

Survey of chemical substances in consumer products

Survey no. 29– 2003

Survey and assessment of chemical substances in hobby adhesives

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Waste

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Table of contents

TABLE OF CONTENTS	3
PREFACE	5
SUMMARY AND CONCLUSIONS	7
1 THE METHOD	11
1.1 DEFINITION	11
1.2 THE METHOD	12
1.2.1 <i>Collection of hobby adhesives</i>	12
1.2.2 <i>Retrieval of material safety data sheets etc.</i>	12
1.2.3 <i>Physical-chemical analysis</i>	13
2 COLLECTION	15
2.1 REGISTRATION OF THE ADHESIVES	15
2.2 CLASSIFICATION OF ADHESIVES ACCORDING TO TYPE	16
3 RETRIEVAL OF DATA	17
3.1 MATERIAL SAFETY DATA SHEETS AND INFORMATION ON PACKAGING	18
3.2 LABELLING OF ADHESIVES	21
3.2.1 <i>Danger symbols and MAL-codes</i>	21
3.2.2 <i>CE-labelled products</i>	25
3.2.3 <i>The Joint Council for Creative and Hobby Materials</i>	25
3.2.4 <i>Environmental labelling</i>	26
4 PHYSICAL-CHEMICAL ANALYSIS	28
4.1 ANALYSIS METHODS	29
4.1.1 <i>Determination of the content of dry matter</i>	29
4.1.2 <i>FTIR analysis</i>	29
4.1.3 <i>X-ray analysis</i>	29
4.1.4 <i>Gas chromatography at mass spectrometric detection</i>	29
4.2 ANALYSIS RESULTS AND COMMENTS	30
4.2.1 <i>Infrared spectroscopic analysis (FTIR)</i>	30
4.2.2 <i>Analysis for the content of dry matter</i>	35
4.2.3 <i>GC/MS analyses</i>	36
4.2.4 <i>Analysis results for phthalates</i>	37
4.2.5 <i>Analyses for a content of formaldehyde and acetaldehyde</i>	38
4.2.6 <i>Analysis for Isocyanates</i>	38
4.2.7 <i>X-ray analysis</i>	39
5 REFERENCES	41

Preface

Collection and analyses to the project "Research and assessment of hobby adhesives" has been elaborated for the Danish Environmental Protection Agency (Danish EPA) from October 1, 2001 till December 15, 2001. The present report describes the results obtained in the project.

Danish Technological Institute, Centre for Environment and Waste Technology, Environment Division in co-operation with Centre for Plast Technology from the Industry Division has prepared the project. Project manager for Danish Technological Institute has been M.Sc., Ph.D. Nils H. Nilsson, Centre for Environment and Waste Technology.

The chemical analysis of hobby adhesives has been made in co-operation with the laboratories of Centre for Chemical Technology in Århus and Taastrup and with Plast Technology in Taastrup. M.Sc. (Engineering) Malene Staal Jensen and M.Sc., Ph.D. Nils H. Nilsson Centre for Environment and Waste Technology have been responsible for co-ordination and completion of the project.

The steering group of the project has been as follows: Claus C.C. Ankjærgaard, Danish EPA (chairman), head of section Lea Frimann Hansen, Danish EPA and M.Sc., Ph.D. Nils H. Nilsson.

The purpose of the project has been to investigate hobby adhesives that can be purchased in the Danish retail. The focus has especially been on hobby adhesives for wood, paper, carton, textiles, and plastic surfaces. Adhesives with and without CE-labels are represented in the survey. CE-labelled adhesives are characterised as being an integrated part of toy (e.g. model sets, jigsaw puzzles etc.) or as being recommended for use for a specific toy or playing purpose.

Based on the efforts of Danish EPA of surveying and informing about the health risks that the Danish population may be exposed to when using consumer products based on chemical substances, the purpose of the project has been to survey the chemical constituents in hobby adhesives. The project consists of three phases. A collection phase, where hobby adhesives have been purchased in the retail. An information retrieval phase, where information has been collected from manufacturers and from the internet; and finally a phase, where physical-chemical analysis of a representative selection of the collected hobby adhesives has been made as well as a conclusion of the results of the project.

The report has been sent to producers and importers for comments.

DEHP was found in two products (BH3 and O20). DEHP has recently been classified as dangerous for reproduction and teratogenicity. The collection of products took place before the classification and labelling were in force. For one of the products the producer has stated that the use of DEHP has stopped due to the classification. For the other product the producer has stated that all phthalates have been substituted in their products.

Furthermore it has been stated that the products HH6 and O8 are withdrawn from the market.

The received comments showed good agreement between the report and the information from the producers.

Summary and conclusions

On behalf of the Danish EPA the Danish Technological Institute has purchased a wide range of hobby adhesives which can be bought in the Danish retail. It has primarily been adhesives for wood, paper, textiles, and plastic objects. However, several of the adhesives are all-purpose adhesives, which can also be used to join other materials.

In total 58 different types of hobby adhesives have been collected at purchases in DIY centres, super markets, leisure stores, and bookshops. The adhesives have then been divided into 13 groups according to application purpose or method of application e.g. sprays.

Firstly a number of screening analyses have been performed on a representative segment of the collected hobby adhesives. In this phase, also a determination of the dry matter percentage in 22 adhesives has been performed. Secondly further special analyses have been performed based on the screening analyses and the information given by the manufacturers and importers of the adhesives. For most of the adhesives it has been possible to obtain product descriptions and material safety data sheets either on the Internet or by contacting the manufacturer. For a few of the adhesives it has not been possible to obtain detailed information on the composition of the adhesive. For some adhesives the available information is that the adhesive is water-based and does not contain substances to be notified. Six of the adhesives were CE-labelled.

The analysis methods used for the testing of the adhesives have been based on chromatographic and spectroscopic methods, except the determination of the content of dry matter.

Primarily, an infrared spectroscopic “fingerprint” analysis has been made on a representative number of samples of the adhesives. The method gives an identification of the adhesive after the solvents, if present, have evaporated and the adhesive is solidified. In some cases, information on the presence of plasticizers in the adhesive, e.g. phthalates, can be obtained.

The infrared spectres can be difficult to interpret if the recipe is based on a combination of adhesives or if so-called copolymer adhesives have been used, that is adhesives, where the adhesive consists of several different types of polymer chain monomers. In cases, where the supplier has not given any information of the chemical composition of the adhesive, the infrared analysis can give information on the type of adhesive. Based on the first results, further infrared analyses have been made inter alia to search for phthalate plasticizers.

The results of the determination of dry matter percentage show that the adhesives hold a content of dry matter from 17 to 100%. In the adhesive where the percentage of dry matter is 100%, the result of the analysis corresponds to the information given by the supplier. As for the adhesives based on solvents, the percentage of dry matter gives a good estimate of the quantity of volatile solvents in the adhesive.

A representative number of samples of the adhesives have been analysed using gaschromatographic/mass spectrometric methods (GC/MS). The technique has been used in the screening phase as well as in the following phase where the adhesives have been analysed for specific substances. By using this analytical technique it is possible to analyse for the composition of volatile compounds in the tested adhesives and to obtain a very precise determination of the composition. It is also possible to determine the content of plasticizers in the adhesives if they have a certain volatility, inter alia phthalate plasticizers.

Some wood adhesives have been analysed by high-pressure liquid chromatography (HPLC) for content of formaldehyde and acetaldehyde. The method is very specific and sensitive toward aldehydes and ketones.

Finally, the adhesives have been tested by X-ray analysis. The analysis has been carried out both in the screening phase and in the special analysis phase.

In the following, a summary of the results from the study of the information on the hobby adhesives in the Danish retail, and of the retrieved information such as product information and material safety data sheets, and the screening analyses and special analyses carried out is given

In many of the cases, only very scanty information regarding type of adhesive and contents of solvents can be found on the packaging, which may be a sort of tube, container or blister pack. The content of phthalate plasticizers is neither specified on the adhesive packaging or on the material safety data sheets of the adhesive, but this isn't required by current legislation though. In several wood adhesives and in one vinyl glue and in one "school glue", phthalate plasticizers were detected. The supplier has informed that the chemical content of the "school glue" is diisobutylphthalate. As for the rest of the adhesives in which phthalates have been detected in the analyses no such information is given on the packaging of the adhesive.

