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Survey of chemical substances in toys for animals

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Contents

Preface

This report on toys for animals has been written in connection with Miljøstyrelsen's projects of surveys of chemical substances in consumer products.

The project is split up into two phases. Phase 1, Survey of the market as well as screening of the composition of materials used for the products. Phase 2, Chemical analysis and evaluation of results of the analyses compared to relevant existing legislation.

The project has been performed by FORCE Technology.

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Summary and conclusions

Toys for animals, especially toys designed for cats and dogs, often have the same appearance as toys for children. Contrary to toys for children, there are no requirements for the content of hazardous components in toys for animals. Thus there is a risk that children playing with toys for animals may be exposed to hazardous components.

One of the results of the market survey was that the products sold via the Internet are the same as the products sold in ordinary shops.

50 different pieces of toys for animals have been purchased, based on the criteria that the toy should be designed for a cat or a dog and at the same time appeal to children.

Only a limited number of the purchased products had a written product description, and again only few of these were in Danish. None of the products had a CE-marking (not a requirement, and if they had been marked, they might have been mistaken for toys for children).

All products were screened to evaluate the material of the product, as well as they were screened to find a content of chlorine, indicating PVC, which could suggest the presence of phthalate as plasticizer.

On the surface of some products, a silicone oil was detected, most likely used as a release layer.

The screening showed that the products were made mainly of PVC, rubber and textile materials of polyesters, but also other materials were identified. Approx. 40% of the toys were made of various rubber materials, while approx. 25% of the toys were made of PVC.

All PVC products contained large amounts of phthalate plasticizers. The products were found to contain between 11% and 54% by weight of either DEHP or DINP.

Two of the PVC products were transparent. In one of these a content of tin (Sn) of more than 0.5% by weight was found, probably coming from a stabilizer.

All PVC products were screened for their content of heavy metals.
Some of the PVC products had a relatively high content of heavy metals. These products were exposed to a migration analysis for heavy metals. None of the tested products had a migration of heavy metals exceeding the requirements for toys for children as given in DS/EN 71-3.

Three of the toys, all looking like mice, were made of real fur on a hard body of plastic. All these three had a high content of chromium, probably coming from the tanning process. By the migration analysis for heavy metals, all three mice had a migration of chromium exceeding the requirements given in DS/EN 71-3.

Cr(VI) was not found in any of the three mice.

Some of the rubber products, more than 25%, were found to release MBT (mercaptobenzothiazole), an agent used in the process of vulcanisation. The amount released varied from 0.5 to 5.9 µg MBT/cm^2.

The rubber products were also analysed for the release of volatile organic compounds. In all samples analysed a content of BHT (butylated hydroxytoluene) was found. In half of the samples the content varied from 0.1 to 0.8 µg BHT/g – in the rest of the samples it was only found in trace amounts. In one sample, a relatively high content of tetradecan was found, 1.5 mg C14/g. In addition, trace amounts of various other components were found.

One of the products had a very characteristic and strong smell. Most likely this odour comes from vanillin, often used as an additive in the production of rubber.

All textiles were analysed for their content of formaldehyde. Out of 19 samples (including the filling of the teddy bears), formaldehyde was found in 3 samples in an amount varying from 6 to 10 µg/g.

The textiles were also analysed for their content of brominated flame retardants. By screening it was found that 3 products had a high content of Br (bromine) that might indicate content of bromine-based flame retardants. However, these could not be found or identified.

Analysing the colourful textiles, neither azo-colourants nor aromatic amines could be found.

This project has been limited only to deal with the content of dangerous chemicals in toys for animals. Methods related to EN 71 were primarily used for the analyses. However, no evaluation in relation to the Toy Directive or other legislation has been done, e.g. whether the toy looks like food, or if the toy consists of small parts that may be swallowed.

1 Introduction

58% of the families with children in Denmark have pets. Far the most of these families also possess toys for the animal. Toys for dogs and cats are not very dissimilar from toys for children and will often lie available all over the house. Thus there is an actual risk that small children will play with the animal's toys. Small children often put the toys into their mouth, they bite in it and will, in some cases, suck at it for a while. Children who are playing with toys for animals may be exposed to the chemical substances that the toys give off, if any.

Toys for animals are produced in a wealth of different forms and often in colourful materials, and, as mentioned, they look very much like toys that are produced for babies.

Toys for animals are not required to meet the requirements for safety existing for toys for children. I.e. toys for children at the age 0-3 years are not allowed to hold more than 0.05% phthalates. Phthalates are used as plasticizers in plastics. Therefore the materials were screened for PVC which often contains phthalates already in the first phase of the examination.

1.1 Purpose

To elucidate the chemical effect from toys for animals that children can be exposed to, it is the purpose of this project to map the Danish market for toys for animals. The existing types of toys are found and it is examined which materials have been used. The project must examine the toys for animals in order to state the release of phthalates, heavy metals and other problematic substances according to requirements and guidelines for toys for children.

1.2 Method

The project only comprehends toys for cats and dogs. This has two reasons:

First because most of the toys for animals in the market are aiming at cats and dogs, while only a limited part is for rodents, birds and fish. Secondly because toys for rodents, birds and fish will often be situated in a cage/aquarium, not causing children to be in direct contact with the toys.
Another criteria for the selection of toys for this project was that it was found to appeal to children.
The selection has not been consciously made to pick products made of special materials or from special importers, wholesalers or retailers.

In the first phase of the project, which should examine what products existed in the Danish market and screen for material composition of the products and evaluate the quantity of products sold, the following means were used:

- Internet searching
- Contact to wholesalers

- Visits to pet dealers and supermarkets
- Purchasing of products
- FTIR analyses
- Identification of chlorine (Beilstein's analysis)

In the second phase of the project, analyses have been made which are relevant to the types of materials found in phase 1. All products are thus not analysed for all substances.
For some products consisting of more materials, each of the materials have been analysed, but for the main part of the products only the materials that were found to be most important were analysed.

According to agreement with the MST analyses as stated in Table 1.1 were made.

TABLE 1.1.

Item	**Analysis**	**Method**
PVC with phthalate	Phthalate determination	GC/MS
PVC	Screening, heavy metals	XRF
PVC	Migration, heavy metals	EN 71-3
Transparent PVC	Tin content	XRF
Yellow/orange/red colours in latex, natural rubber, etc.	Cr/Cd	XRF
Fill in stuffed animals and furred animals	Type of material	FTIR
Sundry	Type of material	FTIR
Textiles and fur	Br (flame retardant), screening	XRF
Br-containing	Br (flame retardant), quantitative.	GC/MS + HPLC
Latex/rubber	Screening, organic compounds	GC/MS – Headspace
Depends on the screening	Quantification of organic compounds	Depends of the substances
Very colourful textiles	Azo dyes screening	prEN71-10/ EN ISO105 E04
Textiles that stain	Azo dyes	EN 14362-1 and -2:2003
Furred animals	Chromat (Cr VI)	DIN 53314
Textiles + filling	Formaldehyde	EN ISO 14184-1
CH-elastomers	Characterisation of odours	GC/MS headspace, if any
Latex/rubber	Mercaptobenzothiazol, etc.	HPLC after aqueous extraction

Abbreviations for applied techniques:
GC/MS: Gaschromatography with mass spectrometric detector
XRF: X-ray fluorescence
FTIR: Fourier transform infrared spectroscopy
HPLC: High pressure liquid chromatography

2 Survey

2.1 Market survey

2.1.1 Internet

The internet was used for screening to find out what types of products of toys for animals are sold in Denmark. This was done by visiting net shops selling toys for animals and websites for vets and pet dealers. The same types of toys for animals were sold by the different dealers.
Also different searching machines were used, i.e. Krak and The Yellow Pages, to search for wholesalers, manufacturers and dealers.
Information from Statistics Denmark's was also found by the internet.

