

NPEO is not ready biodegradable (MITI 1992) but degrades slowly to substances of which some are more persistent such as nonylphenol, especially under anaerobic conditions.

7.6.2 Nonylphenol

7.6.2.1 Identification

CAS no. 25154-52-3 Nonylphenol (NP)

84852-15-3 4-Nonylphenol, branched (4-NP)

EINECS no. 246-672-0 NP

284-325-5 4-NP

 $Molecular\ formula \quad \ C_{_{15}}\,H_{_{24}}\,O$

Molecular structure

 HO \longleftarrow $\mathsf{C}_{\scriptscriptstyle{9}}\mathsf{H}_{\scriptscriptstyle{19}}$

Molecular weight 220.3 g/mol

Synonyms Isononylphenol CAS no. 11066-49-2

Nonylphenol, branched CAS no. 90481-04-2 4-Nonylphenol, linear CAS no. 104-40-5

The name "nonylphenol" is used on a large number of isomer substances having a phenol ring structure and alkyl chain of C_9H_{19} . The variation includes the location of the nonyl group (C_9H_{19}) on the phenyl molecule, the number and location of branching of the alkyl chain.

Some of the branched molecules have their own CAS numbers. The CAS no. 25154-52-3 originally covered all nonylphenols but later only the linear molecule while the branched have received a CAS no. of their own. The commercial available nonylphenol is mainly 4-nonylphenol with branched alkyl chain together with other isomers and goes under the CAS no. 84852-15-3.

The melting point is approx. -8°C but may vary a little for the isomers. The boiling point is approx. 300°C but decomposes at slightly lower temperatures. The vapour pressure is approx. 0.3 Pa at 25°C. The water solubility is approx. 10 mg/l (IUCLID) but may be pH dependent. The n-octanol/water distribution coefficient log Kow is 4.48.

Having an adsorption coefficient log Koc 4.4-5.7, NP is expected to adsorb strongly to organic matter.

NP is not very volatile and residues in textile is expected to remain there during use or until it may be washed out.

7.6.2.2 Classification

Nonylphenol and 4-nonylphenol are both classified under EU index no. 601-053-00-8 as:

Xn; R22 Harmful. Harmful if swallowed

C; R34 Corrosive. Causes burns

N;R50/53 Dangerous for the environment. Very toxic to aquatic

organisms, may cause long-term adverse effects in the aquatic

environment

According to 29ATP (ATP 2002) an addition has been made: Repr.Cat.3; R62/63 (Possible risk of impaired fertility, possible risk of harm to the unborn child)

7.6.2.3 Use in textiles

Nonylphenol ethoxylates (NPEO) is manufactured by ethoxylation of nonylphenol. Thus besides being a residue from production, nonylphenol can also be a degradation product from the degradation of nonylphenol ethoxylate.

7.6.3 Health

7.6.3.1 Oral intake

By oral administration nonylphenol is quickly absorbed in the gastrointestinal tract and distributed via the blood stream and finally excreted via urine and faeces (Fennel and McNeela 1997). The amounts are not included in the study.

In Knaak *et al.* (1996), ¹⁴C-labelled nonylphenol administered orally to rats as single dosages of 6.6 mg/kg. Approximately 70% of the administered radioactivity were recovered in faeces and 20% in urine within 4 days. The presence in urine indicates that a substantial absorption has taken place.

In a study including two human volunteers one person was orally administered 5 mg nonylphenol ($66 \mu g/kg$ bw). The concentrations in blood peaked after 1 hour. The study found that the oral bioavailability of nonylphenol was approx. 20%. Approximately 10% of dose were excreted via urine within 8 hours and 1.5% via faeces within 56 hours (Müller 1997).

Bioaccumulation in lipid tissue has not been observed in mammalian studies but only limited data exist.

Based on the available data it is concluded that the major absorption takes place in the gastrointestinal tract. Nonylphenol is distributed in the entire body with the highest concentrations in lipid tissues. The main excretion is via faeces and urine. The bioavailability is indicated to be 10-20% of administered dose. Percutaneous absorption is low based on the few available data but some penetration does take place especially in the upper skin layers (*stratum corneum*).

Data from animal studies are included. Acute oral toxicity in rats LD_{50} is 1200-2400 mg/kg. The lowest dosage with observable adverse effects (LOAEL) by oral administration is determined to 15 mg/kg/day. Histopathological changes in kidneys is observed in repeated toxicity studies lasting 20 weeks and using 3 generations of rat (NTP 1997). The highest oral dosage without any observable adverse effects (NOAEL) is 15 mg/kg/day for reproduction toxicity based on effects in the reproduction cycle of rats (NTP 1997). The report (NTP 1997) concluded that exposure during several generations might result in minor disturbances in the reproduction ability of the offspring.

A direct comparison between exposure and effect is unrealistic due to the reduced bioavailability. If the bioavailability of 10% is compensated for then NOAEL is reduced with a factor of 10, i.e. NOAEL 1.5 mg/kg/day.

For nonylphenol, a TDI (tolerable daily intake) is determined to 0.005 mg/kg bw/day in Nielsen *et al.* (1999). For nonylphenol ethoxylate the same authors has determined a TDI to 0.013 mg/kg bw/day.

7.6.3.2 Dermal absorption

The percutaneous absorption of NP has been studied in rats, pigs and human skin using 14 C labelled NP over 8 hours. The absorption was determined to 0.1% and the penetration approx. 4% of applied dosage at 0.3 mg/cm 2 . The

recovery was 1.7% in *stratum corneum* (Monteiro-Riviere *et al.* 1999). The result indicate that nonylphenol is only absorbed to a minor degree even if limited penetration does happen.

The acute oral toxicity for rabbits LD_{50} was 2031 mg/kg (Smyth *et al.* 1969) indicating a low acute toxicity.

7.6.4 Evaluation

7.6.4.1 Chemical analyses

The consumer does not get into contact with the pure substance unless residues of NPEO, unreacted NP or NP as degradation product is potentially present in the textiles. In the study both substances was recovered at levels above detection level.

TABLE 7.16 SUMMARY OF MEASURED CONCENTRATIONS OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES (MG/KG)

| Textile | NP | NP1 + NP2 | Σ NP, NP1, NP2 |
|-----------------------------------|-------------|------------|----------------|
| B) 100% cotton, yellow (children) | 0.5 ± 22% | 5.0 ± 2.5% | 5.5 |
| G) 100% cotton (animal motive) | 1.8 ± 1.5% | 16 ± 2.5% | 17.8 |
| O) 100% cotton (bear) | <0.1 | <3 | <3.1 |
| Q) 100% cotton (oilcloth) | 6.4 ± 24.5% | 20 ± 5.6% | 26.4 |

NP: Nonylphenol. NP1: Nonylphenol monoethoxylate, NP2: Nonylphenol diethoxylate

7.6.4.2 Dermal absorption

The estimated dermal exposures at the used presumptions indicate that using a 100% absorption could mean an exceeding of the TDI values of 0.005 mg/kg bw/day for nonylphenol and 0.013 mg/kg bw/day for nonylphenol ethoxylate.

However, the absorption is low for nonylphenol which has been observed to be 0.1% (cf. above, Monteiro-Riviere *et al.* 1999). This absorption is included in the estimation (A_{derm} in table below).

Calculation example (textile B in table):

Assuming 100% dermal absorption

Adult absorption: $5.5 \times 0.5 / 70 \times 1 = 0.0393$ mg/kg bw Child absorption: $5.5 \times 0.25/10 \times 1 = 0.1375$ mg/kg bw

T-shirt, child absorption: $5.5 \times 0.16 / 10 \times 1 = 0.088$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A_{derm.} adult): $0.0393 \times 0.001 = 3.9 \times 10^{-5}$ mg/kg bw Child absorption (A_{derm.} child): $0.1375 \times 0.001 = 1.38 \times 10^{-4}$ mg/kg bw T-shirt, child absorption (A_{derm.} Tshirt): $0.088 \times 0.001 = 8.8 \times 10^{-5}$ mg/kg bw

TABLE 7.17 DERMAL ABSORPTION OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATE

| | Sum | 0.5 kg | Adult | Child | Tshirt | A _{derm} , | A _{derm} , | A _{derm} , |
|-----------------------------------|-------|---------|----------|----------|-------------|---------------------|---------------------|---------------------|
| | | textile | | | | adult | child | Tshirt |
| Textile | mg/kg | mg | mg/kg/bw | mg/kg bw | mg/kg bw | μg/kg bw | μg/kg bw | μg/kg bw |
| B) 100% cotton, yellow (children) | 5.5 | 2.75 | 0.0393 | 0.1375 | 0.088 | 0.039 | 0.138 | 0.088 |
| G) 100% cotton (animal motive) | 17.8 | 8.9 | 0.1271 | 0.4450 | 0.284 | 0.127 | 0.445 | 0.284 |
| O) 100% cotton (bear) | <3.1 | <1.55 | <0.0221 | <0.0775 | <0.04 9 | 0.022 | 0.078 | <0.049 |
| Q) 100% cotton (oilcloth) | 26.4 | 13.2 | 0.1886 | 0.6600 | 0.422 | 0.189 | 0.660 | 0.422 |

Assuming 0.01% absorption, none of the estimations are exceeding 1 µg/kg bw/day. Because TDI is not exceeded no further refinements is found necessary. It is noted that the textile with the highest value is oilcloth, which might be a possibility, but still is considered less relevant as a material used in close body contact.

The conclusion is that the estimated amounts of nonylphenol and nonylphenol ethoxylate do not present health risks from textiles at the measured concentrations.

7.6.4.3 Oral intake and inhalation

By oral exposure is presumed a child sucking/chewing on textile equivalent to 400 cm² or 20 g. The body weight of the child is set to 10 kg and the bioavailability 20%. Based on these assumptions, the amount of substance taken up by the body is estimated, cf. equation in section 6.4, example and results in table below.

Calculation example of oral intake by child:

$$I_{oral, child} = 20 \text{ (g)} \times 5.5 \text{ (µg/g)} \times 0.2 \text{ (20\%)} / 10 \text{ (kg)} = 2.2 \text{ µg/kg bw per event}$$

By inhalation it is presumed that the substance evaporates to its maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m^3 , and that inhalation by an adult person takes place 24 hours in the room (Inhalation: $\mu g/kg$ bw/day).

Based on these assumptions, the amount of substance taken up by the body via inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[5.5 \times 220.3/22.4 \times 0.3/101325] \ 10/\ 20 = 8.01 \times 10^{-5} \ \text{mg/m}^3$ Inhalation = $8.01 \times 10^{-5} \times 20/70 = 2.28 \times 10^{-5} \ \text{mg/kg bw/day}$

Table 7.18 Oral intake and inhalation of nonylpenol and nonylphenol ethoxylate

| | NP+NPE | Oral,child | C Inhalation | Inhalation |
|-----------------------------------|--------|------------|--------------|------------|
| Textile | mg/kg | mg/kg bw | μg/m³ | μg/kg bw |
| B) 100% cotton, yellow (children) | 5.5 | 0.0022 | 0.080 | 0.023 |
| G) 100% cotton (animal motive) | 17.8 | 0.0071 | 0.259 | 0.074 |
| O) 100% cotton (bear) | 3.1 | 0.0012 | 0.045 | 0.013 |
| Q) 100% cotton (oilcloth) | 26.4 | 0.0106 | 0.384 | 0.110 |

For oral intake the sample cotton (G) exceeds the TDI value of 0.005 mg/kg, which may be regarded a potential health problem. However, it should be noted that the NP content is approx. 10% of the exposure concentration and NPE the remaining part. Therefore the combined measured concentrations is concluded not to represent any health risks at the measured concentrations.

An exceeding in oral intake was also observed in the sample from oilcloth, (Q). However, it is considered unlikely that a child will be exposed to the same amount of textile as of the other textiles. Oral intake of ¼ would mean the TDI was not exceeded. It is therefore conclude that no health problem exist for oilcloth at the measured concentrations.

Concerning inhalation the estimated values are far below the TDI value.

7.6.4.4 Conclusion

The measured concentrations of nonylphenol and nonylphenol ethoxylate is assessed not to represent any health problems at the measured concentrations from skin contact or inhalation. For oral intake a potential health risk may be existing but it was concluded to be unlikely.

7.7 O-TOLUIDINE

7.7.1 Identification

Name o-Toluidine CAS no. 95-53-4 EINECS no. 202-429-0 Molecular formula $C_7 H_0 N$ NH_2 Molecular structure

.CH₂

Structural formula: CH_3 - (C_6H_4) - NH_3

Molecular weight

107.16 g/mol

Synonyms ortho-toluidine (o-toluidine) 1-amino-2-methylbenzene

2-aminotoluene *o*-methylaniline

2-methylaniline

2-methylbenzenamine

The melting point is -16,3°C. The boiling point is 200°C. The vapour pressure is 42 Pa at 20°C. The water solubility is 16600 mg/l. The octanol/water distribution coefficient log Kow is determined to 1.32.

Toluidine's adsorption is evaluated to be moderate based on measured adsorption coefficients Koc from 40 to 250 (Swann et al. 1983). o-Toluidine is not expected to evaporate from dry surfaces based on its vapour pressure.

The odour threshold is 0.25 ppm, corresponding to 1.1 mg/m³ (Amore and Hautala 1983).

7.7.1.1 Classification

o-Toluidine is classified under EU index no. 612-091-00-X (Miljøministeriet 2002):

Carc2;R45 Carcinogenic. May cause cancer

Toxic. Toxic by inhalation and if swallowed T;R23/25

Xi;R36 Irritant. Irritating to eyes

N;R50 Dangerous for the environment. Very toxic to aquatic

organisms

7.7.1.2 Source

o-Toluidine is used primarily in the manufacture of colorants but also in the production of rubber, other chemicals and pesticides.. The content in textiles probably is caused by colorants.