To get detailed information on the types of adhesive and the composition it is necessary to study either the product sheet or the material safety data sheet for each single adhesive.

For the adhesives based on solvents, the main components of solvents given by the manufacturer agree very well with the gaschromatographic/mass spectrometric analysis. A part of the product sheets of adhesives based on solvents indicate that the adhesives consist of naphtha, which is an oil distillate. Samples consisting of naphtha are characterised at a large content of aliphatic hydrocarbons and a small content of aromatic hydrocarbons. The aliphatic hydrocarbons include n-hexane, cyclohexane, and n-heptane as well as a number of homologue or isomeric hydrocarbons. According to the chemical analysis's many of the adhesives, based on solvents, contain small quantities of volatile compounds. There are no legal demands that require labelling of these on the declaration, which explains why it cannot be found in the information given by the manufacturers.

Chlorinated hydrocarbons have not been found in the tested adhesives based on solvents. However, many of the adhesives consist of acetone, ethylacetate acetic ether, methylisobutylketone (MIBK), butanol, ethanol and other esters, alcohols and ketones, which are normally used in the paint industry. Several of the spray adhesives consist of aromatic hydrocarbons, which should be considered if an exposure scenario were to be constructed.

In one adhesive the diphenylmethane-4,4' diisocyanate (MDI) was detected in the isocyanate analysis. This finding agrees with the information on the material safety data sheet given by the manufacturer.

In some of the adhesives, inter alia super glues/glues, methylmethacrylate or isomers of this acrylmonomer have been detected. This information is also given in the material safety data sheets.

The analysis for formaldehyde in wood adhesives by high-pressure liquid chromatography showed in both cases that the adhesives had a low content of formaldehyde and that the quantities were so small that they do not have to be notified. The highest content was 0,16% and the limit for notifying a content of formaldehyde in a chemical product is 0,2%. When using the same analysis method a content of acetaldehyde of 0,02–0,06% was detected in both wood adhesives and in one leisure adhesive “school glue”. The content may be caused by the presence of polyvinyl formal and polyvinyl acetate in the adhesives. These polymers can liberate formaldehyde as well as acetaldehyde, which preserve the adhesives.

The X-ray screening of the elements with an atomic weight larger than that of fluorine showed that the content of heavy metals in the analysed hobby adhesives is very low. In the X-ray analysis, chlorine has been detected in rather small quantities in some of the samples, but it has not been possible to determine in what form the chlorine is present. However, it is not chlorinated solvents. In one of the epoxy adhesives 14% sulphur has been detected. Nor is it, in this case, possible to detect in what form the sulphur is present in the adhesive. It is likely though that the sulphur is added as a mercaptane, because this type of sulphur compounds accelerates the curing of epoxy.

Generally, it can be concluded that there are many different hobby adhesives to choose among on the Danish retail market. A large number of these adhesives are based on solvents. Some of these solvents contain components that are found on the List of unwanted substances made by the Danish EPA. Some of the adhesives also contain small quantities of volatile compounds, which is not directly listed in the information given by the manufacturer. The chemistry of adhesives is altogether complex. In many adhesives the recipe is based on more than one adhesive compound as well as mixtures of a number of solvents. Some of the adhesives are two-component adhesives. The advantage of using hot-melt adhesives is that they do not contain solvents. Instead the adhesives become liquid when heating by a hand-held heat gun. These hot melt adhesives can, however, not be used as general purpose hobby adhesives, and there will still be a need of different types of adhesives depending on the purpose for which they shall be used.

“Fællesrådet for formnings- og hobbymaterialer”, the Joint Council for Creative and Hobby Materials, has made criteria for classification of the adhesives. The adhesives are divided into four categories. Category A: May be used by children from the age of three. Of all the collected adhesives four have been assessed according to the current criteria for labelling the products in category A. The adhesives in question are two paper glues (BI8 and BI1), one glue stick (BI2) and one wood adhesive (HN2). The labelling appears in all cases on the material safety data sheet and/or on the product information sheet. There is no labelling on the packaging.

Hobby adhesives can obtain the Nordic Ecolabel, the Swan. The scheme sets criteria for the chemical ingredients in the adhesives. However, none of the purchased adhesives were eco-labelled.

It is, however, on a full volunteer basis whether the manufacturer wants to label the products in accordance with the criteria formulated by the Joint Council for Creative and Hobby Materials or the Nordic Ecolabel – the Swan. The manufacturer is on the contrary obliged to classify their products according statutory order on classification and labelling. In addition, if the glue is sold in a spray application. It must comply with the rules in the statutory order on limitation in use of propellants and solvents in aerosol spray cans as well as the rules on Ae-substances in the statutory order on marketing and use restrictions on hazardous substances and products to certain purpose.

1 The Method

1.1 DEFINITION

Hobby adhesives is in the present project defined as a product that can join two solid surfaces together so that they are joined and kept together by a glue joint. The project focuses on types of glue that can be used for gluing wood, paper, carton, textile, and plastic surfaces. However, it should be noted that some of the types of adhesive could be used for joining other types of material such as metals, glassware, and chinaware. In the present project the adhesives that can be purchased by the Danish consumers in the retail for leisure and other DIY activities in the home are assessed.

The types of adhesives can be divided according to hardening mechanism, application method, and the chemical composition. When dividing the adhesives according to the hardening mechanism, three categories are used:

1. Adhesives curing by chemical reaction,
2. Physical drying adhesives, and
3. Physical hardening adhesives.

Category 1:

The types of adhesives curing by chemical reaction are one- or two-component adhesives. When using the latter, the hardening takes place when two reactive substances are mixed and harden to a solid adhesive, whereas one-component adhesives harden by influence of humidity, another catalysis or by heating, where a hardener is released in the adhesive.

Category 2:

The physical drying types of adhesives harden when solvents or water in the adhesive evaporate. The aqueous adhesives are normally emulsion adhesives except adhesives based on starch and cellulose (paste).

Category 3:

Physical hardening adhesives are applied in as a liquid substance and the adhesion takes place by cooling (Hot-Melt). For certain types of adhesives, curing takes place along with the melting.

For hobby purposes, the most commonly used types of adhesives are:

- “White glue” water-soluble (PVA adhesive) for gluing wood and paper (category 2).
- Different types of contact adhesives mainly based on polychloroprene or polyurethane. Contact adhesives based on water as well as on solvents are used in private homes. The contact adhesives are used for gluing plastic, rubber, leather, metal etc. (category 1 and 2).
- Epoxy adhesive; two-component (“Araldit”) are mixed and can join surfaces of metal, concrete, wood etc. together (category 1).

- Office adhesives glue at evaporation of a solvent or water. May consist of PVC, PVC-PVA-copolymers, natural rubber or animal glue, dextrin, starch and cellulose derivatives (category 2).
- Hot-melt adhesives are applied in the melted state and harden at cooling. Hot-melt adhesives are especially used for industrial purposes but is increasingly used by private households for leisure purposes. (Category 3).

For practical reasons the division of the adhesives in the present study is different from the above-mention as the application method is taken into account. Inter alia the spray adhesives and the very popular super adhesives (superlim) based on cyanoacrylate each has a group of its own.

1.2 THE METHOD

The project includes four phases:

1. Collection of hobby adhesives
2. Retrieval of material safety data sheets etc.
3. Physical-chemical analyses
4. Detail analyses.

The four phases are in detail described in chapter 2 – 4. Below a short description of the methods used in the four phases.

1.2.1 Collection of hobby adhesives

The consumers can purchase hobby adhesives in different types of shops. To ensure that the selected adhesives are representative for the Danish marked, the different types of adhesives have been purchased in four types of shops: DIY markets, hobby shops, super markets, and bookshops.

Phase one of the project has been to collect adhesives that fulfil the criteria for hobby adhesives described in section 1.1. The adhesives have been purchased in different types of shops to cover the market as well as possible. The adhesives have been purchased in supermarkets, hobby shops, bookshops, and DIY markets. In each of the shops as many different types of adhesives have been purchased as possible. The intention has been not to purchase adhesives that have already been purchased in other shops.

The purchased adhesives have been categorised by type/function.

1.2.2 Retrieval of material safety data sheets etc.

Product information on the purchased adhesives has been retrieved as material safety data sheets, product sheets or other similar materials. The material safety data sheets have been retrieved at the homepages of the manufacturer or importer or by contacting the supplier or importer by phone or e-mail. Some adhesives have not been clearly labelled with the name of the manufacturers or importer. In these cases the shop, where the adhesive was purchased, was contacted to help finding the supplier or importer.