2.1.2 Wholesalers

A number of wholesalers were contacted by phone, and subsequently they received a questionnaire. Only very few wholesalers responded to the questionnaires; many questionnaires were not replied to and some wholesalers did not want to participate in the survey.
Therefore it is not possible to get an overview of the extent of the Danish import of toys for animals. The wholesalers who responded to the questionnaire use other wholesalers abroad, and have no direct contact to the manufacturers.
Contact with the wholesalers also showed that exactly the same product can be sold under several brand names. This happens because some wholesalers pack the toys themselves and with their own names.
One wholesaler informed that he required information on the content of harmful substances from the suppliers of toys for animals. The wholesaler has analyses made of the toys continuously, and put forward reports on the content of phthalates and heavy metals.

2.1.3 Manufacturers

No manufacturers of toys for animals were found in Denmark. Most of the toys are made in China. Hong Kong also have a production, and one of the brands found in the Danish market is produced in the USA. For a number of products it was not possible to get information on the place of origin.

2.1.4 Visits to dealers

By searching The Yellow Pages at the internet more than 400 pet dealers were found. Eight pet dealers and two supermarkets were visited. The types of toy sold with the different dealers are very similar and are identical with the types found in net shops and with vets with websites.
The products which can be bought in the shops have very little or no information on the materials. In the few products with this information the materials found are
latex, vinyl, rubber or plush.
Other information found on certain products can be summarised as follows:

- May not be used by children
- Not poisonous
- Do not let the animal play alone
- If this toy is broken, it must be removed from the animal
- Do not eat

In approximately half of the products with attached information, this information was not in Danish. The toys were marketed for animals and therefore not comprehended by any particular regulations, and none of it was CE marked which may have indicated that it was meeting the requirements in the Toys Directive.

2.1.5 Products in the Danish market

A very large part of the products found in the Danish market can be split into the following groups:

- Plush toys: Available with or without sound. The toy looks like various teddy bears in plenty of colours. The plush toys have an appearance similar to plush toys for children.
- Whistling toys: Available in either latex or vinyl. The whistling toys look like animals or food, i.e. hotdogs. Whistling toys very much remind of toys for small children (zero to three years old) and rubber beach toys and toy food, which are also used by older children.
- Tennis balls: Available in several sizes and various colours.
- Balls: Available in many sizes and materials with or without sound. The balls are colourful. The balls look like balls for children.
- Activity balls: Balls with a hole to fill with titbits. The balls are colourful and look like balls for children
- Mice: There are mice in many different materials with or without sound and mechanical movement. It is taken for granted that the mice will appeal to children.
- Ropes: There are many ropes in colourful cotton in the market, but also ropes in other materials. Ropes are not spontaneously mistaken for toys for children, and are not expected to appeal much to children.
- Retriever trestles: Produced in wood, plastic and textiles. Retriever trestles are not spontaneously mistaken for toys for children, and are not expected to appeal much to children.

2.1.6 Purchasing of products

Fifty different toys for dogs and cats were purchased. They were bought as twenty-two different brands; three products had not been branded. The products were bought with six different dealers. No products were bought over the internet, as none of these products could not be found with the retailers.
The price for the purchased toys was between 10 and 100 DKK. The average price was 28 DKK.

The criteria for selecting the toys are stated in section 1.2.

The products are anonymised in the report and listed in Table 2.1 with description of what ”they look like”, and the materials they are made of.

Further, the information stated on the packing/product on material and instructions/warnings is shown in Appendix A, Product information.

TABLE 2.1.

FORCE no.	Item	Description
Toy 1	Pink rabbit, whistling	Soft plastic / rubber Approximately 11 cm
Toy 2	Man, whistling	Soft plastic Approximately 13 cm
Toy 3	Hippopotamus	Textile Approximately 15 cm
Toy 4	Broad ring	Hard plastic Approximately 5 cm wide Approximately 25 cm in diameter
Toy 5	Ball	Look like artificial leather Approximately 9 cm i diameter
Toy 6	Rope with knots	Rope in colours Approximately 20 cm
Toy 7	French loaf, whistling	Soft plastic Approximately 40 cm
Toy 8	Mechanical mouse	Textile, eyes and nose of hard plastic Approximately 10 cm
Toy 9	Tennis ball	Tennis ball, yellow/orange Approximately 8 cm
Toy 10	Ball with bell	Melted plastic pearls Approximately 6 cm
Toy 11	Ball with soft quills	Soft plastic, purple Approximately 4 cm
Toy 12	Pig	Soft plastic Approximately 15 cm
Toy 13	Mouse with ball and feather	Soft + hard plastic + fur Approximately 12 cm
Toy 14	Crocodile, whistling	Soft plastic, green Approximately 15 cm
Toy 15	Sheep, whistling	Soft plastic, feet painted Approximately 20 cm
Toy 16	Head of animal with long ”arms” with rope	Textile and rope Head approximately 10 cm
Toy 17	Hollow ball with hole for titbits	Hard plastic Approximately 8 cm
Toy 18	Pig with plush pants, whistling	Soft plastic + textile Approximately 15 cm
Toy 19	Shrimps of pearls	Soft plastic, eyes hard plastic Approximately 5 cm
Toy 20	Fire hydrant with metal bell inside	Soft plastic, red Approximately 11 cm
Toy 21	Rubber cactus, whistling	Soft plastic Approximately 13 cm
Toy 22	Rubber ball	Soft plastic, blue Approximately 6 cm
Toy 23	Ball with a strap	Soft ball, look like artificial leather Approximately 13 cm
Toy 24	Foam rubber ball	Soft ball Approximately 10 cm
Toy 25	Plastic balls with metal bells	Hard plastic Approximately 4 cm
Toy 26	Shoe, whistling	Soft plastic Approximately 13 cm
Toy 27	Cow	Soft plastic Approximately 14 cm
Toy 28	Stick with string and mouse	Fur mouse approximately 10 cm Stick approximately 0.5 m
Toy 29	Ball with hole for titbits	Hard ball Approximately 6 cm
Toy 30	Cat with rope	Soft plastic Approximately 14 cm
Toy 31	Plush turtle with egg	Textile Approximately 30 cm
Toy 32	Plush mouse	Textile Approximately 30 cm

FORCE no.	Item	Description
Toy 33	Dog	Soft plastic Approximately 20 cm
Toy 34	Ball of rubber ring	Rubber, many colours Approximately 10 cm
Toy 35	2 small plush cats	Textile Approximately 5 cm
Toy 36	Plush/rubber telephone	Rubber front Reverse made of textile Approximately 15 cm
Toy 37	Girl doll	Textile Approximately 20 cm
Toy 38	Spider with string	Soft plastic/rubber Approximately 10 cm
Toy 39	Fur mouse	Fur Approximately 10 cm
Toy 40	Soft dog with hard middle	Approximately 16 cm
Toy 41	Porcupine, whistling	Soft plastic Approximately 7 cm
Toy 42	”Rustling” mouse	Plastic strips Approximately 8 cm
Toy 43	2 fur mice	Fur Approximately 6 cm
Toy 44	Rat, whistling	Soft plastic Approximately 16 cm
Toy 45	Plush porcupine	textile / plush Approximately 12 cm
Toy 46	Black tyre	Soft rubber Approximately 16 cm
Toy 47	Retriever stick	“Oblong tennis ball” Approximately 22 cm
Toy 48	”Ball with four handles”	Soft plastic Approximately 20 cm
Toy 49	Hollow ball with hole for titbits	Hard plastic Approximately 13 cm
Toy 50	Rubber snowman	Hard rubber Approximately 9 cm

3 Analyses

As the information collected on materials used for manufacture of toys for animals was very limited, Beilstein's test and IR screening of the purchased products were performed in the first phase of the project.

3.1 Beilstein's test

Beilstein's test is a quick method for determination of halogens. The principle in the test is that volatile copper salts will colour a flame green due to the copper content. Copperhalides (F is excepted) are volatile, and only in very few other cases will the test give a positive reaction. If there are halogens in plastic, the plastic is probably a PVC plastic and could typically have been softened by a phthalate plasticizer.

