Survey of Chemical Substances in Consumer Products

Survey no. 38, 2004

Survey and liberation of chemical substances in joint sealants

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Content

Preface

The project “Survey and liberation of chemical substances in joint sealants” has been carried out for the Environmental Protection Agency during the period 1 July 2002 till 1 December 2002. This report describes the achieved results.

The project has been carried out by the Danish Technological Institute, Environmental Division in cooperation with Plastic Technology, Industrial Division. The project leader for the Technological Institute has been lic.scient in Chemistry Nils H. Nilsson, Environmental Division. The project leader has functioned as contact person at the Technological Institute to the Environmental Protection Agency.

The laboratory analyses of the joint sealants carried out in cooperation with the Chemical Technology and the Plastic Technology’s laboratories in Taastrup. Paul Lyck Hansen, Chemical Technology, Århus has been professional responsible and he coordinated for the screening analyses, quantitative analyses and exposure experiments, where the laboratory measured for liberation of organic volatiles. Ivan Christensen, Chemistry Technology has been responsible for the screening analyses at X-ray analysis. Søren Pedersen, Plastic laboratory has been responsible for the infrared spectroscopic screening analyses.

The project leader has been responsible for the consumer surveys at interviews in the building markets. Student Pernille Hoffmann has been assisting at the interviews.

The pursuing group has consisted of Anette Ejersted, the Environmental Protection Agency (leader) and Shima Dobel, the Environmental Protection Agency and Nils H. Nilsson, the Danish Technological Institute.

The aim of the project has been to examine which problematic substances occur in the different joint sealants which exist in the retail business at the Danish market. Furthermore it has been the aim to carry out a survey of the consumption on a yearly basis by the do-it-yourself people, and illustrate to what extent the consumers know the marking of the products, including danger symbols and code numbers. Finally it has been the aim to illustrate which exposure for problematic substances that takes place at the consumer stage and when using indoor. The project includes three main phases: A screening phase, a phase where the knowledge for marking was revealed, and a phase where exposure experiments were carried out.

The project did not include a total examination of the marking of all the products. The Danish EPA will subsequently follow up on the marking on the products if this does not fully live up to the demands in the laws.

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

The importer of products no. 6 and 7 has stated that they have changed supplier so the information in this report are no longer up-to-date regarding

these products. Likewise has the importer of product 53 stated that they have chanced supplier and that they no longer sell sealants, which contains chloroorganic compounds.

Summary

The Technological Institute has on behalf on the Environmental Protection Agency by shopping in the retail business collected a large assortment of joint sealants that can be bought by the consumers.

Totally there have been collected 53 different types of joint sealants by shopping at building markets, a paint dealer, a low cost supermarket, a whole sale society (LIC) and a ship´s provision shop. Subsequently the joint sealants have been put in 7 groups after their chemical composition.

As a beginning there has been carried out a number of screening analyses on a typical segment of the collected joint sealants. After this, there has been carried out quantitative analyses, as a result of the information from the screening analyses, and the information collected from the producers or importers of the joint sealants. Finally, there has been carried out exposure experiments with joint foam and silicone joint sealant, in an environment close to practical relations. The emissions in these samples have been measured by personal carried monitoring. The analysis methods that have been used when examining the joint sealants have been based on chromatographic and spectroscopic methods.

The joint sealants have first been examined by X-ray analysis. This screening is carried out in 2 steps. First 18 products were screened. On the basis of the results from this and the product sheets further 2 analyses were carried out.

After this, in the screening phase there has been carried out an infrared spectroscopic analysis of the joint sealant types from a typical extract of the samples. By this method you can achieve a finger-print of the joint sealants. In some occasions you can achieve information about presence of plasticisers in the joint sealants – for example phthalates.

The infrared analysis can give some information about the joint sealant type in the cases, where it is not informed by the supplier.

A typical section of the joint sealants have been screened gas chromatographic /mass spectrometric (GC/MS) or with flame ionisation detection (FID). These techniques have been used both in the screening phase and in the following phase, where they have analysed for specific substances quantitatively. By these analysis techniques you can analyse the composition of volatiles in the examined joint sealants, and achieve a precise description of the composition. It is also possible to decide content of plasticisers in the joint sealants by this technique, if they have some certain volatility. That includes among others phthalate plasticisers and chlorine paraffins.

Certain joint sealants have been analysed by high-pressure fluid chromatography for their content of formaldehyde and acetaldehyde. That has been the case for samples, where it has been stated that fungus and bacteria killing additives have been added. The method is very specific and sensitive to aldehydes and ketones.