A selection of manufacturers and suppliers has been contacted for retrieving further information on the content of chemical ingredients and concentrations of the adhesives. These manufactures and suppliers were also asked about their use of and attitude towards labelling adhesives.

1.2.3 Physical-chemical analysis

Concurrently with the collection of material safety data sheets and other information on the content of chemical ingredients in the adhesives, physical-chemical analyses of the adhesives were made. Two different series of physical-chemical analyses were made: One series of screening analyses and one of detail analyses based on the retrieved information on the adhesives and the results of the screening analyses.

In the screening analyses as well as in the detail analyses, chromatographic and spectroscopic analyses methods and –detection techniques have been used. The following analysis methods have been used: Infrared spectroscopy, HPLC with ultraviolet detection, X-ray analysis and gaschromatography with mass spectrometric detection. The percentage of dry matter has been determined by simple evaporation.

2 Collection

Adhesives have been purchased in nine different shops. According to the project definition the intention has been to purchase as many different types of hobby adhesives as possible without purchasing doublets.

Totally, 70 adhesives were purchased, however, eight of them turned out to be doublets. Furthermore, the four of the remaining products turned out to be identical with four other products from the same manufacturer, however, with another product name. Altogether, 58 different adhesives were purchased.

The collected adhesives include CE-labelled adhesives as well as adhesives without a CE-label.

2.1 REGISTRATION OF THE ADHESIVES

The collected adhesives have been registered in accordance with the "Table on purchased products" from the Danish EPA. The registration include product name, product description, name and address of the manufacturer or importer, date of purchase, bar code/other registration number and if possible product register number (PR-no).

Table 2.1 is a list of where adhesives have been purchased and in what type of shop.

TABLE 2.1 PURCHASE OF ADHESIVES

Date	Shop	Type of shop	Number of purchased products
01/11 2001	Superbrugsen	Grocery	1
31/10 2001	GAD	Bookshop	2
31/10 2001	Mid Hobby ApS	Hobbybutik	3
31/10 2001	Salling	Grocery	5
18/10 2001	Harald Nyborg	DIY market	6
20/10 2001	Bauhaus	DIY market	6
31/10 2001	Hoffmann Hobby	Hobbybutik	8
18/10 2001	Bilka	Grocery	9
18/10 2001	OBS	Grocery	30
Total	Nine shops		70

2.2 CLASSIFICATION OF ADHESIVES ACCORDING TO TYPE

The registered adhesives were divided into different groups according to their area of application. The groups and the number of different adhesives are shown in Table 2.2.

Table 2.2 Adhesives divided into groups according to their application and method of application

Group	Number
Textile adhesive	2
"School glue" (for paper)	7 (plus one doublet of another brand)
Glue sticks (for paper)	6 (plus one doublet of another brand)
Plastic adhesives	4
Vinyl adhesives	2
Wood adhesives	6
Adhesives for general purposes	5 (plus one doublet of another brand)
Contact adhesives	6 (plus one doublet of another brand)
Two-component adhesives	3
Adhesive gun (Hot-Melt adhesive)	2
Super glue	8
Adhesive sprays	4
Adhesives for special purposes	3

In total, 13 different types of paper adhesives were purchased. The adhesives are divided into the following groups: "school glue" and "glue sticks". The "school glue" includes in the present project adhesives in plastic containers and tubes as well as a "adhesive filler".

3 Retrieval of data

Efforts have been made to retrieve information on the content of chemical ingredients in the purchased adhesives from all the suppliers of adhesives in question. The manufacturers and importers of the adhesives, who have been registered for manufacturing more than one of the collected adhesives, are shown in Table 3.1. About 15 different companies manufacture the 58 collected adhesives.

TABLE 3.1 MANUFACTURER OR IMPORTER OF ADHESIVES

Manufacturer	Number of adhesives	Note
Bostik	2	Material safety data sheets available on the Internet
Bison	3	Material safety data sheets forwarded by request
Loctite	3	The importers (Henkel) forwarded the requested material.
Pritt	3	Some material safety data sheets delivered by the former importer Henkel. A new importer has been appointed.
Not noted	3	Three of the collected adhesives did not have a clear identification of either the manufacturer or the importer. As for one of the adhesives, the supplier of the shop in question could help procuring a material safety data sheet.
UHU	4	Material safety data sheets were forwarded by request over the telephone.
Manufacturers from whom only one adhesive was purchased	6	Manufacturer or importer forwarded the safety data sheets by request.
3M	7	The available ¹ material safety data sheets were forwarded by request.
Danalim	12	Product information on the internet. Material safety data sheets forwarded on request.
Casco	15	Material safety data sheets and product information were available on the internet.
Totally	58	

There are different ways in how information on adhesives can be obtained. Some of the manufacturers have made their material safety data sheets and/or product sheets available on the Internet free of charge. Product sheets presents information on how and for what purpose the adhesive can be used and on the precautions needed when using the product. The Danish material safety data sheets with 16 items giving the consumers of the products instructions on how to use them, are determined in Statutory Order on substances and materials, no. 540, September 2nd, 1982 and the amended statutory order, no. 485, June 16, 1995. The material safety data sheets must be available on products for industrial purposes, if it's considered to be dangerous or in any other way harmful to safety or health. They give information on chemical composition, special precautions, educational demands as well as hazard identification such as danger symbols and R- and S-phrases.

¹ For some of the adhesives no material safety data sheet was prepared, as there are no requirements in the law due to the chemical composition of the product.

In most cases, material safety data sheets for the products do exist. It is generally glue sticks and “school glue” for which it has not been possible to retrieve material safety data sheets.

For some of the adhesives it has not been possible to find the manufacturer. Few other adhesives are apparently outdated, and it has been difficult to retrieve the right material safety data sheet. Because they have been replaced by new updated material safety data sheets covering the improved products.

3.1 MATERIAL SAFETY DATA SHEETS AND INFORMATION ON PACKAGING

In the present section, information on chemical components given on the packaging and the material safety data sheets is specified for each group of adhesives. Generally, the information on the packaging of the adhesives is not sufficient to determine the composition of the adhesive.

TABLE 3.2 TEXTILE ADHESIVES

No	Content	Basis
BI 3	Water-based, ammoniac <2%	Natural rubber latex
HH 7	Water-based	Natural rubber latex

TABLE 3.3 “SCHOOL GLUE”

No	Content	Basis
BI 1	Water-based, no duty to disclose all material facts on substances. CE-labelled	Polyvinyl acetate
BI 4	No duty to disclose all material facts on substances. CE-labelled	Mixture of polymers
BI 8	Water-based, no duty to disclose all material facts on substances. CE-labelled	Polyvinyl acetate
HH 2	Water-based, no duty to disclose all material facts on substances above triviality limit	Water-based
HH 5	No solvents. CE-labelled	No information
HH 6	Water 30%-60% benzyl alcohol 1%-5%,	Vinyl acetate Maleic acid Copolymer
O 17	Water 40%-50% Polyvinyl acetate 40%-50% diisobutyl phthalate 5%-10%, Polyvinyl alcohol 1%-5%	Polyvinyl acetate

TABLE 3.4 GLUE STICKS

No	Content	Basis
BI 2	No duty to disclose all material facts on substances. CE-labelled	No information
GAD 1	Aqueous glue. CE-labelled	No information
GAD 2	Water-based adhesive	No information
O 13	Water 54%-60%, glycerine 8%-15%, N-Vinyl-pyrrolidinone Polymer 14%-19%, Acryle Copolymer 7%-11%, 2-Amino-2-Methyl-1-Propanol 0,75%-1,25%	No information
O 6	No solvents	No information
O 14	Water 10%-30%, Acryl polymer 30%-60%, Polyethylene glycol 1%-5%, N-Vinylpyrrolidinone Polymer 1%-5%, Emulgators 1%-5%, Thiazolybenzimidazole 1,0%-1%	No information