7.7.1.3 Chemical analyses

o-Toluidine is only found in sample M (100% wool) in a concentration of 0.82~mg/kg. In no other sample, toluidine was observed above the detection limit of 0.3~mg/kg.

7.7.2 Health

7.7.2.1 Acute toxicity

Several acute data were present. Of these a few is mentioned:

| Acute oral, rat | LD_{50} | 670 mg/kg | HSDB 2002 |
|-----------------------|------------------------|-----------------------------------|-----------|
| Acute oral, mouse | LD_{50}^{5} | 515 mg/kg | HSDB 2002 |
| Acute oral, rabbit | LD_{50}^{50} | 844 mg/kg | HSDB 2002 |
| Acute oral, cat | LD_{50}^{50} | 300 mg/kg | HSDB 2002 |
| Acute dermal, rabbit | LD_{50}^{50} | 3250 mg/kg | HSDB 2002 |
| Intraperitoneal, | LC_{50} | 150 mg/kg | HSDB 2002 |
| mouse | | | |
| Acute inhalation, rat | LC_{50} (4 h) | 862 ppm (3780 mg/m ³) | HSDB 2002 |
| Acute inhalation, rat | $LC_0^{(4 h)}$ | 606 ppm (2670 mg/m ³) | |

The acute oral toxicity values LD₅₀ vary between 300 and 800 mg/kg.

The acute dermal toxicity is high with LD_{50} above 3000 mg/kg, which is not considered very harmful.

An inhalation toxicity value for human has been found with the lowest effect concentration TC_{lo} 25 mg/m³ (Lewis and Sweet 1984, US-NTP 2002).

o-Toluidine is toxic to humans when absorbed through skin, by inhalation or gastrointestinal tract. o-Toluidine affects the haemoglobin and may develop methemoglobine anaemia, i.e. lead to a reduced oxygen supply to the tissues.

Toluidine is a skin and eye irritant.

7.7.2.2 Long-term effects

o-Toluidine is classified carcinogenic. An increased risk of bladder cancer has been reported for workers exposed to dyes and dye intermediates including otoluidine (IPCS 1998). However, due to a mixed exposure including other substances as well means that the concentrations can not be used in this context. No description exists on workers only exposed to o-toluidine (HSDB 2002).

7.7.2.3 Bioavailability/absorption

Absorption via gastrointestinal tract is fast and the main part excreted via urine. Rats administered subcutaneously for prolonged periods with ¹⁴C-2-methylaniline excreted 79%, 3.3% and 1.4% in urine, faeces and by respiration, respectively. In another study exposures through the gastrointestinal tract >92% of the dosage was excreted via urine within 24 hours. 10-26% of the dosage was excreted as unchanged o-toluidine. (HSDB 2002).

No data for dermal exposure or absorption fraction were found. Most references, however, agrees that percutaneous absorption does take place (IARC 1978, ILO 1983).

7.7.2.4 Threshold limit values

TWA (8 hours time-weighted average): 2 ppm skin (ACGIH 2002). TLV: 2 ppm (9 mg/m³) with notion HK indicating skin penetrating and carcinogenic (AT 2002).

7.7.3 Evaluation

7.7.3.1 Dermal absorption

Dermal absorption is estimated for the textile where it was observed and for a concentration equivalent to the detection limit. Because the dermal absorption is unknown 100% absorption is used in the estimation.

Calculation example:

Assuming 100% dermal absorption

Adult absorption: $0.82 \times 0.5 / 70 \times 1 = 0.0059$ mg/kg bw Child absorption: $0.82 \times 0.25/10 \times 1 = 0.0205$ mg/kg bw

T-shirt, child absorption: $0.82 \times 0.16 / 10 \times 1 = 0.0131$ mg/kg bw

TABLE 7.19 DERMAL ABSORPTION OF O-TOLUIDINE

| Sampl | Textile | o-Toluidine | 0.5 kg textile | Adult | Child | Tshirt |
|-------|-----------|-------------|----------------|----------|----------|----------|
| e | | | | | | |
| | | mg/kg | mg | mg/kg/bw | mg/kg bw | mg/kg bw |
| М | 100% wool | 0.82 | 0.41 | 0.0059 | 0.0205 | 0.0131 |
| | DL | 0.3 | 0.15 | 0.0021 | 0.0075 | 0.0048 |

o-Toluidine was only observed above the detection limit in one textile sample. No dermal values for comparison exist. In general, any contact with the compound is considered undesirable, as it is carcinogenic, even if the acute effect values are high.

However if the presence of o-toluidine (and other carcinogenic acrylamines) is as a result of degradation of azocolourants, a Directive on restriction of use of azocolourants include o-toluidine. The directive states that the release of o-toluidine should not exceed detectable concentrations, i.e. above 30 ppm in the finished textile articles or in the dyed parts thereof which may come into direct and prolonged contact with the human skin or oral cavity (EC 2002).

7.7.3.2 Oral intake and inhalation

By oral intake it has been presumed that a child sucks/chews on textile corresponding to 400 cm² or 20 g. The body weight of the child is set to 10 kg and bioavailability to 100%. Based on this, the amount of compound absorbed by the child is estimated.

Calculation example of oral intake by child:

$$I_{oral child} = 20 \text{ (g)} \times 0.82 \text{ (µg/g)} \times 1 \text{ (100\%)} / 10 \text{ (kg)} = 1.64 \text{ µg/kg bw per event}$$

By inhalation it is presumed that the substance evaporates to its maximum achievable concentration and is distributed equally in the entire room (C inhalation in the table below). Furthermore, it is presumed that 10 kg of textile is present in the room, the room air volume is 20 m³, and that inhalation by an adult person takes place 24 hours in the room (Inhalation: µg/kg bw/day).

Based on these assumptions, the amount of substance taken up by the body via inhalation is estimated, cf. equations in section 6.5, example and results in table below.

Calculation example of inhalation by adult:

C inhalation = $[0.82 \times 107.16/22.4 \times 42/101325] \ 10/\ 20 = 8.13 \times 10^{-4} \ mg/m^3$ Inhalation = $8.13 \times 10^{-4} \times 20/70 = 2.32 \times 10^{-4} \ mg/kg \ bw/day$

TABLE 7.20 ORAL INTAKE AND INHALATION OF O-TOLUIDINE

| | ,.20 0 | | 0 0. 0 .010.1 | - | |
|-------|-----------------|-----------|---------------|--------------|------------|
| Sampl | Textile | 0- | Oral, child | C inhalation | Inhalation |
| e | | toluidine | | | |
| | | mg/kg | mg/kg bw | µg/m³ | µg/kg bw |
| M | 100% wool | 0.82 | 0.00164 | 0.813 | 0.232 |
| | Detection limit | 0.3 | <0.00060 | <0.297 | <0.085 |

o-Toluidine is only detected in one sample above the detection limit. No oral value for comparison exists. The estimated concentration in air is approx. 10,000 times less than the threshold limit value for the working environment (9 mg/m³) which should be a sufficient margin of safety. In general, any contact with the compound should be avoided, as it is carcinogenic.

7.7.3.3 Conclusion

o-Toluidine was discovered above the detection limit in only one sample. It is not possible to evaluate its health risks at dermal contact, oral uptake or inhalation. The substance is classified carcinogenic and any contact with the substance should be avoided even at low concentrations.

However, relating to the directive on azocolourants (EC 2002) the measured concentrations in the textile samples was far below 30 mg/kg and thus no health problems may be expected at the measured concentrations and the current knowledge.

7.8 SUMMARY OF CONCLUSIONS

In the table below is presented a summary of the conclusions from the estimations of consumer exposure based on measured concentrations.

Table 7.21 Summary of conclusions of organic compounds

| Compound | Detection limit | Analyses results | Dermal | Oral | Inhalation |
|--|----------------------|---|--|---|--|
| Bis (ethylhexyl) phthalate (DEHP) 117-81-7 | 0.7 mg/kg | From 2.2 to 7.7 mg/kg | No health risks | No health risks | No health risks |
| 4-chloroaniline 106-47-8 | 0.5 mg/kg | 1 sample 1.2 mg/kg, remaining samples below detection limit | The compound is carcinogenic. Assessment not performed | The compound is carcinogenic. Assessment not performed | The compound is carcinogenic. Assessment not performed |
| Formaldehyde 50-00-0 | <20 mg/kg | 3 samples above 20 mg/kg and up to 82 mg/kg | No health risks by comparison to chronic data. | No health risks by comparison to chronic data. | No health risks by comparison to chronic data. |
| Naphthalene 91-20-3 | 0.01 mg/kg | 4 samples containing up to 3 mg/kg, remaining samples below detection limit | No health risks | No health risks | No health risks |
| Nicotine 54-11-5 | o.o2 mg/kg | 9 samples containing up to 0.2 mg/kg, remaining sample below detection limit | No health risks | No health risks | No health risks |
| Nonylphenol, 25154-52-3 Nonylphenolethoxylat, 9016-45-9 | 0.1 mg/kg 3 mg/kg | 4 samples above detection limit | No health risks if assumed absorption at or below 0.1% | No health risk if an absorption of 0,1% is presumed and NP/NPE distribution remains unchanged | No health risks |
| o-Toluidine 95-53-4 | o.3 mg/kg | 1 sample 0.8 mg/kg, remaining below detection limit | The compound is carcinogenic. Assessment not performed | The compound is carcinogenic. Assessment not performed | The compound is carcinogenic. Assessment not performed |

8 Evaluation of metals

The result of the analyses is presented in table 8.1. Cadmium and mercury were not found above the detection limit.

TABLE 8.1 SUMMARY OF MEASURED RESULTS ON METALS

| | Metal (mg/kg) | As | Ва | Cd | Co | Cr | Cu | Hg | Ni | Pb | Sb | Sn |
|-----|--------------------------------|----|-------------|------|------------|-----------|-----------|------|-----|-----------|----------|------|
| San | nple: | | | | | | | | | | | |
| В | 100% cotton, yellow (children) | - | 1.2 | - | 2.2 / 0.45 | 7.4 / 4.7 | 25 | - | - | - | - | - |
| С | Acrylic / nylon | - | 0.76 | - | - | 0.31 | - | - | 1.1 | - | - | |
| D | 100% cotton, blue | - | 0.67 | - | - | 0.24 | 680 | - | - | - | - | |
| F | 100% PET, colourful | - | 1.6 | - | 21 | 0.4 | - | - | - | 1.2 / 1.6 | 110 | |
| G | 100% cotton, animal motive | - | 2.3 | - | - | 0.69 | - / 1.5 | - | - | - | - | 4.9 |
| Н | 100% PET, white | - | 0.85 /1.2 | - | - | - | - | - | - | - | 200 | |
| I | 100% cotton, flowers | - | 2.8 /0.7 | - | - | 0.2 / - | - | - | - | - | 0.63 / - | |
| J | 100% flax | - | 1 | - | - | 0.2 | 20 | - | - | - | - | - |
| L | 100% viscose | 1 | - | - | 43 | - | - | - | - | - | - | |
| М | 100% wool | - | 9.9 | - | 5.6 | - | 5 | - | - | 0.73 | - | |
| N | 100% cotton, versage | - | 1.1 | - | 48 / 32 | 64 / 44 | 1.6 / 1.1 | - | - | - | - | |
| 0 | 100% cotton (bear) | - | 1.1 | - | - | 0.51 | 5.3 | - | - | 0.51 | - | - |
| Р | 100% wool, furniture | - | 0.66 / 0.44 | - | - | 65.2 | 4.9 | - | - | 0.63 | - | |
| Q | 100% cotton (oilcloth) | - | 0.95 | - | - | 0.5 / 1.7 | 260 | - | - | - | - | |
| R | Cotton / PET (napkins) | - | 2 | - | - | 0.2 | 11 | - | - | - | 35 | |
| Det | ektion limit: | 1 | 0.3 | 0.05 | 0.2 | 0.2 | 1 | 0.05 | 1 | 0.5 | 0.5 | 0.05 |

^{-:} Below detection limit. Blanks: not measured

All results are based on double measurements. If the variation exceeds 20% of the average of the double measurements both values are presented. Variation of this size may be caused by inhomogeneity of the sample material.

For all analysed metals apply that the measured concentrations are referring to total metal and not which metal compound that was in the textile. Since the specific metal compound is unknown it is not possible to relate the concentrations to specific data on health as for the organic compounds in previous section.

Below is presented physico-chemical properties for each metal, classification of relevant metal compounds and the data relating to health which are considered relevant.

The health risk at the measured concentrations is evaluated based on three scenarios (cf. section 6):

- a scenario where a child sucks/chews on the textile (oral exposure)
- a scenario where dust released from the textile is inhaled
- a scenario where the textile gets into skin contact.

8.1 ANTIMONY

8.1.1 Identification

Name Antimony CAS no. 7440-36-0 EINECS no. 231-146-5

Molecular formula Sb

Atomic weight 121.75 g/mol Synonym Stibium (Sb)

The melting point of antimony is 630°C. The boiling point is 1635°C. (Budavari 1989). The vapour pressure is 133 Pa (1 mmHg) at 885°C (ATSDR 1992).

Antimony is typically present in textiles for two reasons: Antimony is used as catalyst in the manufacture of polyester and antimony is used as synergist to flame retardants in textiles.

8.1.1.1 Classification

Antimony compounds are classified under several index numbers.

Antimony trioxide (CAS no.: 1309-64-4, EINECS no.: 215-175-0) is

classified under EU index no.: 051-005-00-X:

Carc3;R40; Harmful. Possible risks of irreversible effects.