3.1.1 Method of analysis

A microburner and a strong copper wire were used. The microburner must have full air intake (almost colourless flame). The copper wire is annealed, the hot wire is rubbed at the sample so that some of the sample melts on the wire. The wire is led into the outer zone of the flame. If the sample is lightened and burns, it should burn out outside the flame. The wire is again led into the flame and shortly before annealing, the green colour is obvious if the sample holds halogens.

3.2 FT-IR examinations

3.2.1 Used equipment and techniques

The FT IR analyses were made by a Nicolet Impact 400 FT IR spectrometer.

As many samples showed signs of silicone oil which has probably been used as release layer, these samples were washed in petrol ether to remove residues of the release layer etc. before the actual test preparation.

At first a screening analysis to estimate the type of material was made. Where a toy consisted of more than one type of material, the part of the toy that was considered largest/most considerable was analysed.

Different techniques were used according to the product. Flat, smooth materials were examined by use of ATR technique. Materials that were not smooth or flat were examined by rubbing a silicium carbide sandpaper against the sample and take the spectrum by DRIFT (diffuse reflectance) with the clean sandpaper as reference. Textiles were also examined by DRIFT technique with KBr powder as reference.

Both ATR and DRIFT are reflection techniques and the spectra become a little distorted compared to normal transmission spectra.

For identification of plastic types primarily electronic reference libraries were used (Hummel-Scholl or Sadtler Know-it-all) combined with FORCE Technology's general experience.

Plasticizers as phthalates are normally used in large quantities (30%) and will be visible in the spectra immediately. Often these substances will camouflage the spectra of basis polymer. Phthalates present in few percentages of another ester will usually not be visible. Other additives used in 0.1% to few percentages will not be detected during the screening analysis under normal conditions, unless they have absorptions in areas where basis polymer and possible plasticizer with certainty do not absorb.

Fillers with characteristic spectra, i.e. chalk, can be established at levels of 10-30%, while other fillers most often cannot be proven with certainty.

3.2.2 Results of Beilstein's test and IR analyses

The detailed results of the Beilstein's test and FTIR analyses are shown in Appendix B, Analysis of materials.

As it appears from Appendix B, Analysis of materials, the purchased toys for animals are made of a number of different types of material:

1. Soft and half-stiff plastic: PVC with phthalate as plasticizer
2. Rubber (natural rubber, latex, polyisoprene)
3. Textiles (polyesters, acrylonitrile, viscose/cotton)
4. Real fur
5. Hard plastic types (polypropylene, polystyrene, EPDM)

In the below table the products are divided according to type of material:

TABLE 3.1.

Type	Polymer type	Samples
Soft and half-stiff plastics	PVC with phthalate	2, 5, 11, 13, 18, 19, 23, 30, 33, 36 front, 41, 49
Elastomers	CH-elastomers (i.e. latex, natural rubber, isoprene)	1, 7, 12, 14, 15, 20, 21, 22, 24, 26, 27, 34, 38, 40 front and reverse, 44, 46, 48, 50
Textiles	Polyester types	3, 3 filling, 9, 16, 16 filling, 24, 24 filling, 31, 31 filling, 32, 35, 36 reverse, 42, 47, 48 filling
	Viscose/cotton	6, 37
	Copolymer with acrylonitrile	8, 18 pants, 31, 35, 45,
Fur	Real fur	28, 39, 43
Hard and half-stiff plastics	Polypropylene	4
	Copolymer (ethylene: vinyl acetate)	10
	Copolymer (vinyl chloride: vinyl acetate)	17
	Polystyrene	25
	Methacrylate	29
	PUR	40 middle

It is concluded that approx. 25% of the materials are made of PVC, approx. 35% is made of natural rubber/synthetic rubber, approx. 30% are textiles, excluding all the filling used for stuffing. Finally approx. 10% is a mixture of various hard types of plastic.

The preliminary examination did not check for (or observe) other harmful substances than phthalate, this could have been other plasticizers, heavy metals, dyes, amines, monomers, residues of solvents, etc. However, it was noted that some of the rubber products might hold a content of mercaptobenzothiazol (MBT).

3.3 Survey of further analyses for each type of products

According to prEN 71-9:2002, table 1, it is recommended that polymer materials are analysed for monomers, solvent migration and plasticizers, while leather products (including fur) should be analysed for dyes and primary aromatic amines. It is recommended that textile materials are analysed partly as leather, partly for their content of brominated flame retardants.

Based on the above FTIR screening and Beilstein's test as well as prEN 71-9:2002 it was decided, in agreement with the MST, to analyse each sample as stated in Appendix C, Survey of analyses.

3.3.1 PVC products

Heavy metals
All the PVC products are screened for their content of heavy metals by XRF, as it is not expected in advance that the other products will show a too large content of heavy metals.

Migration of heavy metals
Based on the heavy metals screening the products where the content of heavy metals exceeds the limits for migration as stated in DS/EN 71-3, table 1, were tested for migration of heavy metals in accordance with DS/EN 71-3.

Tin
The transparent PVC products are screened by XRF for their content of tin that may typically be added transparent PVC as stabiliser.

Phthalates
The FTIR analyses of the PVC samples all clearly demonstrated content of phthalates. The PVC samples are therefore also analysed for qualitative and quantitative content of phthalates by extraction and subsequent analysis by use of GC-MS.

3.3.2 Rubber products

Organic compounds
Products of natural rubber/synthetic rubber are all screened for volatile organic compounds by use of GC-MS and headspace technique.

Chromium and cadmium
Rubber products with transparent yellow, orange or red colours are screened by XRF for their content of chromium or cadmium. These two heavy metals have been used in exactly these colours.

Mercaptobenzothiazol (MBT)
This substance is typically used as accelerator in production of natural rubber. A number of selected rubber products have been analysed by use of HPLC for release of MBT (migration to water according to prEN71-10).

Odours
One product had a characteristic odour, which was determined partly by GC-MS with headspace technique, partly by "trained" noses.

3.3.3 Textiles

Brominated flame retardants
All textiles are screened for their content of Br as indication of content of brominated flame retardants. Screening is made by XRF.
In samples with high Br content flame retardants, if any, are attempted identified and quantified by extraction and GC-MS analysis.

Formaldehyde
All textiles, including fill in teddy bears, are tested for their content of formaldehyde according to DS/EN ISO 14184-1.

Azo dyes
According to prEN71-10, annex A, strongly dyed textiles have, at first, been screened for their coming off on different textile materials. The colours where the coming off was observed, are further analysed according to EN ISO 14362 for content of azo dye and/or aromatic amines.

3.3.4 Fur

Chromium
Three of the samples are made of real fur. These three samples are analysed for their content of heavy metals by XRF and migration of heavy metals according to DS/EN 71-3. Finally the three furs have been analysed quantitatively for content of Cr (VI) by a spectro photometric method used for examination of leather products for personal safety devices (DIN 53314).

3.3.5 Other hard and half-stiff types of plastics

Further to identification of types of material only a few analyses have been made within this group.

3.4 XRF screening

3.4.1 Method of analysis

X-LAB 2000 instrument (Spectro) was used for the X-ray analyses (XRF). For quantification of the content, the programme TURBO-QUANT was used. By this technique all elements larger or equal to no. 11, Sodium, can be analysed. The minimum quantity to be determined depends on matrix and element, but is for certain elements <10 ppm.

No actual sample preparation was made. The sample was either placed directly in the instrument, or a piece has been cut/carved out of approximately 5 cm x 5cm. These test samples have been analysed directly in the instrument. The analysis is a surface analysis which means that the analysis goes to a depth of approximately 100µm, depending on the material.

3.4.2 Result of XRF screening

The results of the XRF screening appear from Appendix D, XRF results. Thirty-five products have been screened. In one sample two XRF analyses were made. The requirements for migration of heavy metals according to DS/EN 71-3 can be seen in Appendix D, XRF results, and all samples in which the XRF result for a heavy metal exceeds the requirement for migration are stressed.

Heavy metals

The below table 3.2 shows the total of seven samples (out of thirty-five) where the result shows a content of heavy metal exceeding the requirements for migration. These seven samples have therefore been further analysed according to DS/EN 71-3, see section 3.5, Migration of heavy metals.