TABLE 3.5 PLASTIC ADHESIVES

No	Content	Basis
HH 8	Ethyl acetate 50%-100%	Polystyrene in organic solvents
M 2	Acetone >30% ethyl acetate >30%, butanone >10%, Bisphenol-A-diglycidylether <1%	Epoxy 0.2%
O 8	Heptanes Kelator	(Activator)
O 8	(No solvents) Ethyl cyanoacrylate 65%-95%	Cyanoacrylate
S 4	Butyl acetate >50%, Acetone <40%, Solvent naphtha light aromatic 5%,	Epoxy resin

TABLE 3.6 VINYL ADHESIVE

No	Content	Basis
BH 3	Tetrahydrofuran 60%-100% methyl ethyl ketone 5%-10%	vinyl adhesive
BH 4	Acetone 30%-60 %, Ethyl acetate 10%-30%	vinyl adhesive

TABLE 3.7 WOOD ADHESIVE

No	Content	Basis
HN 1	(No solvents) Isocyanates (4,4'-Diphenylmethandiisocyanate, mixture of isomers)	Polyurethane one-component, moisture cure
HN 2	Water-based, no duty to disclose all material facts on substances	PVAc dispersion
O 12	Water-based, 2-metoxy-1-metyletylacetate, Polyvinyl acetate	Polyvinyl acetate
O 19	Butyl diglycol acetate <2,5%	Polyvinyl acetate dispersion
O 20	Butyl diglycol acetate <2,5%	Polyvinyl acetate dispersion
O 21	Butyl diglycol acetate 2,5%-10%	EVA/acrylic ester (product data sheet) Acryl-copolymer dispersion glue (safety data sheet)

TABLE 3.8 HOBBY ADHESIVE

No	Content	Basis
BI 6	Acetone >20%, naphtha 1%-5% cellulose nitrate 10%-15%, butyl acetate 1%-5% n-butanol 1% -5%, ethanol 5%-10%	Cellulose glue
M 1	Acetone >25% acetic ether >40% solvent naphtha <5%	Epoxy <1%, (ketonaldehydesin 50% in ethyl acetone) <5%
O 29	Water-based	Vinylacetatethen copolymer
O 30	Toluene 10%-25%, butanone 10%-25% acetone 25%-50%	Polyurethane elastomer
O 5	No solvents	No information

TABLE 3.9 CONTACT ADHESIVE

No	Content	Basis
HN 3	Toluene >20%, acetic ether <20% naphtha >20%	Polychloroprene (neoprene)
HN 4	Acetic ether >20 %	Polyurethane one-component
O 18	Toluene 10%- 25%, technical grade heptane 25%-50%, acetone 25%-50%	Polychloroprene
O 28	Technical grade heptane 25%-50%, acetic ether 25%-50%, Toluene 2,5%-10%	Polychloroprene
S 1	Acetone, butyl acetate, acetic ether	No information

S 5	Methyl acetate >60%, Butyl acetate >5% Ethanol	Cellulose nitrate
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TABLE 3.10 TWO-COMPONENT ADHESIVE

No	Content	Basis
BH 6	(No solvents) Bisphenol-A-diglycidylether Copolymer 70%-82%, Bisphenol-F-diglycidylether 4%-10%, epoxy compounds	Epoxy
BH 6	(No solvents) N-3-dimethylaminopropyl)-1,3-propylendiamin 5%-10%	(curing agent)
O 23	(No solvents) Alkylaminophenol, aminoester	(curing agent)
O 23	(No solvents) Epoxy resin	Epoxy resin
O 24	((No solvents) N-(3-dimethylaminopropyl)-1,3-propylendiamine 2,5%-10%	(curing agent)
O 24	(No solvents) Epoxy resin, 2,2-bis(p-(2,3-epoxypropoxy)phenyl)propane 50%-100%, Bisphenol-A-diglycidylether 2,5% - 10%	Low-molecular epoxy resin

TABLE 3.11 SPRAY GUN

No	Content	Basis
HH 3	It has not been possible to procure any information on the chemical substances in the product.	Melt adhesive
HH 4	It has not been possible to procure any information on the chemical substances in the product.	Melt adhesive

As Table 3.11 shows it has not been possible to procure information on the chemical substances in the product on product or material safety data sheets.

TABLE 3.12 SUPER GLUE

No	Content	Basis
BH 5	Ethylcyanoacrylate 60%-100%	Ethylcyanoacrylate
BI 9	Ethyl-2-cyanoacrylate >80%	Cyanoacrylate
HN 6	Polymethyl methacrylate 1%-5%, Ethylcyanoacrylat 80%-99%	Cyanoacrylate
M 3	Ethyl-2-cyanoacrylate 60%-95%	Cyanoacrylate
O 15	Ethyl-2-cyanoacrylate 90%-100%, Amorphous silica 5%-10%, Polymethyl methacrylate 1%-5%	Cyanoacrylate
O 16	Ethyl-2-cyanoacrylate 90%-100%, Poly(methyl-methacrylate) 1%-10%, Hydroquinone <1%	Cyanoacrylate
O 26	Ethyl-2-cyanoacrylate 50%-100%	Ethylcyanoacrylate
O 27	Ethyl-2-cyanoacrylate 50%-100%	Ethylcyanoacrylate

TABLE 3.13 ADHESIVE SPRAY

No	Content	Basis
HH 1	Butane, Propane, Acryl-Harz, Dimethoxymethane	Acrylic
O 11	Propane 5%-20% butane 5%-15%	No information
S 3	Petroleumdestillate, cyclohexanone 10%-20%, propane 10%-20%, nahtha 20%-40%, dimethylether, synthetic rubber 5%-10%, isobutane 1%-5%, isopentan1%-3%	
O 9	Does not contain any classified substances above the triviality limit	No information

TABLE 3.14 ADHESIVES FOR SPECIAL PURPOSES

No	Content	Basis
HN 5	Acetone >20%, cellulose nitrate 1%-5%, ethanole1%-5%	Polyvinyl acetate
O 22	Technical grade heptane (Naphtha (crude oil) Hydro desulphurized light, dearomatises (Solvent naphtha 80/110)) 25%-50%, toluene 2,5%-10%	Synthetic rubber

O 25	Hydroxypropyl methacrylate 10%-25%, Methacrylate 10%-25%, 2-Hydroxyethyl methacrylate 5%-10%	Acrylate adhesive
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3.2 LABELLING OF ADHESIVES

There are different possibilities for and demands regarding the labelling of adhesives. However, all adhesives have to comply with the rules of the statutory act on classification and labelling.

Adhesives, which can be characterised as an integrated part of a toy or are recommended for use for specific kinds of toys or playing purposes, have to be CE-labelled. The CE-labelling has to comply with current standards described in the statutory order on toys.

Some products to occupational use have to be labelled with a codenumber (MAL-codes). The codenumber consist of two figures with a hyphen. The figure before the hyphen divides the products in seven groups from 00- to 5-. The higher figure the higher risk by inhalation. The figure after the hyphen (1 to 6) gives the danger of the substances in direct contact with the skin, eyes and ingestion. Then there are the voluntary labelling systems such as the Nordic Environmental Labelling – The Swan, and The Joint Council for Creative and Hobby Materials (“*Fællesrådet for formnings- og hobbymaterialers*”) Shopping Guide.

3.2.1 Danger symbols and MAL-codes

A great deal of the collected adhesives are labelled with danger symbols and/or codenumber (MAL-code), as well as with risk and safety phrases occur extensively on many of the products. However some groups of adhesives – textile adhesive, “school glue” and glue sticks – are practically without these labelling. The labelling of the adhesives is shown in **Fejl! Henvisningskilde ikke fundet.** to Table 3..