Antimony compounds other than antimony chlorides, oxides and sulphides are classified under EU index no.: 051-003-00-9:

Xn;R20/22 Harmful. Harmful by inhalation and if swallowed

N;R51/53 Dangerous for the environment. Toxic to aquatic organisms,

may cause long-term adverse effects in the aquatic

environment.

8.1.1.2 Measurements

In the analysed textiles, antimony was found at the highest concentrations in polyester (PET). The reason is probably as residues from the production of the fibres. Other metal compounds could be used as catalyst but for economic reasons mainly antimony compounds are used (mainly antimony trioxide and antimony triacetate). It is estimated that more than 90% of produced PET is manufactured using antimony based catalysts. Polyester fibres contain typically between 160 to 240 ppm antimony. However, a large part is washed out in the wet finishing processes (Hansen *et al.* 2002).

The detection limit for antimony is 0.5 mg/kg. In 2 samples of PET, a colourful and a white, a concentration of antimony of 110 and 200 mg/kg was detected. Napkins of cotton/PET contained a concentration of 35 mg/kg while the remaining contained close to or below the detection limit.

8.1.2 Health

Antimony can migrate out of PET textiles, even at low temperatures, into liquids like sweat, saliva and synthetic blood (Hansen *et al.* 2002).

Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes or dust (Budavari 1989).

As oral threshold limit value ATSDR (1992) has derived a RfD of 4×10^{-4} mg/kg bw/day based on a LOAEL 0.35 mg/kg bw/day in a chronic rat study (IRIS 2002).

WHO has derived an acceptable daily dose (ADI) 8.6×10^{-4} mg/kg bw/day (WHO 1996). The latter value is the most recent and is used in this report.

The threshold limit value for air is 0.5 mg/m³ (AT 2002). Because the threshold limit value is relevant for the working environment it is considered reasonable to use a margin of safety of 100, i.e. to use a $TLV/100 = 5 \mu g/m^3$.

Data on dermal toxicity threshold values have not been found.

Information on bioavailability at inhalation has not been found. The fraction of bioavailability at oral intake (BIO_{oral}) is estimated to 0.1 (10%). The value is based on an absorption from gastrointestinal tract of 2-7% (MST 2002).

8.1.3 Evaluation

8.1.3.1 Oral intake

If a child sucks or chews on textile equal to 400 cm² or 20 gram of textile it corresponds to an oral intake estimated for the highest measured concentration of 200 mg/kg textile to:

[0.020 kg x 200 mg/kg x 0.1] / 10 kg body weight = 0.04 mg/kg bw.

At the concentration of 35 mg/kg the oral intake is:

[0.020 kg x 35 mg/kg x 0.1] / 10 kg body weight = 0.007 mg/kg bw.

At a concentration on level with the detection limit 0.5 mg/kg the oral intake is:

 $[0.020 \text{ kg x } 0.5 \text{ mg/kg x } 0.1] / 10 \text{ kg body weight} = 0.1 \,\mu\text{g/kg bw}.$

Using the acceptable daily dose of 0.86 µg/kg bw, it is observed that the value has been exceeded for textiles of or containing PET.

The Danish Environmental Protection Agency therefore decided to perform further studies on the migration of antimony from textiles in situations expected to present the highest exposure to the consumer: oral and dermal contact. The analytical methods are described in section 4.3.6.

In analyses where antimony containing textiles (PET) were extracted by artificial saliva (cf. section 4.3.6) simulating a child that sucks or chews on the textile no sample released above the detection level of 0.5 mg Sb/kg textile (cf. analytical results in section 5, table 5.8).

Based on the migration results the maximum oral intake is estimated to:

[0.020 kg x 0.5 mg/kg x 0.1] / 10 kg body weight = 0.0001 mg/kg bw.

Because this value $0.1~\mu g/kg$ bw is below the WHO ADI-value $0.86~\mu g/kg$ bw, no health risk is expected from children's oral exposure to textiles containing the measured concentrations.

8.1.3.2 Inhalation

Assuming a person reside in a room of 20 m³ containing 30 m² textile equivalent to a weight of 10 kg, the concentration of antimony in dust based on the highest concentration in textile 200 mg/kg is estimated to:

Concentration in air = $[10 \text{ kg x } 200 \text{ mg/kg x } 0.0001^{#}] / 20 \text{ m}^{3} = 10 \text{ x} 10^{-3} \text{ mg/m}^{3}$

The suggested threshold limit value TLV/100 of 5×10^{-3} mg/m³ means that the concentration in air is exceeded in two samples (i.e. above 100 mg Sb/kg).

Amount of inhaled compound =

bioavailability x conc. in air x inhalation rate x duration / body weight

Because the bioavailability factor is unknown it is set to 1 (100% absorption).

Then the amount of inhaled compound is:

 $1 \times 10 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour } \times 24 \text{ hours} / 70 \text{ kg} = 2.7 \times 10^{-3} \text{ mg/kg bw}.$

Since the ADI is 0.86 x 10⁻³ mg/kg bw., the estimated amount absorbed via inhalation is exceeded for the two samples with the highest concentrations. For the remaining samples, the amount absorbed by inhalation is below the ADI. However, the possibility of 10 kg polyester or PET containing fabrics being present under the given circumstances is assumed to be negligible. The absorption is set to 100% and may well be less. The release to air is estimated to 0.01% mainly as dust but the actual inhalable part is unknown. As the distance from the estimated concentrations to the suggested threshold limit values (TLV/100) are small and considering the uncertainties in general, it is assessed that there is no reason to assume immediate health problems from textiles at the measured concentrations

8.1.3.3 Dermal absorption

It is presumed that an adult wears 0.5 kg clothes and weighs 70 kg. A child is presumed to wear 0.25 kg clothes and weighs 10 kg. At skin contact a dermal absorption of 100% is used as first tier. Second tier was to use what was considered a more realistic dermal absorption for metals of 0.1% cf. note^{\$}.

The estimated potential dermal absorption is presented below.

Calculation example:

Assuming 100% dermal absorption

Adult absorption: $110 \times 0.5 / 70 \times 1 = 0.786$ mg/kg bw Child absorption: $110 \times 0.25 / 10 \times 1 = 2.75$ mg/kg bw

T-shirt, child absorption: $110 \times 0.16 / 10 \times 1 = 1.76$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption ($A_{\text{derm,}}$ adult): $0.786 \times 0.001 = 0.786 \times 10^{-3}$ mg/kg bw Child absorption ($A_{\text{derm,}}$ child): $2.75 \times 0.001 = 2.75 \times 10^{-3}$ mg/kg bw T-shirt, child absorption ($A_{\text{derm,}}$ Tshirt): $1.76 \times 0.001 = 1.76 \times 10^{-3}$ mg/kg bw

78

^{#:} Presumed that 0.01% is released as dust, cf. section 6.5

 $^{^{\}rm s}$: The absorption for metals presumed very small. For metals is used 0.1% for all metals, cf. section 6.3.

TABLE 8.2 DERMAL ABSORPTION OF ANTIMONY

| Sample | | 0.5 kg textile | Adult | Child | Tshirt | A _{derm} , | A _{derm} , |
|---------------------|-------|----------------|--------------|-------------|-------------|---------------------|---------------------|
| | ny | | | | | adult | child |
| | mg/kg | mg | mg/kg/b w | mg/kg bw | mg/kg bw | µg/kg bw | μg/kg bw |
| 0/ PET C | - | | | | | 0.0 | |
| 100% PET, colourful | 110 | 55 | 0.7857 | 2.7500 | 1.7600 | 0.786 | 2.750 |
| 100% PET, white | 200 | 100 | 1.4286 | 5.0000 | 3.2000 | 1.429 | 5.000 |
| 100% cotton flowers | 0.63 | 0.315 | 0.0045 | 0.0158 | 0.0101 | 0.005 | 0.016 |
| Cotton / PET | 35 | 17.5 | 0.2500 | 0.8750 | 0.5600 | 0.250 | 0.880 |
| (napkins) | | | | | | | |
| DL | 0.5 | 0.25 | 0.0036 | 0.0125 | 0.0080 | 0.004 | 0.013 |

Using a presumed maximum dermal absorption of 0.1% the estimated absorptions are presented in the last two columns (A_{derm}).

Because potential exceedings of the ADI were observed for textiles containing PET in skin contact further investigations were performed. To study the migration from textiles in wet conditions artificial sweat were used as extraction solution (cf. results in section 5).

In 5 samples, only in one detectable amount was observed above the detection limit of 1 mg/kg. In a PET textile containing between 35 and 48 mg Sb/kg, 3.5 mg/kg was measured i.e. 7 to 10% migrated during one hour of extraction.

The absorption is then estimated using 3.5 mg/kg textile as the exposure concentration and assuming 0.1% absorption:

Adult absorption: $3.5 \times 0.5 / 70 \times 0.001 = 2.5 \times 10^{-5}$ mg/kg bw (0.025 µg/kg bw)

Child absorption: $3.5 \times 0.25 / 10 \times 0.001 = 8.75 \times 10^{-5}$ mg/kg bw T-shirt, child absorption: $3.5 \times 0.16 / 10 \times 0.001 = 5.6 \times 10^{-5}$ mg/kg bw

The estimated dermal absorption is below the ADI value of 8.6×10^{-4} mg/kg bw/d

8.1.3.4 Conclusion

A variety of concentrations up to 200 mg/kg were measured in textiles consisting of or containing PET. Because of the results from the first estimates a further refinement was decided. The study on migration of antimony in artificial sweat showed that up to 10% of antimony was able to migrate from the textile into the liquid. Based on the used scenarios the estimated absorptions were below the ADI value. In migration studies using artificial saliva, antimony did not migrate from the textile to an extent where it resulted in concentrations above the detection level of 0.5 mg/kg textile. Therefore no health problems are expected from the textiles at the measured concentrations.

It is concluded that there is no immediate health risks expected in relation to the measured concentrations of antimony.

8.2 ARSENIC

8.2.1 Identification

 Name
 Arsenic

 CAS no.
 7440-38-2

 EINECS no.
 231-148-6

Molecular formula As

Atomic weight 74.92 g/mol

The melting point is 818°C at 36 atm (Budavari 1989).

8.2.1.1 Classification

Arsenic is classified under EU-index no.: 033-001-00-X

T;R23/25 Toxic. Toxic by inhalation and if swallowed

N;R50/53 Dangerous for the environment. Very toxic to aquatic

organisms, may cause long-term adverse effects in the aquatic

environment

8.2.1.2 Measured concentrations

Arsenic was only detected in one sample consisting of 100% viscose at a concentration close to the detection limit 1 mg/kg.

8.2.2 Health

Most forms of arsenic are toxic to humans at low concentrations, which vary according to the specific arsenic compound (Budavari 1989).

The bioavailability factor at inhalation (BIO_{inh}) is 0.32 and by oral intake (BIO_{oral}) the bioavailability is high and estimated to be 0.98 (Baars *et al.* 2001).

WHO has derived a provisional tolerable weekly oral intake, PTWI of 15 µg/kg bw/week, corresponding to a provisional maximum tolerable daily intake (PMTDI) of 2.1 µg/kg bw/day (WHO 1996).

The tolerable daily intake dose for humans (TDI) has later been re-evaluated by RIVM, which derived at 1×10^{-3} mg/kg bw/day (Baars *et al.* 2001).

The highest acceptable concentration in air for humans (HAC_{air}) is 1×10^{-3} mg/m³ (Baars *et al.* 2001). The threshold limit value in air for arsenic 0.01 mg/m³ (AT 2002).

8.2.3 Evaluation

8.2.3.1 Oral intake

The acceptable oral intake for a child of 10 kg body weight is 0.01 mg/day (10 \times 1×10⁻³ mg/kg bw/day). The bioavailability is approx. 1 (100% absorption).

If a child sucks or chews on textile corresponding to 400 cm² or 20 gram of textile, this would correspond to an oral intake of:

0.020 kg x 1 mg/kg = 0.020 mg by 100% absorption.

An oral intake of 0.02 mg is above the tolerable daily intake for a 10 kg child of 0.01 mg. Since 1 mg/kg was the detection limit it is concluded that even concentrations below the detection limit may cause concern.

8.2.3.2 Inhalation

If it is assumed that a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x 1 mg/kg x 0.0001}] / 20 \text{ m}^3 = 0.05 \text{x} 10^{-3} \text{ mg/m}^3$.

The acceptable concentration in air is $1x10^{-3}$ mg/m³, which is above the estimated value.

The amount of inhaled arsenic = bioavailability x conc. in air x inhalation rate x duration / body weight.

Then the amount of inhaled arsenic is:

 $0.32 \times 0.05 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.004 \times 10^{-3} \text{ mg/kg}$ bw.

Thus, the acceptable daily intake 0.001 mg/kg bw is not exceeded.

8.2.3.3 Dermal absorption

The estimations of potential uptake by skin contact are calculated below.

Assuming 100% dermal absorption

Adult absorption: $1 \times 0.5 / 70 \times 1 = 0.0071$ mg/kg bw Child absorption: $1 \times 0.25 / 10 \times 1 = 0.025$ mg/kg bw

T-shirt, child absorption: $1 \times 0.16 / 10 \times 1 = 0.016$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A $_{derm,}$ adult): $0.0071 \times 0.001 = 0.0071 \times 10^{-3}$ mg/kg bw Child absorption (A $_{derm,}$ child): $0.025 \times 0.001 = 0.025 \times 10^{-3}$ mg/kg bw T-shirt, child absorption (A $_{derm,}$ Tshirt): $0.016 \times 0.001 = 0.016 \times 10^{-3}$ mg/kg bw

Using a presumed maximum dermal absorption of 0.1% the estimated concentration are all below the TDI of 1 μ g/kg bw/day. Therefore it is considered that there is no immediate health risk to the consumers using textiles containing arsenic at the measured concentrations.