In the selection of products the guidelines in DS/EN 71-3 for adjustment of the analytical result have been taken into consideration. "The adjusted analytical result" is obtained by deducting a correction from the analytical result.

E.g. is the analytical correction for Ba 30%. The found value for Ba of 1011 ppm for Toy 34 will thus corrected be considerably below the requirement of 1000 ppm. For this reason no migration analysis was made on Toy 34.

TABLE 3.2 – Content of "EN 71-3 heavy metals", ppm, by XRF analysis

Element	**Cr**	**As**	**Se**	**Cd**	**Sb**	**Ba**	**Hg**	**Pb**
*EN 71-3 requirements**	*60*	*25*	*500*	*75*	*60*	*1000*	*60*	*90*
Toy 5	7	8	0.5	-	10	36	-	222
Toy 18	128	-	-	94	-	249	-	537
Toy 23	648	17	0.3	4	10	379	-	2269
Toy 28	14370	-	0.7	-	-	-	-	10
Toy 33	68	-	0.6	-	1	-	0.5	271
Toy 39	202	0,7	0.5	-	-	-	-	14
Toy 43	470	0,6	0.6	0.4	-	-	-	24

*Maximum migration from materials from toys in mg/kg

Tin

Organic tin compounds are often used as stabilisers in particularly transparent PVC.

Out of the two samples of transparent PVC analysed for content of tin (Sn), one showed a large content; see table 3.3.

TABLE 3.3 – Content of Sn, ppm

Sample no.	**Sn**
Toy 13	-
Toy 19	661

No attempt has been made to identify the tin component in detail.

Chromium/Cadmium

Chromium (Cr) and cadmium (Cd) have previously entered into the composition of yellow/red/orange colours.

Nine samples, all yellow, red or orange, have been screened for their content of Cr and/or Cd, see table 3.4.

The found contents of Cr and Cd are so low that they do not indicate the use of Cr and Cd-containing pigments in the analysed samples.

TABLE 3.4 - Content of Cr and Cd, in ppm

Sample no.	**Cr**	**Cd**
Toy 1	11	-
Toy 12	16	-
Toy 20	21	-
Toy 21	-	-
Toy 24	4	0.5
Toy 26	5	-

Toy 27	5	-
Toy 34	-	2
Toy 48	-	-

Nickel

DS/EN 71-3 comprehends no requirements for the content of Ni. However, the nickel statutory states requirements for both maximum content and release of nickel under certain conditions. A comparison between the values found in the samples analysed, see table 3.5, and the requirements in the nickel statutory (which is being revised at present), where the requirement for content of nickel in e.g. ear stickers is maximum 500 ppm, it can be concluded that the content found is considerably below the allowed value.

TABLE 3.5 – Content of Ni, ppm

Sample no.	Ni
Toy 1	3
Toy 2	5
Toy 3	72
Toy 5	45
Toy 6	6
Toy 7	10
Toy 8	52
Toy 11	7
Toy 12	4
Toy 13	9
Toy 16	49
Toy 18	8
Toy 19	11
Toy 20	4
Toy 21	48
Toy 23	5
Toy 24	52
Toy 26	3
Toy 27	14
Toy 28	21
Toy 30	6
Toy 31.1	80
Toy 31.2	139
Toy 32	65
Toy 33	6
Toy 34	4
Toy 35	128
Toy 36	9
Toy 37	60
Toy 39	9
Toy 41	5
Toy 43	17
Toy 45	47
Toy 47	10
Toy 48	4
Toy 49	5

Flame retardants

As it appears from Appendix D, XRF results, a content of bromine (Br) was

also found in the three products, see table 3.6. A content of Br may indicate a content of brominated flame retardant. Antimon (Sb) is also used as flame retardant, and is used together with brominated flame retardants as well. The content of Sb is therefore also stated in table 3.6. Yet nothing indicates the use of Sb in the analysed samples. Therefore the mentioned products were analysed further to identify the content and type of flame retardants, see section 3.10 for analysis for brominated flame retardants.

TABLE 3.6 - Content of Br and Sb, in ppm

Sample no.	Br	Sb
Toy 3	426	24
Toy 31.2	217	7
Toy 32	771	21

3.5 Migration of heavy metals

3.5.1 Method of analysis

The applied method is DS/EN 71-3. This method simulates contact with gastric juice when a material has been swallowed. Soluble substances are extracted from the sample under simulated conditions that the sample remains in contact with the gastric juice for a period after it has been swallowed. Sample preparation for most of the samples followed DS/EN 71-3, 8.2. The sample preparations for the three fur mice followed DS/EN 71-3, 8.6.
All samples were analysed according to DS/EN 71-3, 8.1.2, where the analytical result is stated to be "The adjusted analytic result" obtained by deducting a correction from the analytical result. Table 3.7 shows the results above the limit in DS/EN71-3, before and after correction.

3.5.2 Result of migration analysis

Table 3.7 shows requirements as well as results.

TABLE 3.7 - Migration, ppm

Element	Emne	Cr	As	Se	Cd	Sb	Ba	Hg	Pb
*EN 71-3 requirements**		*60*	*25*	*500*	*75*	*60*	*1000*	*60*	*90*
Analytical correction (in %)		30	60	60	30	60	30	50	30
Toy 5	Ball	<1	<5	<10	2	<10	77	<5	77
Toy 18	Pig with plush pants, whistling	<1	<5	<10	1	<10	1	<5	<5
Toy 23	Ball with strip	<1	<5	<10	<1	<10	2	<5	<5
Toy 28	Stick with string and mouse	230	<5	<10	<1	<10	3	<5	<5
Corrected		161							
Toy 33	Dog	<1	<5	<10	<1	<10	<1	<5	<5
Toy 39	Fur mouse	349	<5	<10	<1	<10	<1	<5	<5
Corrected		244							
Toy 43	2 fur mice	495	<5	<10	<1	<10	<1	<5	<5
Corrected		347							

*Maximum migration from toy material in mg/kg.

Results for the three fur mice (Toy 28, Toy 39 and Toy 43) are also shown as "adjusted analytical result", that is corrected with the stated analytical correction. Only in these three samples migration exceeds the allowed limit for toys for children.

3.6 Cr(VI)

3.6.1 Method of analysis

The applied method is DIN 53314, which in a modified version is used for determination of chromate in leather used for personal safety devices.
The principle of the method is that the sample is extracted in a buffer with neutral pH and the content of Cr(VI) is then determined colorimetric by a spectrophotometer.

3.6.2 Results of analyses

The three samples of real fur, Toy 28, Toy 39 and Toy 43, have been analysed.
None of the samples demonstrated a content of Cr(VI).
The detection limit for the analysis is 3 mg Cr(VI)/kg.

Cr(III) is used for leather tanning, and if the tanning process is controlled correctly, no Cr(VI) is formed. (MST, survey no. 3, 2002 "Examination of the content of Cr(VI) and Cr(III) in leather articles in the Danish market").

3.7 Phthalates in PVC

3.7.1 Method of analysis

50 mg of the sample are weighed in tiny pieces in a 20 ml screw-capped glass.
The samples are extracted with CH_2Cl_2 at indoor temperature overnight.
Dissolved PVC, if any, is precipitated by addition of methanol.
The sample is centrifuged and the extract is analysed by gaschromatography with mass spectrometric detector (GC-MS). Butyl-hydroxy-toluen (BHT) is used as internal standard.
For the GC-MS analyses is used Varian Saturn 2000 iontrap system.
The detection limit is considerably below the found levels. The uncertainty of the quantification is approximately 10% relative.

3.7.2 Results of analyses

All thirteen PVC-containing products have been analysed. The content of phthalates varies between 11 and 54 weight %.
Table 3.8 demonstrates the found content of phthalates. Results have been sorted according to their content of diisononyl phthalate (DINP) respectively diethylhexyl phthalate (DEHP). Note that DINP is a mixture of isomers with many components.