TABLE 3.15 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR TEXTILE ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
BI 3	-	-	-
HH 7	-	-	00-1

TABLE 3.16 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR “SCHOOL GLUES”

No	Danger symbols	R and S phrases	MAL-codes
BI 1	-	-	-
BI 4	-	-	-
BI 8	-	-	-
HH 2	-	-	1-1
HH 5	-	-	-
HH 6	-	-	-
O 17	-	S26 –R36	-

TABLE 3.177 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR GLUE STICKS

No	Danger symbols	R and S phrases	MAL-codes
BI 2	-	-	-
GAD 1 ²	-	-	-
GAD 2 ³	-	-	-
O 13	-	-	-
O 6	-	-	-
O 14	-	S26	-

TABLE 3.18 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR PLASTIC ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
HH 8	Irritant Highly flammable	R11-36-67 S2-16-46-51	3-1
M 2	Irritant Highly flammable	R11-36 S9-16-23-25	3-1
O 8	Harmful Highly flammable	R11-38-65-67 S2-28-62	-
O 8	Irritant	R36/37/38 S23-24/25-26	-
S 4	Irritant Highly flammable	R11-36 S7/9-16-23-51	3-1

TABLE 3.19 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR VINYL ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
BH 3	Irritant Extremely flammable	R12-36/37 S2-9-16-29-33	4-1
BH 4 ⁴	Irritant Highly flammable	R11-36-66-67 S2-16-26-46	3-1

TABLE 3.20 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR WOOD ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
HN 1	Harmful	R20-36/37/38-42/43 S2-23-36/37-45	00-3
HN 2	-	-	00-1
O 12	-	-	1-1
O 19	-	-	00-1
O 20	-	-	00-1
O 21	-	-	00-1

TABLE 3.21 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR HOBBY ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
BI 6	Irritant Highly flammable	R11-36-66-67 S2-7/9-16-25-29-46	-
M 1	Irritant Highly flammable	R11-36 S7/9-16-23-51	3-1
O 29	-	-	00-1
O 30	Harmful Highly flammable	R11-20-36-67 S2-16-29-46	4-3
O 5	-	-	-

² Based on product information, not a material safety data sheet.

³ Material safety data sheet could not be retrieved.

⁴ The PR-no on the material safety data sheet differs from the one on the purchased product, which indicates that the information may not be correct.

TABLE 3.18 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR CONTACT ADHESIVES

No	Danger symbols	R and S phrases	MAL-codes
HN 3	Harmful Highly flammable	R11-20-66 S2-7/9-16-29-46	4-3
HN 4	Irritant Highly flammable	R11-36-66-67 S2-7/9-16-26-46	3-1
O 18	Harmful Highly flammable	R11-20-36/38-67 S2-9-16-46-51	4-3
O 28	Irritant Highly flammable	R11-36/38-67 S2-16-23-24/25-46-51	3-1
S 1	Highly flammable	R11 S2-16-23-24/25	3-1
S 5	Irritant Highly flammable	R11-36 S9-16-23-33	3-1

TABLE 3.19 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR CONTACT ADHESIVE TWO-COMPONENT ADHESIVES⁵

No	Danger symbols	R and S phrases	MAL-codes
BH 6 Epoxy	Irritant, Dangerous for the environment	R36/38-43-51/53 S2-24-26-37-46-61	00-5
BH 6 curing agent	Irritant	R36/38-43 S2-24-26-37-46	00-1
O 23 Epoxy	Irritant	R36/38-41-43 S2-24/25-26-37/39-46	00-5
O 23 curing agent	Irritant	R36/38-41-43 S2-24/25-26-37/39-46	00-5
O 24 Epoxy resin	Irritant	R36/38-43 S2-26-28-37	00-5
O 24 curing agent	Irritant	R36/38-43 S2-26-28-37	00-5

TABLE 3.20 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR CONTACT ADHESIVE GLUE PISTOL

No	Danger symbols	R and S phrases	MAL-codes
HH 3	-	-	-
HH 4	-	-	-

⁵ Symbols, R and S-phrases and MAL-codes concern the final mixture of hardening and adhesive. Therefore the two different components must be regarded as a pair.

TABLE 3.21 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR SUPER GLUES

No	Danger symbols	R and S phrases	MAL-codes
BH 5	Irritant	R36/37/38 S2-26-46	5-5
BI 9	Irritant	R36/37/38 S2-24/25-26-46	-
HN 6	Irritant	R36/38 S26-28	-
M 3	Irritant	R36/37/38 S23-24/25-26	5-5
O 15	Irritant	R36/37/38 S2-23-24/25-26-51	-
O 16	Irritant	R36/37/38 S2-23-24/25-26-51	-
O 26	Irritant	R36/37/38 S2-23-26-37	-
O 27	Irritant	R36/37/38 S2-23-26-37	-

TABLE 3.26 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR ADHESIVE SPRAYS

No	Danger symbols	R and S phrases	MAL-codes
HH 1	Extremely flammable	-	-
O 11	Extremely flammable	R12 S9-16-23-24-33	3-1
S 3	Irritant, Dangerous for the environment, Extremely flammable	R12-38-52/53-67 S2-15-16-23-24/25-26-28-38-47-51-61	
O 9	-	-	00-1

TABLE 3.27 DANGER SYMBOLS, R AND S PHRASES AND MAL-CODES FOR ADHESIVES FOR SPECIAL PURPOSES

No	Danger symbols	R and S phrases	MAL-codes
HN 5	Irritant Highly flammable	R11-36-66-67 S2-7/9-16-26-46	-
O 22	Irritant Highly flammable	R11-38-67 S2-16-23-29-46-51	3-1
O 25 ⁶	Irritant	R36/37/38-43 S2-26-28-37/39-46	-

Epoxy resin and isocyanates may cause allergic skin irritations and eczema. Therefore regulations have been laid down implying that professionals must have a special training before working with these types of adhesives. The training is offered at schools for semi-skilled workers. The Danish legislation is described in:

- Appendix 2 in the Statutory order on Classification and Labelling. No. 1065 of September 30, 2000.
- Arbejdsministeriets bekendtgørelse nr. 199 af 26. marts 1985 om epoxyharpikser og isocyanater m.v., som ændret ved Arbejdstilsynets bekendtgørelse. No. 779 of October 15, 1999.
- At-meddelelse. Nr. 3.01.3. Juni 1988. Erstatte januar 1986. Epoxyharpikser og isocyanater.
- At-VEJLEDNING C.0.2. January 2001. Sekundær udsættelse for isocyanater

⁶ Is UV-hardening.

Several of the purchased adhesives contain epoxy resins or isocyanates. In these cases it is mentioned on the material safety data sheet that there are regulations implying that a special training is needed before using the adhesives professionally. The same adhesives can be purchased for personal use.

3.2.2 CE-labelled products

The CE-label states that the product complies with a European standard. The manufacturer or the importer applies the label on their products. It informs the user that the product fulfils the European legislation on demands on safety, adapted for the type of product in question. Adhesives, which form an integrated part of toy sets or are recommended for specific toys must fulfil the demands on safety for toys. These demands are implemented in the "Statutory order on toys" and appendix 3 of this statutory order.

Especially, the regulations on chemical properties are relevant of adhesives. The regulations indicate that when using the adhesive may not cause a health risk for the user such as damages due to ingestion, inhalation or contact with the skin, mucous membranes or eyes. The adhesives must not contain dangerous substances. Furthermore, there are demands on a maximum level on bioavailability for different heavy metals per day according to CEN-standard no. EN71-3 listed in appendix 3 of the statutory order on toys.

There are six CE-labelled adhesives among the registered adhesives. Two of the six adhesives are labelled with a warning that only children from the age of three may use the adhesive. Four of the labelled adhesives are "school glues", and the two adhesives above-mentioned with the warnings are in the same group of adhesives. The remaining two CE-labelled adhesives are glue sticks. One of the CE-labelled glue sticks is labelled on the packaging not on the product. The CE-label is mentioned on the material safety data sheet and the product information

3.2.3 The Joint Council for Creative and Hobby Materials

The Joint Council for Creative and Hobby Materials is a union of companies that purchase, market, manufacture or import creative and hobby materials.

The council has made a number of criteria for creative and hobby materials to ensure that the materials do not unnecessarily affect the health and prosperity of children as well as the environment in general. At the same time the criteria ensure a solid foundation on which to evaluate and compare the existing products.

The criteria imply among others that for each product there must be prepared a Danish Material Safety Data Sheet in accordance with the regulations of the National Working Environment Authority.

The products are categorised into one of the four categories (A, B, C or D). According to the criteria, the grading in categories can be found store shelves, in catalogues and other materials related to creative and hobby materials. The guidelines for understanding the four categories are shown in Table 3.22.

TABLE 3.22 THE CRITERIA OF THE JOINT COUNCIL FOR CREATIVE AND HOBBY MATERIALS (FFFH)

Category	Interpretation
A	May be used by children from the age of three. The product complies with the strict safety criteria of the FFFH.
B	May be used by children from the age of 3 under the supervision of an adult. The content of hazardous substances is extremely low. Yet, the product does not comply with the strict criteria of the FFFH.
C	May not be used by children under the age of 15. The product neither comply with the Toy Directive (EU Regulation) nor with the criteria of the FFFH.
D	May only be used by adults. The product is labelled with a danger symbol.