8.2.3.4 Conclusion

Only one sample contained arsenic at concentrations at the detection limit of 1 mg/kg.

Oral intake of arsenic even at low concentrations even below the detection limit may cause concern. It is considered that concentrations above 0.5 times the detection level 1 mg/kg may cause problems under the conditions of the scenario. However, the toxicity depends of the specific arsenic compound.

Inhalation of arsenic containing dust was not considered a health risk according to the scenario used. Skin contact to textiles containing arsenic at the measured concentrations did not cause any health concerns.

8.3 BARIUM

Barium compounds e.g. barium acetate is used in dyes for textiles (Budavari 1989).

8.3.1 Identification

 Name
 Barium

 CAS no.
 7440-39-3

 EINECD no.
 231-149-1

Molecular formula Ba

Atomic weight 137.33 g/mol

The melting point is 710°C. The boiling point is 1600°C (Budavari 1989). The vapour pressure is presumed low and the water solubility insignificant.

8.3.1.1 Classification

Barium and barium compounds are not classified.

8.3.1.2 Measured concentrations

Barium was detected in all but one sample at concentrations varying from the detection limit of 0.3 mg/kg to 10 mg/kg in one sample. Most samples varied between 1 and 2 mg/kg (cf. section 5 or table 8.1).

8.3.2 Health

US-EPA has recommended an acceptable daily oral intake dose (RfD) of 0.070 mg/kg bw/day (IRIS 2002). WHO has recommended a TDI of 0.050 mg/kg bw/day based on a chronic rat study (WHO 1996).

RIVM has re-evaluated the tolerable daily oral intake and derived at a TDI of 0.020 mg/kg bw/dag (Baars *et al.* 2001). An acceptable daily inhalation concentration in air (HAC) is recommended at 1×10^{-3} mg/m³ (Baars *et al.* 2001).

The bioavailability at inhalation (BIO_{inh}) is 0.75 and the bioavailability at oral intake (BIO_{oral}) is estimated to 0.1 (Baars *et al.* 2001).

8.3.3 Evaluation

8.3.3.1 Oral intake

If a child sucks or chews on a piece of textile equivalent to 400 cm² or 20 g textile, this corresponds to a maximum oral intake of:

 $0.020 \text{ kg} \times 10 \text{ mg/kg} \times 0.1 / 10 \text{ kg bw} = 0.002 \text{ mg}$ at the highest measured concentration.

The recommended acceptable daily oral intake values vary between 0.020 and 0.070 mg/kg body weight indicating that the limit for acceptable oral intake is not exceeded.

8.3.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x } 10 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 0.5 \text{ x } 10^{-3} \text{ mg/m}^3$.

The acceptable concentration is higher than the estimated.

Amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled barium is:

 $0.75 \times 0.5 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.1 \times 10^{-3} \text{ mg/kg bw}.$

The acceptable dose is 0.02-0.07 mg/kg and the estimated value is significantly below.

The results demonstrate that in relation to inhalation no health risk is expected.

8.3.3.3 Dermal absorption

The estimation for potential absorption by skin contact is estimated as for antimony.

Calculation example:

Assuming 100% dermal absorption:

Adult absorption: $1.2 \times 0.5 / 70 \times 1 = 0.0086$ mg/kg bw Child absorption: $1.2 \times 0.25 / 10 \times 1 = 0.03$ mg/kg bw

T-shirt, child absorption: $1.2 \times 0.16 / 10 \times 1 = 0.0192$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A_{derm}, adult): $0.0086 \times 0.001 = 0.0086 \times 10^{-3}$ mg/kg bw Child absorption (A_{derm}, child): $0.03 \times 0.001 = 0.03 \times 10^{-3}$ mg/kg bw

Table 8.3 Dermal absorption of barium

| Tex | tile | Ва | 0.5 kg | Adult | Child | Tshirt | Aderm, | Aderm, |
|-----|-----------------------------------|-------|---------|---------|--------|--------|--------|--------|
| | | | textile | | | | adult | child |
| | | mg/kg | mg | mg/kg/b | mg/kg | mg/kg | µg/kg | µg/kg |
| | | | | W | bw | bw | bw | bw |
| В | 100% cotton, yellow (children) | 1.2 | 0.6 | 0.0086 | 0.0300 | 0.0192 | 0.009 | 0.030 |
| C | Acrylic / nylon | 0.76 | 0.38 | 0.0054 | 0.0190 | 0.0122 | 0.005 | 0.019 |
| D | 100% cotton, blue | 0.67 | 0.335 | 0.0048 | 0.0168 | 0.0107 | 0.005 | 0.017 |
| F | 100% PET, colourful | 1.6 | 0.8 | 0.0114 | 0.0400 | 0.0256 | 0.011 | 0.040 |
| G | 100% cotton, animal | 2.3 | 1.15 | 0.0164 | 0.0570 | 0.0368 | 0.016 | 0.057 |
| | motive | | | | | | | |
| Н | 100% PET, white | 1.2 | 0.6 | 0.0086 | 0.0300 | 0.0192 | 0.009 | 0.030 |
| I | 100% cotton, flowers | 2.8 | 1.4 | 0.0200 | 0.0700 | 0.0448 | 0.020 | 0.070 |
| J | 100% flax | 1 | 0.5 | 0.0071 | 0.0250 | 0.0160 | 0.007 | 0.025 |
| М | 100% wool | 9.9 | 4.95 | 0.0707 | 0.2475 | 0.1584 | 0.070 | 0.248 |
| N | 100% cotton, versage | 1.1 | 0.55 | 0.0079 | 0.0275 | 0.0176 | 0.008 | 0.028 |
| 0 | 100% cotton (bear) | 1.1 | 0.55 | 0.0079 | 0.0275 | 0.0176 | 0.008 | 0.028 |
| Р | 100% wool, furniture | 0.66 | 0.33 | 0.0047 | 0.0165 | 0.0106 | 0.005 | 0.017 |
| Q | 100% cotton (oilcloth) | 0.95 | 0.475 | 0.0068 | 0.0238 | 0.0152 | 0.007 | 0.024 |
| R | Cotton / PET (napkins) | 2 | 1 | 0.0143 | 0.0500 | 0.0320 | 0.014 | 0.050 |

The estimated concentrations for dermal intake are below 20 μ g/kg bw/dag. Therefore it is concluded that no immediate health risk is expected at the measured concentrations.

8.3.3.4 Conclusions

Barium was measured above the detection limit in all samples except one consisting of viscose.

Regarding oral intake, inhalation and skin contact it is assessed that no potential health risk for the consumer existed.

8.4 CADMIUM

8.4.1 Identification

 Name
 Cadmium

 CAS no.
 7440-43-9

 EINECS no.
 231-152-8

Molecular formula Cd

Atomic weight 112.41 g/mol

The melting point is 321°C. The boiling point is 765°C (Budavari 1989)

8.4.1.1 Classification

Cadmium compounds are classified different, depending on the specific substance. Some compounds are classified carcinogenic and/or mutagenic and/or reprotoxic.

Cadmium compounds are as a minimum classified harmful and dangerous for the environment containing the risk phrases: Harmful by inhalation, in contact with skin and if swallowed and Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

8.4.1.2 Measured concentrations

In no sample was cadmium detected above the detection limit of 0.05 mg/kg.

8.4.2 Health

Cadmium is a toxic substance. One of the main problems is that cadmium is accumulated in the body especially in the kidneys. The accumulation already begins at birth. When the kidneys reach a concentration of approx. 200 mg/kg or more the kidneys reduce their function (ECB: Risk Assessment of cadmium, draft 2002).

WHO has derived a PTWI (provisional tolerable weekly intake) for cadmium of 7 μ g/kg bw/week (corresponding to 1 μ g/kg bw/day) for en adult (WHO 1996).

Another reference has derived an acceptable daily intake dose (TDI) to 0.5 µg/kg bw/day (Baars *et al.* 2001).

The highest acceptable inhalation concentration (HAC) is recommended to be $0.0004 \,\mu\text{g/m}^3$ (IRIS 2002).

The bioavailability by inhalation (BIO_{inh}) is 0.4 and the bioavailability by oral intake (BIO_{oral}) is estimated to 0.06 (Baars *et al.* 2001).

8.4.3 Evaluation

The health risks are evaluated based on the detection limit 0.05 mg/kg.

8.4.3.1 Oral intake

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake of:

 $[0.020 \text{ kg x } 0.05 \text{ mg/kg x } 0.06]/10 \text{ kg body weight} = 0.006 \mu\text{g/kg bw using detection limit as highest concentration value.}$

The estimated oral intake is a factor 100 below the acceptable daily intake value.

8.4.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x } 0.05 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 2.5 \text{ x } 10^{-3} \text{ } \mu\text{g/m}^3$

This concentration is a little above the recommended acceptable level 4 x 10^{-4} $\mu g/m^3$.

Amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight.

the amount of inhaled cadmium is:

 $0.4 \times 2.5 \times 10^{-3} \,\mu\text{g/m}^3 \times 0.8 \,\text{m}^3/\text{hour} \times 24 \,\text{hours} / 70 \,\text{kg} = 0.3 \times 10^{-3} \,\mu\text{g/kg} \,\text{body}$ weight.

The acceptable daily intake value was $0.5 \mu g/kg$ bw and thus higher than the estimated value.

8.4.3.3 Dermal contact

Using the detection level as maximum concentration it is estimated that the maximum dermal uptake is $0.0004~\mu g/kg$ for adults and $0.0013~\mu g/kg$ for children. Both values are below the acceptable value. Therefore, it is assessed that no immediate health risks are expected at the measured concentrations.

Assuming 0.1% dermal absorption:

Adult absorption: $0.05 \times 0.5 / 70 \times 0.001 = 4 \times 10^{-7}$ mg/kg bw Child absorption: $0.05 \times 0.25 / 10 \times 0.001 = 1.3 \times 10^{-6}$ mg/kg bw

8.4.3.4 Conclusions

In none of the analysed samples cadmium was detected above the detection limit 0.05 mg/kg.

Regarding oral intake, inhalation of textile dust, and by dermal contact it is assessed that no potential health risk exists.

8.5 CHROMIUM

8.5.1 Identification

Name Chromium CAS no. 7440-47-3 EINECS no. 231-157-5

Molecular formula Cr

Atomic weight 52.0 g/mol

The melting point is 1900°C. The boiling point is 2642°C (Budavari 1989).

Chromium exists mostly in the two oxidation stages Chromium(III) and Chromium(VI) and the two forms each are included in several chemical complexes.

8.5.1.1 Classification

Chromium(VI) compounds are classified Toxic and Dangerous for the environment and some compounds such as e.g. chromium trioxide may as pure substance be corrosive and oxidising. Chromium(VI) compounds are carcinogenic by inhalation and may cause allergy at skin contact. Chromium(VI) compounds are toxic to aquatic organisms and not ready biodegradable (Fairhurst and Minty 1989, Miljøministeriet 2002).

Chromium(III) compounds are not recognised as carcinogenic and are less harmful than chromium(VI) compounds (Fairhurst and Minty 1989, Miljøministeriet 2002).

8.5.1.2 Measured concentrations

The detection limit for chromium is 0.2 mg/kg. In the analysed samples, a chromium level above the detection limit was observed in 10 out of 14 samples.

In two samples, cotton versage and wool furniture, were measured a concentration around 60 mg/kg. In one sample, cotton yellow (children), was measured 7 mg/kg while the remaining samples had low levels.

By the analyses it could not be determined whether the measured chromium was chromium(VI) or chromium(III).

8.5.2 Health

The tolerable daily intake dose (TDI) is recommended to 5 μ g/kg bw/day for Cr(III) and 3 μ g/kg bw/day for Cr(VI) (Baars *et al.* 2001).

The bioavailability by inhalation (BIO_{inh}) is 0.1 for Cr(III) and 0.25 for Cr(VI). The bioavailability by oral intake (BIO_{oral}) is estimated to 0.01 for Cr(III) and 0.05 for Cr(VI) (Baars *et al.* 2001).

8.5.3 Evaluation

8.5.3.1 *Oral intake*

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake of:

 $[0.020 \text{ kg x } 65 \text{ mg/kg x } 0.05] / 10 \text{ kg body weight} = 6.5 \mu\text{g/kg bw at the highest measured concentration and based on chromium(VI).}$

Based on chromium(III) the oral intake is estimated:

 $[0.020 \text{ kg x } 65 \text{ mg/kg x } 0.01] / 10 \text{ kg body weight} = 1.3 \mu g$ at the highest measured concentration.

Using the detection limit value, the oral intake would be:

[0.020~kg~x~0.2~mg/kg~x~0.05]~/~10~kg body weight = 0.02 $\mu g/kg$ bw for chromium(VI).

Using the acceptable daily oral intake as 3 μ g/kg bw for chromium(VI) would result in an exceeding for the two samples with the highest measured concentrations of chromium (N and P). The TDI for chromium(III) is set to 5 μ g/kg body weight and that is higher than the maximum estimated intake (1.3 μ g/kg bw).

8.5.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x } 65 \text{ mg/kg x } 0,0001] / 20 \text{ m}^3 = 3 \text{ x} 10^{-3} \text{mg/m}^3$.