TABLE 3.8 – Phthalate content in weight %

Sample	%DEHP	%DINP
Toy 7	0	14.8
Toy 36	0	20.3
Toy 33	0	21.0
Toy 18	0	21.3
Toy 11	0	27.0
Toy 13	0	28.5
Toy 30	0	30.6
Toy 49	0	50.4
Toy 2	0	54.0
Toy 5	11.1	6.9
Toy 23	12.3	0.0
Toy 19	21.9	0.0
Toy 41	39	0.0

Further to the main component (DEHP or DINP) a small content (< 1%) of compounds as methyl-(2-ethylhexyl)-phthalate was also found in many of the samples. No attempt has been made to quantify this content.
Very small quantities of nonylphenol were found in several of the samples. The content has not been quantified.

Nonylphenole is used for e.g. production of antioxidants for rubber and plastics, surface active substances and in plasticizers for PVC.

3.8 Screening for organic compounds

3.8.1 Method of analysis

Approximately 0.5 g of the sample is cut into small pieces. The samples are placed in a closed test tube.
The samples are analysed by GS-MS using the headspace technique.
The samples are heated at 50°C for ten minutes and shaken intermittently. Hereafter 1000 µl of the air above the sample (headspace) is injected in the GC.
The Varian Saturn 2000 ion-trap GC-MS system is used for the GC-MS analyses. By the headspace technique only substances with a certain vapour pressure are observed.
The detection limit is approximately 10 µg/g for BHT, but depends on the substance.

3.8.2 Results of analyses

The twenty identified elastomer products have been analysed. See the results in Appendix E, Screening of organic compounds.
The only organic compounds found in large quantities in this analysis is BHT (butylated hydroxytoluene) and alifatic hydrocarbon with tetradecan in the largest quantity.
Further to this, N-butyl benzensulfonamid and cyclohexanon have been detected in several samples and one single not-identified amine compound in one sample.

3.9 Quantitative organic analysis

3.9.1 Method of analysis

As the only measurable quantities found in the samples were BHT (butyl hydroxytoluen) and tetradecan, it was chosen to quantify by use of the headspace technique.

3.9.2 Results of analyses

The content of BHT in selected samples, in accordance with 3.8.2, determined by the headspace technique.
Uncertainly of this method is 50% relative.
The detection limit is 0.005 µg/g.

TABLE 3.9

Sample	µg BHT/g
Toy 1	0.2
Toy 14	0.1
Toy 15	0.1
Toy 20	0.1
Toy 27	0.8
Toy 34	0.6
Toy 38	1.1
Toy 40	0.4
Toy 48	0.1

The content of tetradecane in selected samples determined by the headspace technique.

TABLE 3.10

Sample	Mg C14/g
Toy 7	1.5
Toy 48	0.01

3.10 Brominated flame retardants

3.10.1 Method of analysis

GC-MS
0.5 g sample is extracted in 9 ml dichlormethan and is placed on ultrasound for 30 minutes.
2,4,6-tribrom-anisol (TBA), 100 µg/sample is used as internal standard.
The extracts have been analysed by the Varian Saturn 2000 GC-MS system.

HPLC, decabromdiphenylether
Waters HPLC system with UV detector at 220 og 240 nm.
RP-C18 column with 100% methanol eluent 1 ml/minute.

0.5 – 0.6 g sample is extracted with 9 ml dichlormethane in ultrasound for 30 minutes. The extract is filtered and injected without further treatment.

3.10.2 Results of analyses

GC-MS
As mentioned in the XRF-analyses, a content of Br was found in three samples, Toy 3, Toy 31.2, and Toy 32. Therefore these samples have been analysed further by the above GC-MS method.

This technique has not made it possible to identify or quantify flame retardants, if any, in the three samples.
A frequently used flame retardant, decabromdiphenylether, could not be detected by this system and has therefore been analysed by the HPLC method.

HPLC, decabromdiphenylether
The detection limit by the applied method (without concentrating) is 0.25 µg/ml, corresponding to 4 µg/g textile or 4% of the expected content in sample 31. Sample 31 had the smallest content of bromine by the XRF examination.
Decabromdiphenylether was not detected by this method in any of the three samples.

3.11 Mercaptobenzothiazol (MBT)

3.11.1 Method of analysis

According to the FTIR spectra, nine of the rubber products indicated a possible content of mercaptobenzothiazol (MBT). It was chosen to select the migration procedure in EN 71-10, §6 followed by an HPLC analysis of the extract.

Pieces of the products with a surface of approximately 10 cm^2 were shaken with 25 ml distilled water for at least 1 hour. The filtered migration liquid was then analysed by HPLC on an RP18 column with UV detection at 320 nm ("Microbial and photolytic degradation of benzothiazoles in water and wastewater ", Dissertation von M.Sc. Hafida Kirouani-Harani, Fakultät III der Technischen Universität Berlin, 2003).

An external standard was used.

3.11.2 Results of analyses

The results of the nine tested rubber products are stated in the below table 3.11.
There is a considerable uncertainty about the actual surface area due to the shape of the samples. An attempt was made to have 10 cm^2, but some were approximately 25 cm^2 (the areas have been taken into consideration in the calculations).

The uncertainty of the calculation is approximately 6 µg/sample.

TABLE 3.11 – MBT release

Sample	µg MBT / cm^2
Toy 7	n.d.
Toy 21	1.8
Toy 26	n.d.
Toy 27	n.d.
Toy 34	0.6
Toy 40	2.1
Toy 46	5.9
Toy 48	n.d.
Toy 50	0.5

n.d. = not detected

As it appears, five samples release significant quantities of MBT.

3.12 Screening for azo dyes

3.12.1 Method of analysis

Stain effect according to prEN 71-10:2002, Annex A (slightly modified EN ISO 105 E04).
The sample material in pieces of approximately 5 cm x 15 cm were analysed for their staining by applying acid and caustic artificial sweat. The samples were tested for staining at 37°C on several different textiles by contact while they were being dipped in the two kinds of "sweat".

The degree of staining is estimated on a scale from 1 – 5, where 5 means ”not staining”.

3.12.2 Results of analyses

See Appendix F, Screening for azo dyes.
Seven samples/partial samples with transparent colours were selected for analysis for azo dyes. Out of the seven analysed samples, three samples showed class 4 under some conditions, while the rest of the samples showed class 4-5 or 5.
The analysis does not reveal if it is due to azo dyes, but exclusively if the colours stain.

For further analysis for content of azo dyes the three samples were picked that got the classification 4 one or more times: Toy 16 yellow, Toy 16 green and Toy 31 green.

3.13 Azo dyes

3.13.1 Method of analysis

The analyses have been made according to SS-EN 14362-1: 2003 (without extraction of fibres) or SS-EN 14362-2:2003 (with extraction of fibres).
Toy 31 green is tested according to SS-EN 14362-1:2003, while Toy 16 yellow and Toy 16 green is tested according to SS-EN 14362-2:2003.
The principle of the method is that azo dyes, if any, are reduced to aromatic amines by a citrate-buffer, pH 6.00 and sodium dithionite.
Detection of aromatic amines is made by GC-MS, and quantification is made by use of internal standard and calibration solvents of amines.
Sample quantity: 1.0 g per sample
Detection limit per amine: 20 mg/kg

Toy 31 green held two colours, a green and a beige. The two colours were analysed together as one sample.

3.13.2 Results of analyses

No traces of aromatic amines could be detected in any of the analysed dye samples. Thereby it can be concluded that the three samples held no azo dyes.

3.14 Formaldehyde analysis

3.14.1 Method of analysis

Formaldehyde determination in textiles are made according to EN/ISO 14184-1:1998.
The principle of the analysis is that the content of formaldehyde, if any, is extracted from the textile sample with water at 40°C. The quantity of formaldehyde is determined spectrophotometrically after reaction with acetylacetone for formation of a yellow colour. Calibration takes place in a series of calibrations of reference solutions of formaldehyde in water.
The detection limit is 5 mg/kg. Uncertainty at this level is also 5 mg/kg.

3.14.2 Results of analyses

From the results in table 3.12 it can be concluded that only samples 3, 6 and 8 contain traces of formaldehyde.