Of all the collected adhesives four have been assessed according to the current criteria for labelling the products in category A. The adhesives in question are two paper glues (BI8 and BI1), one glue stick (BI2) and one wood adhesive (HN2). The labelling appears in all cases on the material safety data sheet and/or on the product information sheet. There is no labelling on the packaging.

There is no information on any of the collected adhesives implying that the adhesive can be categorised in one of the other categories (B, C or D).

3.2.4 Environmental labelling

The Nordic Environmental Labelling Scheme, the Swan, has made criteria for adhesives. The product group includes adhesives for hobby, creative, office and professional purposes.

In the criteria document of the Swan the following demands are 1. The general properties, and 2. The chemical composition.

1. According to the general criteria an eco-labelled adhesive may not be classified as harmful, oxidising, explosive or dangerous for the environment. Besides, there is a maximum limit for the content of different classified substances.
2. According to the criteria document for the chemical substances an eco-labelled adhesive may not contain.
 - Phthalates
 - Alkyl phenoethoxylates
 - Alkyl phenols
 - Halogenated solvents

None of the collected adhesives carry an eco-label.

4 Physical-chemical analysis

Concurrently with the retrieval of data on the purchased adhesives physical-chemical analyses have been made, partly as opening screening analyses and partly as detail analyses as a follow-up on the screening. In the phase of screening as well as in the following-up phase chromatographic and spectroscopic methods have been used. Therefore the results from both phases are dealt with in the present chapter.

The selected screening analyses have been made up of the type of adhesive and the information retrieved from the manufacturers and importers.

As for water-based hobby adhesives and for those based on solvents the determination of the content of solid materials has been made by simple evaporation of the dilution medium. For the types of adhesives based on solvents it gives unit of measurement for the quantity of volatile solvents and the compounds.

The infrared spectroscopic (FTIR) characterisation of the adhesives has taken place after evaporation of the dilution medium of either water or organic solvents. When using the infra red analysis method it is possible to an identification of the type of adhesive and in some cases an identification of the added plasticizing agents. As for types of adhesives that are not diluted the FTIR-analysis has been made directly on the adhesive.

For two-component adhesives the characterisation has been made on the adhesive as well as on the hardening agent.

Furthermore, an element analysis has been made using x-ray detection screening following the same procedure as described for the FTIR-analysis. When using this type of analysis the presence of possible heavy metals or other relevant elements, e.g. chlorine is determined. The method does not bring forward information on the type of chemical compound in which the element appears.

For the adhesives based on solvents a gas chromatographic/mass spectrometric (GC/MS) screening on the composition of the solvent has been made. The same method has been used in the following special analyses.

The selected water-based hobby adhesives have been screened for the presence of formaldehyde, added as a preservative agent, by using a high-pressure liquid chromatographic analysis. The analysis is carried out after extraction and derivation.

An analysis for detection of phthalate plasticizing agents has been made on the adhesives if the screening analysis has indicated the presence of this type of plasticizing agents or in the types of adhesives in which this type of agents is normally used (PVA-wood adhesives).

4.1 ANALYSIS METHODS

In the present section the used analysis methods are described.

Detection limits for the different analysis methods are very dependent on types of compounds that have to be analysed, interfering components, and the method that has been used. In Table 4.1 the empirical and typical detection limits for the used analyses are shown.

TABLE 4.1 DETECTION LIMITS BASED ON EXPERIENCE

Substance	Detection limit	Uncertainty % rel.
Organic compounds by GC/MS	0,001 W/V%	10
Element analysis by X-ray analysis	0,0005 W/W%	10
Formaldehyde by HPLC	0,0001 W/W%	10
Phthalates	0,2-1 µg/g	10
Isocyanates	0,1 W/W%	-

4.1.1 Determination of the content of dry matter

A solid material is determined by evaporation of the solvents at 45°C for 24 hours. Then all water-based adhesives have been tried for another 24 hours at 105°C. The test quantity was between 10-50 g before evaporation.

4.1.2 FTIR analysis

The samples of the adhesives have been dehydrated at 50°C and grinded to powder with potassium bromide. The analysis has been made using a Nicolet Magna 550 Fourier Transform Infrared spectrometer by screening the potassium bromide tablet.

4.1.3 X-ray analysis

The analysis has been made on a wavelength-dispersive Phillips PV 2400 instrument. The analysis has been made directly on the sample of adhesive without any pre-treatment. The instrument immediately prints out the total composition of elements of the sample.

4.1.4 Gas chromatography at mass spectrometric detection

4.1.4.1 Headspace analysis

The method is in principle as follows: The sample of the adhesive is weighed in a vial with Teflon coated cap and is then heated up till 45°C for an hour. Then a gas sample is taken using a gas tight syringe, which is analysed using a capillary gas chromatography combined with a mass spectrometry.

4.1.4.2 Other GC/MS analysis

The analyses of phthalates have been made by using extraction with dichloromethane and with an added deuterium marked internal standard of dibutyl phthalate – d4. The extraction took place by an hour's extraction using ultrasound. The extracts were analysed by using a capillary gas chromatography combined with a mass spectrometry in scan-mode (GC/MS-scan). The uncertainty is evaluated to be 10% at the maximum at concentrations larger than five times the detection limit.

The analyses of isocyanates have been made a sample of the adhesive diluted in 10% methanol in dichlormethane. The solution was analysed by using GC-MS at a HP 5890 II/MS 5971 instrument and by using a CP-Sil 5CB, 0,25 mm ID column with 0,25 µm thickness of the stationary phase coat.

4.1.4.3 High pressure liquid chromatographic (HPLC) analysis for formaldehyde

The HPLC analysis for formaldehyde was made on a HP 1100 instrument with a diodearray detector. The analysis was made after conversion of formaldehyde to a dinitrophenylhydrazone derivate.

The separation took place on a RP 18 column, 25 cm × 4.6 mm.

As a mobile phase a tetrahydrofuran, acetonitrile and water gradient has been used.

The detection wave-length 360 nm.

Extracting the adhesive with dichlormethane and heptane in ratio 30/70 after derivatising carried out the sample preparation. The extract was rinsed for chloride and the solution was dehydrated at a rotation evaporator. After the evaporation of the adhesive the remains were dissolved in 96% alcohol and injected on the chromatography.

4.2 ANALYSIS RESULTS AND COMMENTS

In the present section the results of the various analyses are discussed. The analysis results from the screening and the detail analyses are discussed collectively.

4.2.1 Infrared spectroscopic analysis (FTIR)

During the first screening an FTIR-analysis has been made on a selection of the adhesives from the groups spray adhesives and adhesives for special purposes.

During the following detail analysis another two adhesives were analysed: M2, because the X-ray analysis indicated a high content of chlorine, O23, because the X-ray analysis indicated a high content of sulphur. The FTIR-analyses did, however, not give an indication of the presence of the detected elements. However, in the first analysis the chlorine in question was not chlorinated hydrocarbons and the sulphur may be derived from a hardening system based on mercapto, which is typically used at "five minutes epoxy adhesives" to obtain a quick hardening.

In the second phase BI1, HN3 and HN4 were FTIR analysed, too. The results for the contact adhesives showed that one of the types (HN3) is based on chloroprene and the other transparent type (HN4) is based on poly(vinylacetate).

In general, the FTIR-analysis corresponds very well with the information retrieved from the manufacturer/supplier. In a few cases the information is not in accordance with the analysis and that is the adhesives with a complex composition. In one of the cases the adhesive was assessed to be an adhesive based on polyurethane. However, the adhesive was based on epoxy and on ketonealdehyde resin. In another case the FTIR-analysis implies the adhesive is based on polyvinylalcohol, but the supplier informs that the adhesive is polyvinylacetate. However, the transition is stepwise from polyvinylacetate to polyvinylalcohol depending on the degree of acetylation.

In cases where the manufacturer or the supplier has not informed about the composition of the adhesive components, the FTIR-analysis suggests the composition of the adhesive.