The amount of inhaled substance = bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled substance assuming chromium(VI): $0.25 \text{ x } 3\text{x}10^{-3} \text{ mg/m}^3\text{ x } 0.8 \text{ m}^3\text{/hour x } 24 \text{ hours / } 70 \text{ kg} = 0.23 \text{ µg/kg body weight.}$

The amount of inhaled substance assuming chromium(III): $0.1 \times 3 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.09 \text{ µg/kg body weight.}$

The estimated maximum intake by inhalation is lower than the TDI-values. Therefore it is assessed that inhalation of textile dust containing chromium is not considered a health risk to the consumers at the measured concentrations.

8.5.3.3 Dermal contact

The potential absorption of chromium by skin contact is presented below.

Calculation example (using max. measured concentration):

Assuming 100% dermal absorption:

Adult absorption: $65.2 \times 0.5 / 70 \times 1 = 0.4657$ mg/kg bw Child absorption: $65.2 \times 0.25 / 10 \times 1 = 1.63$ mg/kg bw T-shirt, child absorption: $65.2 \times 0.16 / 10 \times 1 = 1.0432$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A_{derm.}, adult): $0.4657 \times 0.001 = 0.4657 \times 10^{-3}$ mg/kg bw Child absorption (A_{derm.}, child): $1.63 \times 0.001 = 1.63 \times 10^{-3}$ mg/kg bw

TABLE 8.4 DERMAL ABSORPTION OF CHROMIUM

| Tex | tile | Cr | 0.5 kg textile | Adult | Child | Tshirt | A _{derm} , adult | A _{derm} , child |
|-----|-----------------------------------|-----------|-------------------|--------------|-------------|-------------|------------------------------|------------------------------|
| | | mg/k g | mg Cr | mg/kg/b w | mg/kg bw | mg/kg bw | μg/kg bw | μg/kg bw |
| В | 100% cotton, yellow (children) | 7.4 | 3.7 | 0.0529 | 0.1850 | 0.1184 | 0.053 | 0.185 |
| C | Acrylic / nylon | 0.31 | 0.155 | 0.0022 | 0.0078 | 0.0050 | 0.002 | 0.008 |
| D | 100% cotton, blue | 0.24 | 0.12 | 0.0017 | 0.0060 | 0.0038 | 0.002 | 0.006 |
| F | 100% PET, colourful | 0.4 | 0.20 | 0.0029 | 0.0100 | 0.0064 | 0.003 | 0.010 |
| G | 100% cotton, animal motive | 0.69 | 0.345 | 0.0049 | 0.0173 | 0.0110 | 0.005 | 0.017 |
| I | 100% cotton, flowers | 0.2 | 0.1 | 0.0014 | 0.0050 | 0.0032 | 0.001 | 0.005 |
| J | 100% flax | 0.2 | 0.1 | 0.0014 | 0.0050 | 0.0032 | 0.001 | 0.005 |
| Ν | 100% cotton, versage | 64 | 32 | 0.4571 | 1.6000 | 1.0240 | 0.457 | 1.600 |
| 0 | 100% cotton (bear) | 0.51 | 0.255 | 0.0036 | 0.0128 | 0.0082 | 0.004 | 0.013 |
| Р | 100% wool, furniture | 65.2 | 32.6 | 0.4657 | 1.6300 | 1.0432 | 0.466 | 1.630 |
| Q | 100% cotton (oilcloth) | 1.7 | 0.85 | 0.0121 | 0.0425 | 0.0272 | 0.012 | 0.043 |
| R | Cotton / PET (napkins) | 0.2 | 0.1 | 0.0014 | 0.0050 | 0.0032 | 0.001 | 0.005 |

The estimated concentration s for dermal absorption are below the lowest TDI of 3 μ g/kg bw/day assuming 0.1% dermal absorption. The textiles wool furniture and cotton versage (N and P) are estimated to be closest to the TDI values.

For the furniture textiles it is assumed they are not used in close body contact to the whole body surface. Assuming half exposure (one side of the body) the margin of safety to the TDI-values will be increased.

It is therefore assessed that there is no immediate health risk from textiles containing chromium at the measured concentrations. No information has been recovered on the levels necessary to exclude possible allergy at skin contact. The level is individual and depending on sensitisation of the exposed person.

8.5.3.4 Conclusions

In 2 samples, cotton (versage) and wool (furniture), relatively high concentrations of chromiumn were measured.

If the chromium consisted of chromium(VI), there may be a health risk by oral intake for the two textile samples. In case a significant part of the chromium is chromium(III) there will be no immediate health risk.

Inhalation of chromium containing textile dust is not considered a health risk at the measured concentrations of chromium.

Dermal contact is assessed that there is no immediate health risk from textiles containing chromium at the measured concentrations. No information has been recovered on the levels necessary to exclude possible allergy at skin contact. The level is individual and depends on sensitisation of the exposed person.

86 CORALT

8.6.1 Identification

Name Cobalt CAS no. 7440-48-4 EINECS no. 231-158-0

Molecular formula Co

Atomic weight 58.93 g/mol

The melting point is 1493°C. The boiling point is ca. 3100°C (Budavari 1989).

8.6.1.1 Classification

Cobalt as metal is classified under EU index no. 027-001-00-9.

R42/43 May cause sensitisation by inhalation and skin contact

R53 May cause long-term adverse effects in the aquatic environment.

Cobalt compounds are classified different depending on the specific cobalt compound. Most compounds are classified according to the characteristics of cobalt relating to allergy, sensitisation by inhalation and skin contact.

Some cobalt compounds such as e.g. chlorides and sulphates are classified Toxic if swallowed.

8.6.1.2 Measured concentrations

The detection limit for cobalt is 0.2 mg/kg. In 10 of the analysed samples, no concentrations above the detection limit were measured.

In two samples, viscose and cotton versage (L and N) were measured a concentration of approx. 40 mg/kg while the remaining samples contained between 2 and 5 mg/kg.

8.6.2 Health

Only little information on cobalt was available. Besides allergenic effects the substance depending on the specific cobalt compound may cause different effects on organs.

The acceptable daily intake dose (TDI) is derived at 1.4 μ g/kg bw/day (Baars et al. 2001).

The highest acceptable daily concentration in air for inhalation (HAC) is recommended to $0.5 \,\mu\text{g/m}^3$ (Baars *et al.* 2001).

No information was available on the bioavailability factors which are therefore set to 1 (100%).

8.6.3 Evaluation

8.6.3.1 *Oral intake*

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake of:

 $[0.020 \text{ kg x } 40 \text{ mg/kg x } 1] / 10 \text{ kg body weight} = 80 \mu\text{g/kg bw at the highest measured concentrations.}$

Using the detection limit an oral intake would be estimated to 0.4 µg/kg bw.

The acceptable daily dose by oral intake is at the level of the detection limit. It is therefore considered that for two samples (N and L) a considerable health risk exists and for two samples (F and M) a health risk may exist for consumers according to the used exposure scenario.

8.6.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x } 40 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 2 \text{ x} 10^{-3} \text{ mg/m}^3$.

The estimated concentration exceeds the acceptable concentration a little.

The amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled cobalt is:

 $1 \times 2 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.57 \text{ µg/kg body weight.}$

By comparison of the above value with the acceptable dose of $1.4 \mu g/kg$ body weight it is observed that the estimated highest value is below the TDI.

8.6.3.3 Dermal contact

The potential dermal absorption is estimated below.

Calculation example:

Assuming 100% dermal absorption:

Adult absorption: $48 \times 0.5 / 70 \times 1 = 0.3429$ mg/kg bw Child absorption: $48 \times 0.25 / 10 \times 1 = 1.2$ mg/kg bw

T-shirt, child absorption: $48 \times 0.16 / 10 \times 1 = 0.768$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A $_{derm,}$ adult): $0.3429 \times 0.001 = 0.3429 \times 10^{-3}$ mg/kg bw Child absorption (A $_{derm,}$ child): $1.2 \times 0.001 = 1.2 \times 10^{-3}$ mg/kg bw

TABLE 8.5 DERMAL ABSORPTION OF COBALT

| Tov | +ila | Со | | Adult | Child | Tshirt | ۸ | ۸ |
|-----|----------------------|------|---------|----------|--------|---------|--------------|--------------|
| Tex | Гextile | | 0.5 kg | Adult | Critic | 1211111 | A_{derm} , | A_{derm} , |
| | | | textile | | | | adult | child |
| | | mg/k | mg Co | mg/kg/bw | mg/kg | mg/kg | μg/kg bw | μg/kg bw |
| | | g | 8 | 81 81 3 | bw | bw b | 1010 | 1010 |
| В | 100% cotton, yellow | 2.2 | 1.1 | 0.0157 | 0.0550 | 0.0352 | 0.0157 | 0.0550 |
| | (children) | | | | | | | |
| F | 100% PET, colourful | 21 | 10.5 | 0.1500 | 0.5250 | 0.3360 | 0.1500 | 0.5250 |
| L | 100% viscose | 43 | 21.5 | 0.3071 | 1.0750 | 0.6880 | 0.3071 | 1.0750 |
| М | 100% wool | 5.6 | 2.8 | 0.0400 | 0.1400 | 0.0896 | 0.0400 | 0.1400 |
| Ν | 100% cotton, versage | 48 | 24 | 0.3429 | 1.2000 | 0.7680 | 0.3429 | 1.2000 |
| | DL | 0,2 | 0,1 | 0,0014 | 0,005 | 0,0032 | 0,0014 | 0,005 |

The estimated concentrations for dermal absorption (A_{derm}) are below TDI of 1.4 µg/kg bw/day although N and L are close. It is considered that no immediate health risk is expected at the measured concentrations.

However, the possibility of allergy and sensitisation by skin contact is considered to be an existing potential.

8.6.3.4 Conclusions

In 5 samples, cobalt was measured above the detection limit of 0.2 mg/kg, in two samples the cobalt concentration was approx. 40 mg/kg.

A significant health risk regarding oral intake is expected for the samples containing cobalt concentrations above the detection limit. Regarding inhalation of textile dust no health risk is expected under the conditions used. The same applies to dermal absorption. However, a potential for allergy or sensitisation could not be excluded.

8.7 COPPER

8.7.1 Identification

 Name
 Copper

 CAS no.
 7440-50-8

 EINECS no.
 231-159-6

Molecular formula Cu

Atomic weight 63.55 g/mol

The melting point is 1083°C and the boiling point is ca. 2590°C (Budavari 1989).

Copper can be found at two oxidation stages Copper(I) and Copper(II) and the two are each included in several different chemical compounds.

8.7.1.1 Classification

Copper compounds are classified differently according to the specific copper compound. Most copper compounds are classified Harmful if swallowed because copper may cause liver damage (Larsen *et al.* 2000).

Some compounds such as copper(I) chloride and copper sulphate a classified Dangerous for the environment and Toxic to aquatic organisms and May cause long-term adverse effects in the aquatic environment. Other copper compounds are classified Irritant but not with risks for allergy and sensitisation (Miljøministeriet 2002).

8.7.1.2 Measured concentrations

The detection limit in the analysis is 1 mg/kg. In 10 samples concentrations above the detection limit were observed.

In a sample, blue cotton, a concentration of 680 mg/kg was observed and in another sample, cotton oilcloth, 260 mg/kg.

In the remaining samples concentrations were below 25 mg/kg.

8.7.2 Health

Copper is mainly harmful by oral intake. The acceptable daily intake dose (TDI) is derived at 0.14 mg/kg bw/day (Baars *et al.* 2001).

the highest acceptable concentration in air by inhalation (HAC) is recommended to 1×10^{-3} mg/m³ (Baars *et al.* 2001).

In the available data on acceptable daily intake, no distinction between the copper compounds was made. The two forms are therefore treated as one.

Merian (1991) refers that approx. 50% is absorbed via the gastrointestinal tract. The bioavailability factor by inhalation (BIO_{inh}) is 0.5 and the bioavailability by oral intake (BIO_{oral}) is estimated to 0.5 (Baars *et al.* 2001).

8.7.3 Evaluation

8.7.3.1 Oral intake

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake of:

[0.020 kg x 680 mg/kg x 0.5] / 10 kg body weight = 0.7 mg using the highest measured concentration.

Using the concentration of 25 mg/kg textile the oral intake is: [0.020 kg x 25 mg/kg x 0.5] / 10 kg body weight = 0.025 mg.

Since the acceptable daily intake dose is 0.14 mg/kg body weight it can be concluded that the two textile samples with the high concentrations of copper, D with 680 mg/kg and Q with 260 mg/kg, exceeds the TDI value.

8.7.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = $[10 \text{ kg x } 680 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 34 \text{ x} 10^{-3} \text{ mg/m}^3 \text{ for the highest concentration.}$

The acceptable concentration in air is $1 \times 10^{-3} \text{ mg/m}^3$ and an exceeding in the two samples with the highest concentrations is observed.

The amount of inhaled substance = bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled copper is: $0.5 \times 34 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 5 \times 10^{-3} \text{ mg/kg bw}.$

The TDI of 1.4×10^{-3} mg/kg was exceeded in the two samples with high concentrations of copper (D and Q).

8.7.3.3 Dermal absorption

The potential for dermal absorption is estimated below.