TABLE 3.12

Sample no.	µg/g
3	10
3 fill	< det. limit
6	8
8	6
9	< det. limit
16	< det. limit
16 fill	< det. limit
18	< det. limit
24 black	< det. limit
24 fill	< det. limit
31	< det. Limit
31egg	< det. Limit
31 fill	< det. Limit
32	< det. Limit
35	< det. Limit
36	< det. Limit
37	< det. Limit
45	< det. Limit
47	< det. Limit

3.15 Smell

3.15.1 Method of analysis

Approximately 0.5 g of the sample is cut into small pieces. The samples are put into a closed sample bottle.
The samples are analysed by GS-MS using the headspace technique.
The samples were heated at 50°C for ten minutes and shaken at regular intervals.
Then 1000 µl of the air above the sample is injected (headspace) by the GC.
The Varian Saturn 2000 ion-trap GC/MS system is used for the GC-MS analyses. By the headspace technique only substances with a certain vapour pressure can be observed.

To supplement the above method, also ”trained noses” have been used for determination/characterisation of the smell.

3.15.2 Results of analyses

One sample, Toy 34, had a very penetrating and characteristic smell.

GC-MS
Trace amounts of cyclohexanone, a C-14 hydrocarbon and a not identified amine were found.

”Nose” method
The smell was characterised as a mixture of liquorice allsorts, caramel, and particularly vanilla.
A rubber manufacturer informed that vanillin (4-hydroxy-3-methoxybenzaldehyd) is used as smelling substance in rubber.

No traces of vanillin could be found by the GC-MS analysis. However, this does not exclude that the smell in the toys derives from added vanillin.

By the internet and in literature, different values for the smell limit for vanillin have been found. The smell limit for vanillin in air is stated to be $1.1x10^{-8}$ ppb (http://cira.ornl.gov/documents/vanillin.pdf) or $2 \cdot 10^{-7}$ mg/m^3 (Am.Ind.Hyg.Assoc., March 1986).

Table 3.13 shows a short summary of the gathered Results of analyses.

TABEL 3.13 – Summary of results

Items	**Analysis**	**Result**
PVC with phthalate	Determination of phthalate	Phthalate was found in all PVC products. Content varied between 11 and 54%
PVC	Screening, heavy metals	7 out of 35 samples showed a content of heavy metals which is higher than the migration requirements
PVC	Migration, heavy metals	3 fur animals had migration which is higher than the migration requirements
Transparent PVC	Tin content	In 1 out of 2 samples there was a high content of Sn
Yellow/orange/red colours in latex, natural rubber etc.	Cr/Cd	No Cr/Cd-containing pigments were found in any of the samples
Textiles and fur	Br (flame retardants), screening	Br was found in 3 samples
Br-containing	Br (flame retardants), quant.	No brominated flame retardants were found in any of the samples
Latex/rubber	Screening, organic compounds	BHT was found in 9 products and alifatic hydrocarbon was found in 2 products
Strongly coloured textiles	Azo dyes	No azo dyes were found in any of the strongly coloured products
Fur animals	Chromate (Cr VI)	All three fur animals contained large quantities of Cr(III), but no Cr(VI)
Textiles + fill	Formaldehyde	Small quantities of formaldehyde were found in 3 out of 19 samples
CH-elastomers	Characterisation of smell	A strong smell could not be identified with certainty, but is probably caused by vanillin as most characteristic
Latex/rubber	Mercaptobenzothiazol, etc.	5 samples showed migration to water of MBT

4 References

Statistics Denmark's: www.dst.dk

DS/EN 71-3:1995 Legetøj. Sikkerhedskrav. Del 3: Migration af særlige stoffer [Safety of Toys – Part 3: Migration of particular substances]

prEN 71-9:2002 Safety of Toys – Part 9: Organic Chemical Compounds - Requirements.

prEN 71-10:2002 Safety of Toys – Part 10: Organic Chemical Compounds – Sample Preparation and Extraction.

prEN 71-11:2003 Safety of Toys – Part 11: Organic Chemical Compounds – Methods of Analysis.

PVC Informationsrådet, [The PVC Information Council] www.pvc.dk

1 Product information

FORCE no.	Item	Description	Material as informed on the items	Information on the product
Toy 1	Pink rabbit, whistling	Soft plastic / rubber Approximately 11 cm	Latex	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 2	Man, whistling	Soft plastic Approximately 13 cm	Vinyl	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 3	Hippopotamus	Textile Approximately 15 cm	-	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 4	Broad ring	Hard plastic Approximately 5 cm wide Approximately 25 cm in diameter	-	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 5	Ball	Look like artificial leather Approximately 9 cm i diameter	-	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 6	Rope with knots	Rope in colours Approximately 20 cm	-	Always buy toys that fit the size of the dog. The dog should always be under supervision when playing with toys. (DK)
Toy 7	French loaf, whistling	Soft plastic Approximately 40 cm	-	Do not let the animal play alone.
Toy 8	Mechanical mouse	Textile, eyes and nose of hard plastic Approximately 10 cm	-	Toy for cats. (DK)
Toy 9	Tennis ball	Tennis ball, yellow/orange Approximately 8 cm	-	
Toy 10	Ball with bell	Melted plastic pearls Approximately 6 cm	-	
Toy 11	Ball with soft quills	Soft plastic, purple Approximately 4 cm	-	
Toy 12	Pig	Soft plastic Approximately 15 cm	-	Do not let the animal play alone. Broken toy must be removed from the animal. This toy is not for children.

FORCE no.	Item	Description	Material as informed on the items	Information on the product
Toy 13	Mouse with ball and feather	Soft + hard plastic + fur Approximately 12 cm	-	
Toy 14	Crocodile, whistling	Soft plastic, green Approximately 15 cm	-	Not poisonous. Do not let the animal play alone. Broken toy must be removed from the animal. This toy is not for children.
Toy 15	Sheep, whistling	Soft plastic, feet painted Approximately 20 cm	Latex	Do not let the animal play alone.
Toy 16	Head of animal with long "arms" with rope	Textile and rope Head approximately 10 cm	-	
Toy 17	Hollow ball with hole for titbits	Hard plastic Approximately 8 cm	-	Animals should not play with the toy if it is worn or broken.
Toy 18	Pig with plush pants, whistling	Soft plastic + textile Approximately 15 cm	Vinyl+Plush	
Toy 19	Shrimps of pearls	Soft plastic, eyes hard plastic Approximately 5 cm	Latex	
Toy 20	Fire hydrant with metal bell inside	Soft plastic, red Approximately 11 cm	Rubber	Non-poisonous. Rubber is not digestible; if it is broken, the toy must be removed from the dog. (DK)
Toy 21	Rubber cactus, whistling	Soft plastic Approximately 13 cm	-	Non-poisonous. Latex is not digestible; if it is broken, the toy must be removed from the dog. (DK)
Toy 22	Rubber ball	Soft plastic, blue Approximately 6 cm	-	Toy for dogs. Do not let the animal play alone. Not edible.
Toy 23	Ball with a strap	Soft ball, look like artificial leather Approximately 13 cm	-	Toy for dogs. Do not let the animal play alone. Not edible.
Toy 24	Foam rubber ball	Soft ball Approximately 10 cm	-	
Toy 25	Plastic balls with metal bells	Hard plastic Approximately 4 cm	-	Shines in the dark. Do not let the animal play alone. Not edible.
Toy 26	Shoe, whistling	Soft plastic Approximately 13 cm	-	For puppies. Do not let the animal play alone. Not edible.
Toy 27	Cow	Soft plastic Approximately 14 cm	Latex	Pay attention that the toy is not bit to pieces and swallowed. This toy is not for children.