TABLE 4.2 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF TEXTILE ADHESIVES

No	Content	Basis	FTIR
HH 7	Water-based	Natural rubber latex	Mixture of e.g. poly(isoprene)

TABLE 4.3 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF "SCHOOL GLUES"

No	Content	Basis	FTIR
O 17	Water 40%-50%, Polyvinylacetate 40%-50%, diisobutyl phthalate 5%-10%, Polyvinyl alcohol 1%-5%	Polyvinyl acetate	Mixture of (polyvinyl acetate copolymer)
BI 8	Water-based, no duty to disclose all material facts on the substances	Polyvinyl acetate	Polyvinyl acetate
HH 6	Water 30%-60%, Benzyl alcohol 1%-5%,	Vinylacetate maleic acid copolymer	Poly(vinyl acetate)
BI 1	Water-based. no duty to disclose all material facts on the substances	Polyvinyl acetate	Polyvinyl alcohol

TABLE 4.4 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF GLUE STICKS

No	Content	Basis	FTIR
BI 2	No duty to disclose all material facts on the substances	No information	Suggests contents of glycyglycin
O 13	Water 54%-60%, glycerine 8%-15%, N-Vinylpyrrolidinone Polymer 14%-19%, Acryle Copolymer 7%-11%, 2-Amino-2-Methyl-1-Propanol 0,75%-1,25%	No information	Suggests contents of glycyglycin

TABLE 4.5 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF PLASTIC ADHESIVES

No	Content	Basis	FTIR
M 2	Acetone >30% ethylacetate >30%, butanone >10%, Bisphenol-A-diglycidylether <1%	Epoxy 0.2%	Acryllatex
O 8 Activator	Heptanes kelator	(Activator)	CH ₂ - and CH ₃ -groups
O 8 Adhesive	Ethyl cyanoacrylate 65%-95%	Cyanoacrylate	Poly(ethyl-cyanoacrylate)
S 4	Butyl acetate >50%, Solvent-naphtha light aromatic 5% Acetone < 40%,	Epoxy resin	Poly(methyl-methacrylate)

TABLE 4.6 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF VINYL ADHESIVES

No	Content	Basis	FTIR
BH 4	Acetone 30% -60 % Ethylacetate 10% - 30%	Vinyllic adhesive	Suggests contents of polyurethane

			adhesive
BH 3	Tetrahydrofuran 60%-100% metylethyl ketone 5%-10%	Vinyllic adhesive	PVC with phthalate plasticizer

TABLE 4.7 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF WOOD ADHESIVES

No	Content	Basis	FTIR
O 21	Butyl diglycol acetate 2,5%-10%	EVA/acrylic ester (product sheet) Acrylic-copolymer dispersion adhesive (material safety data sheet)	Acrylic latex
HN 2	Water-based, no duty to disclose all material facts on the substances	PVAc dispersion	Primarily Poly(vinyl-acetate)
O 12	Water-based 2-methoxy-1-metyletylacetate Polyvinylacetate	PVAc	Poly(vinyl-acetate)
O 19	Butyl diglycol acetate <2,5%	Polyvinylacetate dispersion	Poly(vinyl-acetate)
O 20	Butyl diglycol acetate <2,5%	Polyvinylacetate dispersion	Poly(vinyl-acetate)
HN 1	(No solvents) Isocyanates (4,4'-Diphenylmethandiisocyanat, mixture of isomers)	Polyurethane one-component, moisture cure	Polyether urethane

TABLE 4.8 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF HOBBY ADHESIVES

No	Content	Basis	FTIR
BI 6	Acetone >20%, naphtha 1%-5% cellulose nitrate 10%-15% butyl acetate 1%-5% n-butanol 1% -5% ethanol 5%-10%	Cellulose adhesive	Mixture of among others polyvinyl acetate
O 5	No solvents	No information	Mixture of poly(ethyl acrylate)
O 29	Water-based	Vinylacetatethene copolymer	Poly(vinyl-acetate)
M 1	Acetone >25% ethyl acetate >40% solvent naphtha<5%	Epoxy <1% ketone aldehyde resin 50% in ethyl acetone)<5%	Polyester urethane

TABLE 4.9 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF CONTACT ADHESIVES

No	Content	Basis	FTIR
S 1	Acetone, butyl acetate, ethyl acetate		Mixture of among others acrylic

O 28	Technical grade heptane 25%-50%, Ethyl acetate 25%-50%, Toluene 2,5%-10%	Polychloroprene	Mixture of poly(chloroprene)
S 5	Methyl acetate >60%, Butyl acetate >5%, ethanol		Suggests contents of cellulose nitrate
HN 4	Ethyl acetate >20 %	Polyurethane one-component	Poly(vinylacetate)
HN 3	Toluene>20%, ethyl acetate <20%, naphtha >20%	Polychloroprene (neoprene)	Polychloroprene

TABLE 4.10 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF TWO-COMPONENT ADHESIVES

No	Content	Basis	FTIR
BH 6	4,4-Isopropylidendiphenol-Epichlorohydrin Copolymer 70%-82%, Bisphenol-F-diglycidylether 4%-10%, epoxy compounds	epoxy	Adhesive: Epoxy bisphenol-A
BH 6	N-3-dimethylaminopropyl)-1,3-propylendiamin 5%-10%		Hardening agent: Polyaminamide (the aliphatic agent)
O 23	Alkylaminophenol aminoester		A: Poly(propyleneoxid)aminoether
O 23	Epoxy resin		B: Bisphenol A epoxy resin
O 24	N-(3-dimethylaminopropyl)-1,3-propylendiamin 2,5%-10%		Aliphatic amidamine
O 24	Epoxy resin, 2,2-bis(p-(2,3-epoxypropoxy)phenyl)propan 50%-100%, Bisphenol-F-diglycidylether 2,5%.10%	Low- molecular epoxy resin	Epoxy, bisphenol-A

TABLE 4.11 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF ADHESIVE PISTOLS

No	Content	Basis	FTIR
HH 4	No information	Melt adhesive	Poly(ethylen-ethylenvinylacetate)copolymer

TABLE 4.12 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF SUPER GLUES

No	Content	Basis	FTIR
O 16	Ethyl-2-cyanoacrylate 90%-100%, Poly(methyl methacrylate) 1%-10% Hydroquinone <1%	Cyanoacrylate	Poly(ethylcyanoacrylate)
O 27	Ethyl-2-cyanoacrylate 50%-100%	Ethylcyanoacrylate	Poly(ethylcyanoacrylate)
M 3	Ethyl-2-cyanoacrylate 60%-95%	Cyanoacrylate	Poly(ethylcyanoacrylate)

TABLE 4.13 FTIR-RESULTS COMPARED WITH THE INFORMATION FROM THE MATERIAL SAFETY DATA SHEET OF SPRAY ADHESIVES

No	Content	Basis	FTIR
HH 1	Butane, Propane, Acryl-resin, Dimethoxymethane		Mixture of poly(butadien-methylmethacry-

			late)
S 3	Petroleum destillate, cyclohexane 10%-20% propane 10%-20% naphtha 20%-40% dimethyl ether 10%-20% synthetic rubber 5%-10% isobutane 1%-5% isopentane 1%-3%	Epoxy 0,2%	Mixture of poly(isobutene)
O 9	No content of classified substances above the triviality limit		Poly(styrene acrylester) with calcium carbonate

4.2.2 Analysis for the content of dry matter

The content of solid materials has been tested in 22 adhesives. The purpose of the analyses has been to measure the content of solvents. On this basis 22 adhesives have been selected representing all types of adhesives except glue sticks, spray pistol, super glues, spray adhesives and adhesives for special purposes. The surface primers have not been tested for their content of solid materials. The results are shown in Table 4.14.

The content of solid materials in the adhesives varied from 17% to 100%.

In the following samples the content of solid materials was measured to be 100%: BH6, O24 (epoxy adhesive and aliphatic amidamine), O8 (ethylcyanoacrylate) and HN1. The four samples, in which the content of solid materials was measured to be 100%, correspond with the material safety data sheets of the suppliers. They have all stated that there are not solvents in the adhesives.