Calculation example:

Assuming 100% dermal absorption:

Adult absorption: $680 \times 0.5 / 70 \times 1 = 4.847$ mg/kg bw Child absorption: $680 \times 0.25 / 10 \times 1 = 17.0$ mg/kg bw

T-shirt, child absorption: $680 \times 0.16 / 10 \times 1 = 10.88$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A_{derm}, adult): $4.857 \times 0.001 = 4.857 \times 10^{-3}$ mg/kg bw Child absorption (A_{derm}, child): $17.0 \times 0.001 = 17.0 \times 10^{-3}$ mg/kg bw

TABLE 8.6 DERMAL ABSORPTION OF COPPER

| Tex | tile | Cu | 0.5 kg textile | Adult | Child | Tshirt | A _{derm} , adult | A _{derm} , child |
|-----|-----------------------------------|-----------|-------------------|--------------|-------------|-------------|------------------------------|------------------------------|
| | | mg/k g | mg Cu | mg/kg/b w | mg/kg bw | mg/kg bw | μg/kg bw | μg/kg bw |
| В | 100% cotton, yellow (children) | 25 | 12.5 | 0.179 | 0.625 | 0.4000 | 0.179 | 0.625 |
| D | 100% cotton, blue | 680 | 340 | 4.857 | 17.000 | 10.880 | 4.857 | 17.000 |
| G | 100% cotton, animal motive | 1.5 | 0.75 | 0.011 | 0.038 | 0.0240 | 0.011 | 0.038 |
| J | 100% flax | 20 | 10 | 0.143 | 0.500 | 0.3200 | 0.143 | 0.500 |
| М | 100% wool | 5 | 2.5 | 0.036 | 0.125 | 0.0800 | 0.036 | 0.125 |
| Ν | 100% cotton, versage | 1.6 | 0.8 | 0.011 | 0.040 | 0.0256 | 0.011 | 0.040 |
| 0 | 100% cotton (bear) | 5.3 | 2.65 | 0.038 | 0.133 | 0.0848 | 0.038 | 0.133 |
| Р | 100% wool, furniture | 4.9 | 2.45 | 0.035 | 0.123 | 0.0784 | 0.035 | 0.123 |
| Q | 100% cotton (oilcloth) | 260 | 130 | 1.857 | 6.500 | 4.1600 | 1.857 | 6.500 |
| R | Cotton / PET (napkins) | 11 | 5.5 | 0.079 | 0.275 | 0.1760 | 0.079 | 0.275 |

For copper the estimated concentrations for dermal absorption ($A_{\rm derm}$) are below 0.14 mg/kg bw/day. Therefore, it is considered that no immediate health risk exists by the measured concentrations of copper in textile.

8.7.3.4 Conclusions

In two textile samples, blue cotton and cotton oilcloth, relative high concentrations of copper were measured.

For these two samples there may be a health risk by oral intake and inhalation while there was expected no health risks from the remaining textiles. Regarding dermal uptake by skin contact no health risk was expected at the measured concentrations.

8.8 LEAD

8.8.1 Identification

 Name
 lead

 CAS no.
 7439-92-1

 EINECS no.
 231-100-4

Molecular structure Pb

Atomic weight 207.2 g/mol Synonym Plumbum (Pb)

The melting point is 327.4°C. The boiling point is 1740°C. The vapour pressure is low: 236 Pa (1.77 mmHg) at 1000°C.

Lead may be used in pigments for dyes (Budavari 1989). Lead acetate is used for dying and printing cottons (Budavari 1989).

8.8.1.1 Classification

Several lead compounds are classified in the list of dangerous substances (Miljøministeriet 2002).

Lead alkyls are classified very toxic with reprotoxic effects and dangerous to the environment.

Other lead compounds are classified toxic with reprotoxic effects, harmful by inhalation and if swallowed, dangerous for the environment, toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment

8.8.1.2 Measured concentrations

The detection limit for lead was 0.5 mg/kg. In a single sample, PET colourful, a lead concentration of approx. 1.5 mg/kg was measured. The concentration in three samples varied between 0.5 and 1 mg/kg while the remaining was below the detection limit (cf. table 8.1).

8.8.2 Health

Lead is considered a problem due to its effects on the central nervous system in adults, children and the unborn child.

WHO has derived a PTWI (provisional tolerable weekly intake) for children of 25 μ g/kg bw/week without using safety factors (WHO 1996). No information has been found indicating a change necessary of the FAO/WHO's PTWI. Based on the PTWI a tolerable daily intake (TDI) value is derived at 3.6×10^{-3} mg/kg bw/day.

No information on acceptable concentration values by inhalation of lead was available. However, WHO (1996) presents a reference concentration RfC (inhalation) of 0.5 µg/m³.

The bioavailability by inhalation (BIO_{inh}) is 0.5 and bioavailability by oral intake (BIO_{anh}) is estimated to be 0.1 (Baars *et al.* 2001).

8.8.3 Evaluation

8.8.3.1 Oral intake

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g and using the maximum measured concentration 1.6 mg/kg textile this corresponds to an oral intake of:

 $[0.020 \text{ kg x } 1.6 \text{ mg/kg x } 0.1] / 10 \text{ kg body weight} = 0.32 \,\mu\text{g/kg body weight}.$

The acceptable daily intake dose is 3.6 µg per kg body weight and it is observed that estimations based on the maximum measured value do not exceed this value.

8.8.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration of lead in dust in the air based on 1.6 mg/kg is estimated to be:

Concentration in air = $[10 \text{ kg x } 1.6 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 0.08 \mu\text{g/m}^3$.

Amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled lead is:

 $0.5 \times 0.08 \,\mu\text{g/m}^3 \times 0.8 \,\text{m}^3/\text{hour} \times 24 \,\text{hours} / 70 \,\text{kg} = 0.011 \,\mu\text{g/kg} \,\text{body weight}.$

Since the acceptable dose is $3.6 \mu g/kg$ body weight it is observed that the estimated intake is far below that level.

8.8.3.3 Dermal contact

The estimated absorption from skin contact is estimated below

Calculation example:

Assuming 100% dermal absorption:

Adult absorption: $1.6 \times 0.5 / 70 \times 1 = 0.011$ mg/kg bw Child absorption: $1.6 \times 0.25 / 10 \times 1 = 0.04$ mg/kg bw

T-shirt, child absorption: $1.6 \times 0.16 / 10 \times 1 = 0.0256$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption ($A_{derm,}$ adult): $0.011 \times 0.001 = 0.011 \times 10^{-3}$ mg/kg bw Child absorption ($A_{derm,}$ child): $0.04 \times 0.001 = 0.04 \times 10^{-3}$ mg/kg bw

TABLE 8.7 DERMAL UPTAKE OF LEAD

| | The state of the s | | | | | | | | |
|-----|--|-------|---------|----------|----------|----------|----------|----------|--|
| Tex | tile | Pb | 0.5 kg | Adult | Child | Tshirt | Aderm, | Aderm, | |
| | | | textile | | | | adult | child | |
| | | mg/kg | mg | mg/kg/bw | mg/kg bw | mg/kg bw | μg/kg bw | μg/kg bw | |
| F | 100% PET, colourful | 1.6 | 0.8 | 0.0114 | 0.0400 | 0.0256 | 0.0114 | 0.0400 | |
| М | 100% wool | 0.73 | 0.365 | 0.0052 | 0.0183 | 0.0117 | 0.0052 | 0.0183 | |
| 0 | 100% cotton (bear) | 0.51 | 0.255 | 0.0036 | 0.0128 | 0.0082 | 0.0036 | 0.0128 | |
| Р | 100% wool, furniture | 0.63 | 0.315 | 0.0045 | 0.0158 | 0.0101 | 0.0045 | 0.0158 | |
| | DL | 0.5 | 0.25 | 0.0036 | 0.0125 | 0.0080 | 0.0036 | 0.0125 | |

The estimated concentration by dermal uptake (A_{derm}) is below 3.6 µg/kg bw/day. It is therefore considered that no immediate health risk is expected to the consumer at the measured concentrations.

8.8.3.4 Conclusions

In a single sample, PET colourful, a lead concentration of 1.6 mg/kg was measured. Three samples varied between 0.5 and 1 mg/kg while the remaining samples were below the detection limit. It is assessed that even the highest measured concentration did not cause health risks by oral, inhalation or dermal contact to consumers.

8.9 MERCURY

8.9.1 Identification

Name Mercury CAS no. 7439-97-6 EINECS no. 231-106-7

Molecular formula Hg (Hydrargyrum)

Atomic weight 200.59 g/mol

The melting point is -38.9° C. The boiling point is 356.7° C (Budavari 1989). The vapour pressure is 0.25 Pa (2×10^{-3} mmHg). Mercury is the only metal with a vapour pressure that makes evaporation possible.

The water solubility is approx. 20 mg/l at 25°C.

8.9.1.1 Classification

Mercury is classified under EC index no. 080-001-00-0:

T;R23 R33 Toxic. Toxic by inhalation. Danger of cumulative effects N;R50/53 Dangerous for the environment. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

The classification varies according to concentration in the product. For instance the classification for inorganic and organic mercury compounds are presented below (Miljøministeriet 2002):

| Index no. | Compound | Classification | Concentrations |
|-----------|------------------|-----------------|---|
| | mercury with the | R33 N;R50/53 | C ≥ 2: Tx;R26/27/28 R33 0.5% ≤ C < 2%: T;R23/24/25 R33 0.1% ≤ C < 0.5%: Xn; R20/21/22 R33 |
| | mercury with the | R33 R50/53 | C ≥ 1% : Tx;R26/27/28 R33 0.5% ≤ C < 1% : T;R23/24/25 R33 0.05% ≤ C < 0.5% : Xn;R20/21/22 R33 |

It is noted that during the current revision of the annex a minor change is suggested that mostly concern the addition of environmental classification but also a further subdivision of the concentration levels (ATP 2002):

| Indeks no. | Compound | Classification | Concentrations |
|--------------|---------------------|----------------|---|
| | compounds of | R33 R50/53 | $C \geq 25\%: T+,N; R26/27/28-33-50/53 \\ 2.5\% \leq C < 25\%: T+,N; R26/27/28-33-51/53 \\ 2\% \leq C 2.5\%: T+; R26/27/28-33-52/53 \\ 0.5\% \leq C < 2\%: T; R23/24/25-33-52/53 \\ 0.25\% \leq C < 0.5\%: Xn; R20/21/22-33-52/53 \\ 0.1\% \leq C < 0.25\%: Xn; R20/21/22-33$ |
| 080-004-00-7 | of mercury with the | R33 R50/53 | $C \ge 25\% : T+,N; R26/27/28-33-50/53$ $2.5\% \le C < 25\% : T+,N; R26/27/28-33-51/53$ $1\% \le C < 2.5\% : T+; R26/27/28-33-52/53$ $0.5\% \le C < 1\% : T; R23/24/25-33-52/53$ $0.25\% \le C < 0.5\% : Xn; R20/21/22-33-52/53$ $0.05\% \le C < 0.25\% : Xn; R20/21/22-33$ |

8.9.1.2 Measured concentrations

In none of the analysed samples were measured a concentration above the detection limit 0.05 mg/kg.

8.9.2 Health

Mercury is readily absorbed after inhalation, via skin and from the gastrointestinal tract.

WHO has determined a PTWI of 5 μ g/kg bw/week of which no more than 3.3 μ g must be methylated mercury (MST 1994). The PTWI corresponds to approx. 0.72 μ g/kg bw/day.

The acceptable daily intake dose by oral intake (TDI) is determined to 7.2×10^{-4} mg/kg bw/day (WHO 1996). RIVM has later recommended a

separation into inorganic mercury with a TDI of 2 μg/kg bw/day and a TDI of 0.1 μg/kg bw/day for organic mercury (Baars *et al.* 2001).

The highest acceptable daily concentration in air by inhalation (HAC) is recommended to 2×10^{-4} mg/m³ for metallic mercury adsorbed to dust (Baars *et al.* 2001).

The bioavailability by inhalation (BIO_{inh}) is 0.75 and the bioavailability by oral intake (BIO_{anh}) is estimated to 0.07 (Baars *et al.* 2001).

8.9.3 Evaluation

Below is evaluated whether the concentration at the detection limit 0.05 mg/kg would cause any health risk.

8.9.3.1 Oral intake

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake of:

[0.020~kg~x~0.05~mg/kg~x~0.07] / 10 kg body weight = 0.007 $\mu g/kg$ body weight.

The TDI value for methylated mercury is $0.1 \mu g/kg$ and higher for inorganic mercury.

Because all samples contained mercury below the detection limit even the lowest TDI value is not exceeded.

8.9.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated based on the detection limit concentration. As mercury has a high vapour pressure the total amount is in principle volatile and not only the part that is adsorbed to dust. Mercury's vapour pressure is below 0.1 mmHg and therefore it is assumed that 1% of the mercury is available for inhalation (TGD 1996).

Concentration in air = $[10 \text{ kg x } 0.05 \text{ mg/kg x } 0.01] / 20 \text{ m}^3 = 2.5 \text{x} 10^{-4} \text{mg/m}^3$.

The acceptable concentration is 2×10^{-4} mg/m³ and the estimated concentration is thus at the same level as the acceptable daily concentration based on the detection limit concentration. However, it should be noted it is presumed that 1% is released and bioavailable within one day. It may seem unlikely but as the emission rate is unknown it is useful for a first evaluation.

The amount of inhaled substance = bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled mercury is: $0.75 \times 2.5 \times 10^{-4} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.05 \text{ µg/kg body weight}$

WHO's TDI value of $0.72~\mu g/kg$ body weight is not exceeded when it is assumed that mercury corresponding to 1% of 0.05~mg/kg evaporates.

Inhalation of mercury does not present any health risk at the measured concentrations in textiles to the consumer.

8.9.3.3 Dermal absorption

The estimated dermal absorption based on the detection limit is $0.0004 \, \mu g/kg$ for adults and $0.0013 \, \mu g/kg$ bw for children. These intake values are far below even the lowest TDI value. It is therefore considered that there is no immediate health risk to the consumer from the textiles at the measured concentrations.