FORCE no.	Item	Description	Material as informed on the items	Information on the product
Toy 28	Stick with string and mouse	Fur mouse approximately 10 cm Stick approximately 0.5 m	-	Pay attention that the toy is not bit to pieces and swallowed. This toy is not for children.
Toy 29	Ball with hole for titbits	Hard ball Approximately 6 cm	-	
Toy 30	Cat with rope	Soft plastic Approximately 14 cm	-	
Toy 31	Plush turtle with egg	Textile Approximately 30 cm	Plush	
Toy 32	Plush mouse	Textile Approximately 30 cm	-	Pay attention that the toy is not bit to pieces and swallowed. This toy is not for children.
Toy 33	Dog	Soft plastic Approximately 20 cm	-	Playing with the toy should always be supervised. Replace the toy if it is worn or broken.
Toy 34	Ball of rubber ring	Rubber, many colours Approximately 10 cm	-	If the toy is broken, it must be removed. Supervision is recommended.
Toy 35	2 small plush cats	Textile Approximately 5 cm	-	Playing with the toy should be supervised. Stop playing if the toy is broken.
Toy 36	Plush/rubber telephone	Rubber front Reverse made of textile Approximately 15 cm	-	Non-poisonous. Do not let the animal play alone. It the toy is broken, it should be removed from the animal. This toy is not for children.
Toy 37	Girl doll	Textile Approximately 20 cm	Fibre fill, Cotton/Poly	
Toy 38	Spider with string	Soft plastic/rubber Approximately 10 cm	Latex	
Toy 39	Fur mouse	Fur Approximately 10 cm	-	
Toy 40	Soft dog with hard middle	Approximately 16 cm	Latex	Non-poisonous.
Toy 41	Porcupine, whistling	Soft plastic Approximately 7 cm	Vinyl	
Toy 42	”Rustling” mouse	Plastic strips Approximately 8 cm	-	Not edible. Do not let the animal play alone. Replace the toy when worn or broken.
Toy 43	2 fur mice	Fur Approximately 6 cm	-	
Toy 44	Rat, whistling	Soft plastic Approximately 16 cm	Latex	

FORCE no.	Item	Description	Material as informed on the items	Information on the product
Toy 45	Plush porcupine	Textile / plush Approximately 12 cm	Plush	Defective toy should be discarded. (DK)
Toy 46	Black tyre	Soft rubber Approximately 16 cm	Rubber	
Toy 47	Retriever stick	"Oblong tennis ball" Approximately 22 cm	-	
Toy 48	"Ball with four handles"	Soft plastic Approximately 20 cm	Latex	
Toy 49	Hollow ball with hole for titbits	Hard plastic Approximately 13 cm	-	Playing with the toy should be supervised.
Toy 50	Rubber snowman	Hard rubber Approximately 9 cm	Natural rubber	Supervise playing with this toy.

1 FTIR / Beilstein

Results of FTIR analyses and Beilstein's test

FORCE no.	Product name as stated on the product/packing	Beilstein's test	Material determined by IR
Toy 1	Pink rabbit, whistling	neg	Polyisoprene, with chalk and other filling
Toy 2	Man, whistling	pos	Phthalate + possibly PVC
Toy 3	Hippopotamus	Nt	Polyester (possibly PETP (polyethylenterephthalate))
Toy 3, fill		Nt	Polyethyleneterephthalate-type
Toy 4	Broad ring	neg	Polypropylen
Toy 5	Ball	pos	o-phthalacidester + possibly PVC
Toy 6	Rope with knots	Nt	Viscose, cotton
Toy 7	French loaf, whistling	pos	Polyisoprene + o-phthalacidester
Toy 8	Mechanical mouse	neg	Poly (acrylonitrile : methyl acrylate)
Toy 9	Tennis ball	neg	Fabric : Butyleneterephthalatester-type Ball : CH-elastomes with chalk
Toy 10	Ball with bell	nt	Copolymer Poly (ethylen:vinylacetate)
Toy 11	Ball with soft quills	pos	o-phthalacidester (+ PVC)
Toy 12	Pig	neg	CH-elastomes (EPDM, ethylenepropylenedienemodifier), with chalk
Toy 13	Mouse with ball and feather	pos	Soft and hard parts: PVC + phthalate
Toy 14	Crocodile, whistling	neg	Polyisoprene, much chalk
Toy 15	Sheep, whistling	neg	Polyisoprene, with chalk
Toy 16	Head of animal with long "arms" with rope	Nt	Polyester (possibly PETP (polyethylenterephthalate))
Toy 16, fyld		Nt	Polyethyleneterephthalate-type
Toy 17	Hollow ball with hole for titbits	pos	Copolymer with vinyl chloride and vinyl acetate
Toy 18	Pig with plush pants, whistling	pos	Plastic: phthalate + PVC
Toy 18, pants		Nt	Copolymer (acrylonitril : vinyl acetate) -type
Toy 19	Shrimps of pearls	pos	Phthalate + PVC
Toy 20	Fire hydrant with metal bell inside	neg	Polyisoprene filled with chalk
Toy 21	Rubber cactus, whistling	neg	CH-elastomer (polyisoprene-type), with chalk
Toy 22	Rubber ball	neg	CH-elastomer (EPDM-type), with chalk and silicate
Toy 23	Ball with a strap	pos	Phthalate (+ PVC)
Toy 24	Foam rubber ball	neg	Polyester + CH-elastomer
Toy 24, fyld		Nt	Polyethyleneterephthalate-type
Toy 25	Plastic balls with metal bells	neg	Polystyrene
Toy 26	Shoe, whistling	neg	Polyisoprene with Zn-diethyldithiocarbamate
Toy 27	Cow	neg	CH-elastomer
Toy 28	Stick with string and mouse	neg	Real fur

FORCE no.	Product name as stated on the product/packing	Beilstein's test	Material determined by IR
Toy 28, plastic body		Nt	Polyethylene, with inorganic filling
Toy 29	Ball with hole for titbits	neg	Methacrylate-type
Toy 30	Cat with rope	Handle pos, Cat pos	o-phthalacidester (+ PVC)
Toy 31	Plush turtle with egg	Nt	Green fabric: Acrylonitril + PVA ; Egg : Butyleneterephthalateester-type
Toy 31, fill		nt	Polyethyleneterephthalate-type
Toy 32	Plush mouse	nt	Butyleneterephthalateester-type
Toy 33	Dog	pos	o-phtalacidester (+ PVC)
Toy 34	Ball of rubber rings	neg	CH-elastomer (polyisoprene-type), with chalk and silicate
Toy 35	2 small plush cats	nt	White fabric : Butyleneterephthalatester-type; Black fabric: Acrylonitril + vinyl acetate-type
Toy 36, front	Plush/rubber telephone	pos	Black : o-phthalsyreester (+ PVC), White : o-phthalsyreester (+ PVC)
Toy 36, rear side		nt	Polyethyleneterephthalate-type
Toy 37	Girl doll	neg	
Toy 38	Spider with string	neg	CH-elastomer, with chalk
Toy 39	Fur mouse	nt	Real fur
Toy 39 plastic body		nt	Polyethylene, with inorganic filling
Toy 40	Soft dog with hard middle	neg	Middle: PUR ; Head and tail: CH-elastomer with chalk and + silicate
Toy 41	Porcupine, whistling	pos	Phthalate + PVC
Toy 42	"Rustling" mouse	nt	Polyethyleneterephthalate-type
Toy 43	2 fur mice	nt	Real fur
Toy 43, fill		nt	Polyethyleneterephthalate-type
Toy 44	Rat, whistling	neg	CH-elastomer with chalk
Toy 45	Plush porcupine	nt	Black fur: Acrylonitrile + vinyl acetate -type Brown fur: Ditto
Toy 46	Black tyre	neg	CH-elastomer
Toy 47	Retriever stick	nt	Fabric: Butyleneterephthalatester-type Core: CH-elastomer + chalk
Toy 48	"Ball with four handles"	neg	Latex with chalk
Toy 49	Hollow ball with hole for titbits	pos	o-phthalacidester + possibly PVC
Toy 50	Rubber snowman	neg	CH-elastomer

Beilstein's test : pos = positive, neg = negative, nt = not tested.
Polyisoprene = natural rubber
Samples of polyisoprene and PVC were washed with petroleum ether before the IR examination as these samples had silicone oil at the surface (probably release layers from the casting)