TABLE 4.14 RESULTS OF THE ANALYSIS OF SOLID MATERIALS

Type of glue	Adhesive	Content of solid materials
Two-component, hardening agent	O 24	99,6%
Two-component, adhesive	O 24	100%
Two-component	BH 6	100%
Contact adhesive	S 1	21,3%
Contact adhesive	O28	24,9%
Contact adhesive	HN 3	25,5%
Contact adhesive	S 5	35,8%
Plastic adhesive	M 2	22,4%
Plastic adhesive	O 8	100%
"School glue"	O 4	42,3%
"School glue"	HH 6	50,5%
"School glue"	O 17	69,7%
Textile adhesive	HH 7	67,6%
Wood adhesive	O 20	47,1%
Wood adhesive	O 12	47,8%
Wood adhesive	HN 1	98,7%
Hobby adhesive	BI 6	24,3%
Hobby adhesive	M 1	26,2%

Hobby adhesive	O 5	34,0%
Hobby adhesive	O29	58,0%
Vinyl adhesive	BH 3	17,1%
Vinyl adhesive	BH 4	21,8%

4.2.3 GC/MS analyses

GC/MS analyses have been made in the screening phase on a large variety of the collected adhesives to screen the adhesives for the content of volatile compounds that is solvents, monomers and plasticizers.

In the special analysis phase the water-based wood adhesives and a vinyl adhesive have also been tested for the content of phthalate plasticizers.

The analyses have been made on the following types of adhesives: Hobby adhesives, contact adhesives, spray adhesives, plastic adhesives, vinyl adhesives, super glues, adhesives for special purposes, and wood adhesives.

4.2.3.1 Hobby adhesives

The three analysed adhesives for general purposes are all based on solvents. When analysing the adhesives the main components correspond with the information given by the supplier. Besides, other volatile compounds are detected in small quantities. The tested hobby adhesives contain aromatic hydrocarbons, either in the presence of toluene or due to the use of naphtha as diluent. All the adhesives contain aliphatic hydrocarbons and acetone.

4.2.3.2 Contact adhesives

In total, six contact adhesives have been tested by a GC/MS-analysis. The content of solid materials in these adhesives is typically 20%-35%. All the tested contact adhesives contain substances that are on the Danish EPA's list of undesirable substances. The substances in question are aromatic hydrocarbons, cyclohexane and heptane. Besides these solvents other solvents such as acetone and aliphatic esters etc. have been detected, depending on the product.

4.2.3.3 Spray adhesives

Four spray glues have been tested by GC/MS-analyses. In S3 a content of aliphatic hydrocarbons has been detected. According to the material safety data sheet from the supplier there are other solvents in the product among others cyclohexane, which has not been specified at the GC/MS-analysis. The manufacturer has in written on the label of the product that the adhesive must only be purchased for professional use.

In HH1 hexane and toluene have been detected as a part of a mixture of solvents.

In O9 consists a complex mixture of solvents inter alia components of aromatic hydrocarbons. The material safety data for O9 does not bring forward information of chemical ingredients, but only that the substances are below the triviality limit and shall therefore not be classified.

In O11 a content of hexane and toluene has been detected among others. These substances are not mentioned in the material safety data sheet.

4.2.3.4 Plastic adhesives

In the O8-Activator main components are C₅-C₈ aliphatic hydrocarbons. The content of hexane is 0,1%. In the adhesive the content of acrylic ester has been detected (methylmetaacrylate). According to the material safety data sheet of the supplier it is a cyanoacrylate adhesive.

In M2 the content of solvents corresponds with the information from the supplier that is that the content of solvents is primarily acetone, ethyl acetate and 2-butanone.

4.2.3.5 Vinyl adhesives

Both the purchased vinyl adhesives are tested by GC/MS. Vinyl adhesives are especially used for join surfaces of PVC. The main component in BH3 is tetrahydrofuran. The FTIR-analysis also indicates that the adhesive consists of phthalate. As for BH4 the main components and solvents acetone and ethyl acetate. Both results correspond with the information on the material safety data sheet of the supplier. The FTIR-analysis indicates a polyurethane binding agent.

4.2.3.6 Super glues

At the headspace analysis the content of methylmethacrylate has been detected in the two tested super glues O27 and M3. However, according to the material safety data sheet the main component is ethylcyanoacrylate in both adhesives.

4.2.3.7 Adhesives for special purposes

One of the adhesives in the group of adhesives for special purposes has been tested by GC/MS. The adhesive in question is HN5, which is a polyvinyl acetate adhesive based on solvent. The analysis shows that the main content of solvents in the adhesives is acetone. Besides, there is a content of toluene and ethyl acetate as well as vinyl acetate. According to the material safety data sheet of the supplier the adhesive contains acetone, cellulose nitrate and ethanol.

4.2.4 Analysis results for phthalates

In total, five adhesives, four wood adhesives and one vinyllic adhesive, have been analysed for the content of phthalates. The vinyllic adhesive, BH3, was analysed because the FTIR-analysis indicated a content of PVC with phthalate plasticizers. In three samples from the other adhesives phthalates were detected either in the shape of diisobutyl phthalate or diethylhexyl phthalate. The results are shown in Table 4.15.

TABLE 4.15 ANALYSIS RESULTS OF ADHESIVE SAMPLES FOR CONTENT OF PHTHALATES IN µG/G

Adhesive	BH3	HN2	O12	O19	O20
Diethylphthalate	-	-	-	-	-
Diisobutyl-phthalate	-	2,3	17,200	-	-
Dibutylphthalate	-	-	-	-	-
Butyl 2-ethylhexyl-phthalate	34	-	-	-	-
Diethylhexyl-phthalate	87,300	-	-	-	16,000

Diethylphthalate	-	-	-	-	-
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" - ": Not detected – detection limit 0,2-1 µg/g (0,00002 – 0,0001 %)

4.2.5 Analyses for a content of formaldehyde and acetaldehyde

Five of the adhesives have been analysed for the content of formaldehyde. The detection limit is 1.0 mg/l. Formaldehyde was found in all five adhesives and in three of them there was also detected a content of acetaldehyde. As the highest content of formaldehyde is detected in the wood adhesive for outdoor purposes, it is judged to be due to the fact that formaldehyde can be used as a kind of preservative against microbial growth.

TABLE 4.16 ANALYSIS RESULTS OF GLUE SAMPLES FOR CONTENT OF FORMALDEHYDE

Adhesive	Formaldehyde (mg/kg)	Acetaldehyde (mg/kg)	Comments
"school glue" (O 4)	2,1	-	Polyvinyl-acetate
Glue stick (O 13)	3,4	-	Water-based
"school glue" (O 17)	2,4	About 250	
Wood adhesive (outdoors) (O 19)	1.600	About 480	
Wood adhesive (indoors) (O 20)	22	About 640	

A low content of formaldehyde has been detected in BI8, O13, O17 and O20. However, a higher content of formaldehyde, 0.16%, has been detected in O19.

A content of acetaldehyde of 0.05% has been detected in O19 and O20 indoor and a content of acetaldehyde of 0.025% in O17.

4.2.6 Analysis for Isocyanates

Analyses have been carried out for isocyanates in two adhesives, one wood adhesive and one hobby adhesive.

A content of isomers of Diphenylmethan-diisocyanates (MDI) has been detected in the wood adhesive (HN1). The detection corresponds with the supplier's information on the material safety data sheet. MDI is on the Danish EPA's list of undesirable substances.

The GC/MS analysis did not detect any remains of isocyanates M1 although the FTIR-screening analysis indicated it was a polyurethane adhesive. The result from the GC/MS analysis therefore corresponds with the material safety data sheet from the supplier who informs that the product is an epoxy resin mixed with a ketone aldehyde resin. The content of C9- to C11- aromatic compounds corresponds with the information of the supplier on the content of light aromatic solvent naphtha.

4.2.7 X-ray analysis

In the first phase x-ray analyses were made on 11 of adhesives. The adhesives were transversely selected to make sure that all the groups of adhesives are represented. In addition another x-ray analysis was made after the screening analyses. An extra analysis was made on a vinyl adhesive, in which polyvinyl chloride was detected when using the FTIR-analysis.

A content of lead was detected in several of the products, however, detection values are low; 20 mg/kg is the highest detection value.

A high content of chlorine has been detected in the B3, which corresponds with the FTIR-analysis indicating a content of PVC.

In S4, a plastic adhesive, a high content of chlorine has been detected (15 g/kg or 1.5% chlorine). The content of chlorine does neither correspond with the information from the supplier nor the executed analyses.

In the 2-component adhesive, O23, a high content of sulphur of 14% has been detected. There is no immediate relation between this relative high sulphur content and the information from the supplier. It is likely though that the sulphur is added as a mercaptane, because this type of sulphur compounds accelerates the curing of epoxy.

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