Assuming 0.1% dermal absorption:

Adult absorption: $0.05 \times 0.5 / 70 \times 0.001 = 3.57 \times 10^{-7}$ mg/kg bw Child absorption: $0.05 \times 0.25 / 10 \times 0.001 = 1.25 \times 10^{-6}$ mg/kg bw

8.9.3.4 Conclusions

For all textile samples the content of mercury was below the detection limit 0.05 mg/kg.

For textiles containing mercury below the detection limit it is concluded that no significant health risk existed by oral intake, by inhalation or at dermal contact with the textiles used in the study.

8.10 NICKEL

8.10.1 Identification

 Name
 Nickel

 CAS no.
 7440-02-0

 EINECS no.
 231-111-4

Molecular formula Ni

Atomic weight 58.69 g/mol

Nickel has a melting point of 1455°C (Budavari 1989).

8.10.1.1 Classification

Nickel is classified under EU index no. 028-002-00-7:

Carc3;R40 Possible risks of irreversible effects. May cause sensitisation

R43 by skin contact

Most nickel compounds are classified due to the allergenic properties by R43: May cause sensitisation by skin contact (Miljøministeriet 2002).

Some nickel compounds are either recognised as carcinogenic or suspected to be carcinogenic such as e.g. nickel carbonate and nickel sulphate (IPCS 1990).

Besides most nickel compounds are classified Dangerous for the environment and R50/53, very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (Miljøministeriet 2002).

8.10.1.2 Measured concentrations

The detection limit for nickel is 1 mg/kg. In a single sample (acrylic/nylon) was measured 1.1 mg/kg while all other samples were containing nickel below the detection limit.

8.10.2 Health

Skin contact to nickel is essential as most nickel compounds may cause allergic reactions in sensitised humans. An evaluation of skin contact is therefore relevant but relevant data for such an evaluation was not available. EU has included nickel in its risk assessment programme on existing substances but it is not yet finalised (ECB) and the result therefore unknown.

The acceptable daily intake dose by oral intake (TDI) is recommended to 5×10^{-3} mg/kg bw/day (WHO 1996). RIVM however has re-evaluated the value and recommend 0.05 mg/kg bw/day (Baars *et al.* 2001).

The acceptable daily concentration in air for inhalation of nickel containing dust (HAC) is recommended to 5×10^{-6} mg/m³ (Baars *et al.* 2001).

The bioavailability by inhalation (BIO_{inh}) is 0.06 and the bioavailability by oral intake (BIO_{oral}) is estimated to 0.05 (Baars *et al.* 2001).

8.10.3 Evaluation

8.10.3.1 Oral intake

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g this corresponds to an oral intake using a concentration of 1.1 mg/kg to:

 $[0.020 \text{ kg x } 1.1 \text{ mg/kg x } 0.05] / 10 \text{ kg body weight} = 0.11 \mu\text{g/kg body weight}.$

The lowest acceptable daily intake dose is $5 \mu g/kg$ body weight which is higher than the estimated intake value. Therefore, no immediate health risk is expected from oral exposure to the analysed textiles.

8.10.3.2 Inhalation

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air is estimated to be:

Concentration in air = [10 kg x 1.1 mg/kg x 0.0001] / 20 m³ = $0.055 \,\mu\text{g/m}^3$, which is approximately 10 times above the acceptable air concentration of 5 x $10^{-6} \,\text{mg/m}^3$.

The amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight.

The amount of inhaled substance is:

 $0.06 \times 0.055 \,\mu\text{g/m}^3 \times 0.8 \,\text{m}^3/\text{hour} \times 24 \,\text{hours} \,/\,70 \,\text{kg} = 9.4 \times 10^4 \,\mu\text{g/kg}$ body weight.

The acceptable daily intake for nickel is $5 \mu g/kg$ body weight, which is considerably higher than the estimated value.

8.10.3.3 Dermal absorption

The potential absorption of nickel is estimated below.

Assuming 100% dermal absorption:

Adult absorption: $1.1 \times 0.5 / 70 \times 1 = 0.007857$ mg/kg bw Child absorption: $1.1 \times 0.25 / 10 \times 1 = 0.0275$ mg/kg bw

T-shirt, child absorption: $1.1 \times 0.16 / 10 \times 1 = 0.0176$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption (A $_{\text{derm.}}$, adult): $0.00786 \times 0.001 = 0.00786 \times 10^{-3}$ mg/kg bw Child absorption (A $_{\text{derm.}}$, child): $0.0275 \times 0.001 = 0.0275 \times 10^{-3}$ mg/kg bw

The estimated concentrations for dermal absorption (A_{derm}) are below 5 µg/kg bw/day. It is therefore assessed that there will be no immediate health risk to consumers from dermal absorption from textiles at the measured concentrations.

Nickel is recognised as allergenic. No information was available as to the concentration acceptable to exclude the potential as it is individual and depends on the sensitisation of the individual human.

According to Danish regulation on certain nickel containing products (Miljøog Energiministeriet 2000) product that are in repeated and prolonged dermal contact not release more than 0.5 µg Ni/cm²/week. At a maximum measured content of 1.1 mg/kg textile and a density 333 g/m² textile is calculated a maximum content of 0.03 ng/cm². This would result in a margin of safety of 10000. Thus, the possibility of allergic reactions is considered insignificant.

8.10.3.4 Conclusions

Only on sample contained nickel just above the detection limit 1 mg/kg while no other sample contained nickel above the detection limit.

A nickel content at approximately the detection level was not indicated to be of any health risk by oral, inhalation or by dermal contact to the consumer at the measured concentrations. Potential allergenic problems could not be evaluated.

8.11 TIN

8.11.1 Identification

Name Tin

CAS no. 7440-31-5 EINECS no. 231-141-8

Molecular formula Sn

Atomic weight 118.69 g/mol Synonym Stannate

The melting point is 231.9°C. The boiling point is 2507°C.

Stannic oxide is used in the dyeing of textiles just as compounds like the compounds stannic chloride, stannous oxalate and stannous tartrate is used in dyeing and printing textiles (Budavari 1989).

8.11.1.1 Classification

Tin exists in two oxidation stages Sn(II) and Sn(IV) and has different properties depending on the specific compounds, organic or inorganic.

As example stannic chloride (CAS 7646-78-8) is classified Corrosive and R52/53, Dangerous for the environment, Harmful to aquatic organisms and

may cause long-term adverse effects in the aquatic environment (Miljøministeriet 2002).

8.11.1.2 Measured concentrations

The detection limit for tin in the analyses is 0.05 mg/kg. Four samples were analysed for tin. Only in one sample of 100% cotton with animal motive, a concentration of 4.9 mg/kg was observed. In the remaining samples tin was not detected above the detection limit.

8.11.2 Health

In a Dutch exposure assessment of tin in textiles different organic tin compounds in textiles were found in e.g. T-shirts, underpants, shirts, socks and tights (Janssen *et al.* 2000).

In the RIVM report is suggested an acceptable daily oral intake (TDI) of 2.3 μ g/kg bw (equivalent to 0.6 μ g Sn/kg bw/day) based on dioctyl tin compounds and usable for dialkyl tin compounds. For triphenyl tin compounds is calculated an acceptable daily oral intake (ADI) of 0.5 μ g/kg bw/day based on an evaluation of the highest dose without adverse effects (NOAEL) of 1.7 mg/kg/day for rats (Janssen *et al.* 2000).

The threshold limit value (TLV) for 8 hours exposure in the working environment is for organic tin, calculated as Sn, 0.1 mg Sn/m³, for tributylic tin compounds 0.05 mg Sn/m³ and for inorganic tin compounds 2 mg Sn/m³ (AT 2002).

The bioavailability by inhalation (BIO_{inh}) was not available but the bioavailability by oral intake (BIO_{oral}) is estimated to 0.25 (Baars *et al.* 2001).

8.11.3 Evaluation

Assuming a child sucks or chews on textile equivalent to 400 cm² or 20 g, this corresponds to an oral intake of:

[0.020 kg x 4.9 mg/kg x 0.25] / 10 kg body weight = 2.45 ug/kg body weight.

Using the detection limit 0.05 mg/kg, the oral intake is:

[0.020 kg x 0.05 mg/kg x 0.25] / 10 kg body weight = 0.025 ug/kg body weight.

The acceptable oral intake is approx. 0.5 ug/kg body weight indicating that the sample where tin was detected exceeds the ADI while samples below the detection limit do not exceed the ADI value.

8.11.3.1 *Inhalation*

Assuming a person reside in a 20 m³ room containing 30 m² textiles equivalent to a weight of 10 kg and the release to air is 0.01%, the concentration in the air based on 4.0 mg Sn/kg:

Concentration in air = $[10 \text{ kg x } 4.9 \text{ mg/kg x } 0.0001] / 20 \text{ m}^3 = 0.25 \text{ x} 10^{-3} \text{ mg/m}^3$.

The daily acceptable air concentration is unknown but the margin of safety is more than a factor 100 below the TLV. Therefore it is assessed that there is

no immediate health risk by inhalation of textile dust containing tin at the measured concentrations.

The amount of inhaled substance =

bioavailability x conc. in air x inhalation rate x duration / body weight

As the bioavailability factor is unknown it is set to 1 (100%).

The amount of inhaled substance is:

 $1 \times 0.25 \times 10^{-3} \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{hour} \times 24 \text{ hours} / 70 \text{ kg} = 0.07 \text{ ug/kg body weight.}$

Thus the ADI for intake is not exceeded.

8.11.3.2 Dermal absorption

The potential dermal absorption is calculated below.

Assuming 100% dermal absorption:

Adult absorption: $4.9 \times 0.5 / 70 \times 1 = 0.035$ mg/kg bw Child absorption: $4.9 \times 0.25 / 10 \times 1 = 0.1225$ mg/kg bw T-shirt, child absorption: $4.9 \times 0.16 / 10 \times 1 = 0.078$ mg/kg bw

Assuming 0.1% absorption:

Adult absorption ($A_{derm,}$ adult): $0.035 \times 0.001 = 0.035 \times 10^{-3}$ mg/kg bw Child absorption ($A_{derm,}$ child): $0.123 \times 0.001 = 0.123 \times 10^{-3}$ mg/kg bw

The estimated concentration assuming 0.1% absorption resulted in dermal absorption values (A_{derm}) below the ADI 0.6 µg Sn/kg bw/day. Therefore, it is assessed that there is no immediate health risk for the consumer at the measured concentrations.

8.11.3.3 Conclusions

Of the four analysed samples only one contained concentration above the detection limit. The measured concentration of tin in the sample containing 4.9 mg Sn/kg (sample G) may cause a health risk by oral intake. Oral intake by the remaining textiles, inhalation and skin contacts by all samples were not considered to present any health risk to consumers at the measured concentrations.

8.12 SUMMARY

The summary of results on the evaluations and conclusions are presented below.

TABLE 8.8: SUMMARY OF CONCLUSIONS ON METALS

| Metal | Detection limit | Analyses results | Oral intake | Inhalation | Dermal absorption |
|----------|--------------------|---|---|--|---|
| Antimony | 0.5 mg/kg | 35 mg/kg, 110 mg/kg, 200 mg/kg, remaining below detection limit | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Arsenic | 1 mg/kg | Max 1 mg/kg | Health risk may exist below the detection limit, i.e. arsenic above 0.5 times the detection limit may cause a health risk. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Barium | 0.3 mg/kg | 1 sample 10 mg/kg, several up to 2 mg/kg | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Cadmium | 0.05 mg/kg | No samples above detection limit | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Chromium | 0.2 mg/kg | 2 samples approx. 60 mg/kg 1 sample 7 mg/kg, remaining below i mg/kg or detection limit | If the content of chromium in the two samples at the highest levels are chromium(VI) there may be a health risk. Is the chromium mostly chromium(III) no health risk is expected. For the remaining samples no health risks are expected. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. Allergy and sensitisation is not evaluated. |
| Cobalt | 0.2 mg/kg | 2 samples 40 mg/kg 2 samples 2-5 mg/kg, remaining below the detection limit | Health risk exist in the two samples at high concentrations, health risk may exist in two samples at the intermediate values. No risk in samples below detection limit. | No health risks to consumer at the measured concentrations. Allergy and sensitisation is not evaluated | No health risks to consumer at the measured concentrations. Allergy and sensitisation is not evaluated |
| Copper | 1 mg/kg | 2 samples of 680 and 260 mg/kg, remaining below 25 mg/kg | Health risk may exist by the two samples at high concentrations. No risk from the remaining samples. | Health risk may exist by the two samples at high concentrations. No risk from the remaining samples. | No health risks to consumer at the measured concentrations. |
| Lead | 0.5 mg/kg | 1 sample 1.5 mg/kg, 2 samples 0.5-1 mg/kg, remaining below detection limit | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Mercury | o.o5 mg/kg | All samples below detection limit | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |
| Nickel | ı mg/kg | 1 sample 1.1 mg/kg, remaining below detection limit | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. Allergy and sensitisation is not evaluated. |
| Tin | 0.05 mg/kg | 1 sample 4.9 mg/kg, remaining below detection limit | Health risk may exist by the one sample at high concentration. No risk from the remaining samples. | No health risks to consumer at the measured concentrations. | No health risks to consumer at the measured concentrations. |

9 Screening

For the 10 textiles included in the analysis package A, a qualitative screening was performed for other compounds or groups of compounds. The results of the screening are presented in table 9.1.