1 Survey of analyses

Analysis	Items	Method	Samples
Phthalate determination	PVC with phthalate	GC/MS	2, 5, 7, 11, 13, 18, 19, 23, 30, 33, 36, 41, 49
Screening, heavy metals	PVC	XRF	2, 5, 7, 11, 13, 18, 19, 23, 30, 33, 36, 41, 49
Migration, heavy metals	PVC	EN 71-3	Number and items depend on the screening
Tin content	Transparent PVC	XRF	13, 19
Cr/Cd	Yellow/orange/red colours in latex, natural rubber etc.	XRF	1, 12, 20, 21, 24, 26, 27, 34, 48
Br (flame retardants)	Textiles and fur	XRF	3, 6, 8, 9, 16, 18, 24, 2 * 31 (turtle + egg), 32, 35, 36, 37, 45, 47
Chromate (Cr VI)	Fur animal	(EN420)	28, 39, 43
Screening, organic compounds	CH-elastomer	GC/MS Headspace	1, 4, 7, 12, 14, 15, 20, 21, 22, 24, 26, 27, 34, 38, 40, 44, 46, 48, 50
Quantification of organic compounds	Depends on the screening	Depends on substances	Depends on the screening Estimate approximately 10 pieces
Azo dyes Screening	Strongly coloured textiles	(staining) EN ISO 105-E04	3, 3 x 16, 31, 32
Azo dyes	Strongly coloured textiles	EN 14362-1 og – 2:2003	Depends on the screening
Formaldehyde	Textiles + filling	EN ISO 14184-1	3, 6, 8, 9, 16, 18, 24, 2 * 31 (turtle + egg), 32, 35, 36, 37, 45, 47 + filling : 3, 16, 24, 31
Characterisation of smell	CH-elastomer	Possibly GC/MS headspace	34
Mercaptobenzothiazol, etc.	Latex/rubber	HPLC after watery extraction	7, 21, 26, 27, 34, 40, 46, 48, 50

1 XRF results, ppm

Element	Cr	Ni	As	Se	Br	Sr	Cd	Sn	Sb	I	Ba	Hg	Pb
EN 71-3 requirements	*60*		*25*	*500*			*75*		*60*		*1000*	*60*	*90*
Toy 1	11	3				42				4			2
Toy 2		5			1	1							1
Toy 3		72			426				24				13
Toy 5	7	45	8	0.5	17	28		1	10		36		222*
Toy 6	4	6			15	5		4	21	20	56		1
Toy 7	10	10			0.4	38						0.3	0,9
Toy 8		52		0.2	3	2			17				2
Toy 11		7	0.3		1	33		1					1
Toy 12	16	4		0.4	1	42							2
Toy 13	18	9			2	3							1
Toy 16		49			2	1			47				2
Toy 18	128*	8			1	7	94*	3			249		537*
Toy 19	10	11			1	1	2	661					2
Toy 20	21	4				133				3		1	12
Toy 21		48			1	109					118		4
Toy 23	648*	5	17	0.3	2	43	4	4	10		379		2269 *
Toy 24	4	52		0.5	4	5	0.5		27		35		2
Toy 26	5	3				54			5.4		108		1
Toy 27	5	14				41							2
Toy 28	14370 *	21		0.7	6	26							10
Toy 30	12	6			0.4	3			0.4				14
Toy 31.1	11	80			4	1	1		10				3
Toy 31.2	13	139			217	1	0.5		7				3
Toy 32		65			771	1	0.4		21				2
Toy 33	68*	6		0.6	1	3			1			0.5	271*
Toy 34		4			4	47	2				1011*	0.5	2
Toy 35		128			0.7	2							1
Toy 36		9			9	3					17		2
Toy 37	6	60			4	3	0.4		27				3
Toy 39	202*	9	0,7	0.5	11	48							14
Toy 41	8	5		0.3	0.8	2			0.6				3
Toy 43	470*	17	0,6	0.6	9	13	0.4						24
Toy 45		47		0.4	3	2	0.3		5				2
Toy 47	7	10			11	128	1		14		721		24
Toy 48		4			0.3	173							3
Toy 49	12	5			0.7	2							2

* The results state values that are higher than the requirement for migration according to DS/EN 71-3:1995 (requirements for toys for children).

1 Screening of organic compounds by headspace GS-SM

The table shows the four substances found in most of the products. Trace amounts are marked by + or -, measurable quantities with ++, large quantity with +++.

BHT (butylated hydroxytoluene) was in half of the samples of traceable size and in the rest of the samples there were measurable quantities.
Tetradecane ($C_{14}H_{30}$) is identified as the strongest CH compound in most of the samples, but was only measurable in two samples, particularly in Toy 7.

Sample	Cyclohexanon	Tetradecan	BHT	n-butyl-benzen-sulfonamid	Others
Toy 1	+	+	++	-	
Toy 4	-	+	+	+	Octane, xylene etc.
Toy 7	+	++++	+	+	
Toy 12	+	+	+	+	
Toy 14	-	+	++	+	Possibly aliphatic amine
Toy 15	+	+	++	+	
Toy 20	-	+	++	+	
Toy 21	+	+	+	+	More alkanes
Toy 22	+	+	+	+	
Toy 24	-	+	+	+	Ester compound
Toy 26	+	+	+	+	More alkanes
Toy 27	-	+	++	+	
Toy 34	+	+	++	-	
Toy 38	-	+	++	+	Ester compound
Toy 40	+	+	++	+	Toluene
Toy 44	+	+	+	+	
Toy 47	+	+	+	+	Limonen?
Toy 48	+	++	++	+	
Toy 50	+	+	+	+	Alifatic amine compound, low boiling

1 Screening for azo dyes

1.1 Method of analysis

Stain test according to prEN 71-10:2002, Annex A.
The sample material in pieces of approximately 5 cm x 15 cm were analysed for stains by influence of artificial sweat. The samples were tested on a number of textiles under two different pH conditions.
The grade of staining is evaluated on a scale from 1 – 5, where 5 means “no staining”.

1.2 Results of analyses

A total of 7 strongly coloured samples were selected for the analysis.

The scale is 1 – 5, where 5 is ”no staining”.

	Sample material			
	Toy 3		Toy 16 yellow	
	pH 5.5	pH 8.0	pH 5.5	pH 8.0
Staining on				
Acetate	4-5	4-5	4-5	4-5
Cotton	4-5	4-5	4-5	4-5
Polyamide	4-5	4-5	4-5	4-5
Polyester	5	5	4-5	4-5
Acryl	5	5	4-5	4-5
Wool	4-5	4-5	4	4-5

	Sample material			
	Toy 16 green		Toy 16 purple	
	pH 5.5	pH 8.0	pH 5.5	pH 8.0
Staining on				
Acetate	4-5	4-5	4-5	4-5
Cotton	4-5	4-5	4-5	4-5
Polyamide	4	4	4-5	4-5
Polyester	4-5	4-5	4-5	4-5
Acryl	4-5	4-5	4-5	4-5
Wool	4	4	4-5	4-5

	Sample material			
	Toy 31 yellow		Toy 31 green	
	pH 5.5	pH 8.0	pH 5.5	pH 8.0
Staining on				
Acetate	4-5	4-5	4	4
Cotton	4-5	4-5	4-5	4-5
Polyamide	4-5	4-5	4-5	4-5
Polyester	4-5	4-5	4-5	4-5
Acryl	5	4-5	4-5	4-5
Wool	4-5	4-5	4	4-5

	Sample material	
	Toy 32	
	pH 5.5	pH 8.0
Staining on		
Acetate	4-5	4-5
Cotton	4-5	4-5
Polyamide	4-5	4-5
Polyester	5	5
Acryl	5	5
Wool	4-5	4-5

The analysis does not reveal if the staining is caused by azo dyes, but only if the colours stain.
For further analysis in order to find the content of azo dyes, three samples which had been classified as "4" in the classification: Toy 16 yellow, Toy 16 green, and Toy 31 green.