TABLE 9.1 COMPOUNDS OR GROUPS OF COMPOUNDS OBSERVED IN THE SCREENING

| Sample | Detected compounds | |
|------------------------|--|--|
| B) 100% cotton, yellow | Phthalate*, fatty acids, $C_xH_y(C_{8-20})$, $C_xH_y(C_{20-40})$, 2-2`-oxybis ethanol, | |
| (children) | squalene, aliphatic alcohols, aliphatic amide | |
| E) Cotton/PET brown | fatty acids, aliphatic amide | |
| G) 100% (animal | fatty acids, 2-2`-oxybis ethanol | |
| motive) | | |
| I) 100% cotton | fatty acids, $C_xH_y(C_{8-20})$, $C_xH_y(C_{20-40})$,), 2-2`-oxybis ethanol, propylene | |
| (flowers) | glycol, aliphatic amide | |
| J) 100% flax | bis (2-ethylhexyl) maleate, 2-2`-oxybis ethanol, squalene | |
| L) 100% viscose | Phthalate*, 5-hydroxy-methyl-furfural | |
| M) 100% wool | fatty acids, $C_xH_v(C_{20-40})$, 2-2`-oxybis ethanol, 2-(2-butoxy-ethoxy)ethanol | |
| O) 100% cotton (bear) | fatty acids, $C_xH_y(C_{20-40})$ | |
| Q) 100% cotton | C _x H _y (C ₂₀₋₄₀), bis (2-ethylhexyl) maleate, benzylbenzoate, 2-2`-oxybis | |
| (oilcloth) | ethanol | |
| T) 100% PET (pillow) | fatty acids, $C_x H_y (C_{20-40})$ | |

^{*:} presumed to be DEHP

Below is presented data on the individual compounds and groups of compounds relevant to health properties.

9.1 SPECIFIC COMPOUNDS

9.1.1 2,2 '-oxybis ethanol

9.1.1.1 Identification

The compound has CAS no. 111-46-6 and the synonym diethylene glycol. The compound has EU-no. 203-872-2 and Index-no. 603-140-00-6.

The compound is used as intermediate in several industries e.g. in the manufacture of paints, lacquers and in the textile industry.

The boiling point is 245°C and the melting point is -6°C. The density is 1.18 at 20°C (Budavari 1989).

The vapour pressure is 5.7×10^{-3} mmHg at 25° C (0.76 Pa) (Daubert *et al.* 1989).

Diethylene glycol is soluble in water, alcohol, ether, acetone and ethylene glycol while it is insoluble in toluene, kerosene, oils and carbon tetrachloride (Budavari, 1989, Browning, 1965).

9.1.1.2 Classification

The compound is classified Harmful and R22: Harmful if swallowed.

The threshold limit value for diethylene glycol is 2.5 ppm or 11 mg/m³ (AT 2002).

9.1.1.3 Health

The major health risks relate to oral intake of diethylene glycol in relative large amounts. In one case 105 deaths were observed among 353 humans which had swallowed a solution of sulphanil amide in liquid solution containing 72% diethylene glycol (Amdur *et al.* 1991).

Oral intake of a single dose of about 1 ml/kg is lethal to humans (Amdur *et al.* 1991). Another reference estimates the acute lethal dose for humans to be between 0.5 and 5 gram/kg (Gosselin *et al.* 1976).

The compounds may cause depressions and harm liver and kidneys (Gosselin, 1976).

9.1.2 2-(2-butoxylethoxy)ethanol

9.1.2.1 Identification

The compound has CAS no. 112-34-5. It is also named butoxydiethylene glycol, butoxyl diglycol or butyl carbitol. The molecular weight is 162.2 g/mol and the molecular formula is $C_8H_{18}O_3$. The structure is shown below.

The boiling point is 230 °C, the melting point is -68 °C and the density 0.95 at 20°C (Budavari 1989).

The octanol/water distribution coefficient log Kow is measured to 0.56 (Hansch *et al.* 1995).

The compound is miscible in water and most organic solvents.

The vapour pressure is estimated to 0.022 mm Hg at 25°C (2.9 Pa) (Daubert et al. 1989).

9.1.2.2 Classification

The substance is not on the list of dangerous substances. The threshold limit value is 100 mg/m³ (AT 2002).

9.1.2.3 Health

it is noted that butyl diglycol resembles diethylene glycol and may be a little more toxic (Gosselin *et al.* 1984). Data in the database HSDB show that the two glycols in health perspective are closely related.

Clayton and Clayton (1982) states that the compound is most toxic when inhaled or absorbed through skin repeatedly at low doses. It is also mentioned that the compound causes irritation of eyes but not the skin.

9.1.3 Propylenglycol

9.1.3.1 Identification

The CAS no. is 57-55-6. Propylene glycol is also named 1.2-propanediol. The molecular weight is 76.1 g/mol and the molecular formula $C_3H_8O_2$. The structure is shown below.

The boiling point is 188°C and the melting point –59°C (Budavari 1989). The compound is miscible with water and most organic solvents. The vapour pressure is estimated to 0.129 mmHg (15 Pa) at 25°C (Daubert *et al.* 1989)

Based on a determined octanol/water distribution coefficient log Kow -0.92 (Hansch *et al.* 1995) the BCF for propylene glycol is estimated to 3.6.

9.1.3.2 Classification

Propylene glycol is not on the list of dangerous substances (Miljøministeriet 2002).

Propylene glycol is not on the list of threshold limit values (AT 2002).

9.1.3.3 Health

Propylene glycol is used as solvent in food, cosmetics and pharmaceuticals (Clayton and Clayton 1982).

No data from the description in the Hazardous Substance Data Bank (HSDB) indicates that the substance should present any significant health risk.

A lethal dose to humans is given as 15 gram/kg (Gosselin et al. 1976).

9.1.4 Benzyl benzoate

The CAS no. is 120-51-4. The substance is also known as benzoic acid phenylmethyl ester. The molecular weight is 212 g/mol and the molecular formula is $C_{14}H_{12}O_2$. The structure is presented below.

$$H_3C$$
 O
 O
 CH_3
 CH_3

The boiling point is 323°C and the melting point is 21°C. The density is 1.11 (Budavari, 1989).

The octanol/water distribution coefficient Log Kow is measured to 3.97 (Hansch *et al.* 1995) and the vapour pressure is measured to 0.000224 mm Hg (0.03 Pa) at 25°C (Daubert *et al.* 1989).

9.1.4.1 Classification

The substance is not on the list of dangerous substances.

9.1.4.2 Health

Benzyl benzoate is used as additive to food, in cosmetics and other relations. Benzyl benzoate may be added to food in concentrations of 1-100 mg/kg, depending of the specific product.

Benzyl benzoate is relatively non-toxic but may cause irritation of skin and eyes (American Medical Association, 1994).

The lethal dose to humans is estimated to between 0.5 and 5 gram/kg (Gosselin *et al.* 1976).

9.1.5 5-hydroxyl-methylfurfural

9.1.5.1 Identification

The CAS no. is 67-47-0. The molecular weight is 126 g/mol and the molecular formula $C_6H_6O_3$. The structure is shown below.

The melting point is 32-35°C. The boiling point is 114-116°C at 1 mmHg.

The health properties have been described in few details. There are indications that the compound is mutagenic and may cause tumours. The reported Ames tests were positive (Shinohara *et al.* 1986). Damages to DNA in studies on hamsters have been reported (Janzowski *et al.* 2000).

9.1.6 bis(2-ethylhexyl)maleate

The CAS no is 142-16-5. The molecular weight is 340.5 g/mol. The molecular formula is $C_{20}H_{36}O_4$. The structure is shown below.

The compound is liquid at room temperature. The melting point is -60°C. The boiling point at 10 mmHg is 164°C, which mean that the boiling point is

much higher at 1 atm. The density is 0.94 (Clayton and Clayton 1982). The substance is soluble in water.

The substance is used as co-monomer in the production of several polymers such as vinyl acetates, acrylates, and amides and in the manufacture of anionic tensides.

The compound is included in HSDB (Hazardous Substance Databank) in a very short version without description of health risks.

The substance is not classified. No threshold limit values was available.

9.1.7 Squalene

The CAS no. is 7683-64-9. The molecular weight is 410.7 g/mol. The molecular formula is $C_{30}H_{50}$. The molecular structure is given below.

The melting point is about -75°C. Boiling point is 285°C. Squalene is practically insoluble in water but freely soluble in ether, acetone and other organic solvents (Budavari 1989).

Squalene is used as bactericide, intermediate in manufacturing pharmaceuticals, organic colouring materials and surface-active agents (tensides).

Data on health have not been available.

9.2 SUBSTANCE GROUPS

9.2.1 Hydrocarbons

Several hydrocarbons were identified within the two groups C_xH_y (C_{8-20}) and C_xH_y (C_{20-40}).

The short-chained hydrocarbons with a chain length from 8 to 20 may include compounds like octane, nonane, and decane up to eicosane ($C_{20}H_{42}$). The carbon chain of the compounds can be linear or branched. The compounds may contain one or more double bonds.

The simplest compound is octane, which has the molecular formula C_8H_{18} and CAS no. 111-65-9. Octane is classified Irritant at skin contact, may cause lung damage by oral intake and vapours may cause lethargy and dizziness. It

is also classified dangerous for the environment, very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

The compounds $C_{16}H_{34}$, hexadecane and $C_{18}H_{38}$, octadecane are solvents and are used e.g. as intermediates in the chemical industry. Hexadecane has a boiling point of 268°C and octadecane 318°C. When oxidised they may transform to palmitic acid (C_{16}) and stearic acid (C_{18}).

9.2.2 Fatty acids

This group covers a large number of compounds, primarily aliphatic saturated monocarboxylic acids, like e.g. stearic-, palmitic- and oleic acids. Of unsaturated fatty acids could be mentioned oleic acid, linolic acid and linolenic acid. The socalled omega-3-fatty acids are also included under the name fatty acids (C₂₂-compounds, e.g. docosa-4,7,13,16,19-hexanoic acid).

These compounds are not considered a health risk.

9.2.3 Aliphatic alcohols

Aliphatic alcohols comprise in principle all hydrocarbons with one or more hydroxy-groups.

The simplest is methanol, the most common is ethanol, and e.g. 2-propanol is very used for industrial purposes.

The aliphatic alcohols have different properties depending on the carbon chain length. Examples are shown in table 9.2

TABLE 9.2 EXAMPLES OF ALCOHOLS

| Compoun d | CAS no. | Classification | Comments |
|----------------|------------|---|--|
| Methanol | 67-56-1 | F, T; R 11- 23/24/25- 39/23/24/25 | Highly flammable. Toxic by inhalation, in contact with skin and if swallowed Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed. |
| Ethanol | 64-17-5 | F R11 | Highly flammable |
| 1- Propanol | 71-23-8 | F, Xi; R 11-41-67 | Highly flammable Irritant, - Risk of serious damage to eyes. Vapours may cause lethargy. |
| 1-Butanol | 71-36-3 | Xn; R10-22- 37/38-41-67 | Flammable Harmful if swallowed. Irritating to respiratory system and skin. Risk of serious damage to eyes Vapours may cause lethargy. |
| Pentanol | 30899-19-5 | Xn;R10-20 Flammable Harmful by inhalation. | |
| 1-Hexanol | 111-27-3 | Xn; R22 | Harmful if swallowed |
| 1- Heptanol | 111-70-6 | Not on the list of dangerous substances | Risk of health hazard by inhalation and in contact with skin. Not flammable. |
| Octanol | 111.87-5 | Not on the list of dangerous substances | No flammable. |

The alcohols have increasing boiling point and flash point by increasing chain length. Therefore alcohols with chain lengths above 6 carbon atoms are not considered flammable. No direct relation exists between chain length and health hazards even though there is a tendency that compounds with longer chain lengths are less hazardous. Branched carbon chains do not always have the same properties as linear structures.

9.2.4 Aliphatic amides

Aliphatic amides are compounds that contain a ketone-group and an aminogroup and have the principle structure:

$$R - (C=O) - NH$$

The simplest compound is formamide, H-(C=O)-NH₂, CAS no. 75-12-7. The compound is considered toxic as it is reprotoxic.

A short-chained aliphatic amide could be e.g. butylamide, C_3H_7 -(C=O)-N H_2 , CAS no. 541-35-5. No data on health effects were available.

An example of a long-chained aliphatic amide could be e.g. stearic acid amide, $C_{12}H_{35}$ -(C=O)-NH,, CAS no. 124-26-5.

It is assumed that compounds within this group are very different in relation to health hazards.

9.3 SUMMARY

In table 9.3, a summary of the information found in the screening is presented.

TABLE 9.3 SUMMARY OF COMPOUNDS OBSERVED IN THE SCREENING

| Compound / group of compounds | CAS no. | Comments |
|---------------------------------|-----------|---|
| 2,2 '-oxybis ethanol | 111-46-6 | Diethylene glycol Harmful if swallowed. Threshold limit value: 11 mg/m³ |
| 2-(2-butoxyethoxy) ethanol | 112-34-5 | Butoxydiglycol Reminds of diethylene glycol. Threshold limit value 100 mg/m ³ |
| Propylene glycol | 57-55-6 | Limited health hazard. Used in food and cosmetics |
| Benzylbenzoate | 120-51-4 | Limited health hazard. Used in foods |
| 5-hydroxy- methylfurfural | 67-47-0 | Risk of long-term adverse effects. Few data |
| Bis (2- ethylhexyl) maleate | 142-16-5 | No data |
| Squalene | 7683-64-9 | Hydrocarbon, - no specific data |
| Hydrocarboner C ₈₋₂₀ | | Short-chained are considered health hazardous. Long-chained compounds assumed minimum health risk |
| Hydrocarboner C 20-40 | | No specific data, assumed minimum health risk |
| Fatty acids | | Assumed minimum health risk |
| Aliphatic alcohols | | Health hazard depends on the specific compound, some may be toxic while others have little or minimum health risks. |
| Aliphatic amides | | These compounds are very different and the specific compounds are not evaluated |

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