Below this is a short summing up of the results of studying the text on the joint sealants, as they are available in the retail trade and on the collected information in the form of product sheets or safety sheets and the performed analyses and exposure samples.

To get further information on joint sealant type and composition, it is necessary to study either product sheet or safety sheet for the joint sealant.

The infrared spectroscopic analysis showed presence of phthalate plasticisers in one of the purchased acrylic joint sealants and an isocyanine-based joint sealant. There has not been found phthalate plasticisers in four examined MS polymeric-based joint sealants. For one single joint sealant, where it did not appear from the packaging on which basis it was, the infrared analysis showed that it was an acrylic type.

The screening at X-ray technique for elements with atomic weight larger than the weight of fluorine showed that the content of heavy metals in all the examined joint sealants was very low. There has been found chlorine as an element in amounts of 2.4-4.2% in two samples of joint foam and one sample of joint sealant, all three on isocyanate basis. At the gas chromatographic mass spectroscopic analysis it turned out that it is chlorine paraffins. There has been found presence of tin in seven examined samples. The sample that had the largest amount has been examined at GC/MS. Tin turned out to be as dibutyltine in this sample.

In a vegetable oil-based sample cobalt has been found. It is known that cobalt is used in siccatives for this type of joint sealants.

At the gas chromatographic screening analysis for solvents on 14 selected samples within all types of joint sealants, there has been found solvents or propellants. For the silicone and acrylic-based joint sealants it is lower alcohols or acetone that comes forward. For the bitumen/rubber-based types there are larger amounts of turpentine comparable connections, and xylenes. In the vegetable oil-based samples you can find heavy hydrocarbons among others. In two acrylic-based samples phthalate plasticisers have been found. The same can be seen in a silanterinated polyolic (MS)-polymeric-based type. The content has later been defined quantitatively. In one acrylic joint sealant it is a matter about 3% dibutyle phthalate, and in the other it is about 16% diisononyle phthalate.

In the MS-polymer joint sealant there has been measured 32% diisodecyle phthalate and 4% diethylhexyle phthalate (DEHP). In two joint foams there has been found presence of chlorine paraffins. The content has been measured at respectively 5 and 9%. It is estimated from the retention times that it is intermediate chained types. In one of the bitumen-based samples there has been detected nonylphenoles in an amount of 8%.

For one of the isocyanate-based polyurethane foams there has been found diphenylmetan 4.4 diisocyanate (MDI) in accordance with the producer information on the safety data sheet.

An analysis for formaldehyde in 4 silicone joint sealants and one acrylic joint sealant at high-pressure fluid chromatoghraphic showed a low content of formaldehyde and acetaldehyde in five examined samples, so it can be concluded that these samples are not conserved with formaldehyde-based

preservatives. For two samples of silicone joint sealants a high content of a material with retentions time as butanal was found. It has later been stated that it comes from bunanon-2-oxim. The analysis indicates a potential for liberation of butanon-2-oxim close to 10%. Butanon-2-oxim is first formed during the cure of the joint sealants, and can only be found in very small quantities in the actual product (few milligrammes per kg).

It must be concluded that a numberof the examined joint sealants contain chemical substances that are on the signal list of unwanted substances from the Environmental Protection Agency. //3//

In supplement to the chemical analyses that have been carried out, the Technological Institute has made a questionnaire survey in two building markets for painter materials. The aim has been to investigate the consumer's knowledge of classification of painter materials and danger labelling, consumer pattern and information in relation to the environment, both the external and the working hygienic conditions. At the same time the consumption of joint sealants to the "do-it-yourself" activities has been searched. From the survey it must be concluded that there in average are bought approx. 2 joint sealants per "do-it-yourself" people per year. But the bargains are unequally divided, since one of the 59 interviewed persons had bought 150 joint sealant patrons. The Joint Trade Cooperation and Information Council estimate that the consumption is equally divided between professionals and people that use joint sealants on amateur basis. The total consumption of joint sealants is in the order of 6.000 – 8.000 t.

It appears from the survey that environmental considerations take a part for choice of painter materials for far the greater part of the consumers. Most consumers also read the information on the packaging about the right use of new types of painter materials, which they have not tried before, and the information about cleaning of tools. Besides the packaging, the personnel in the shop are the most important information source you can use if you need advice. The Internet is another information source, but not near as important in the answers.

There are used comparatively rare protective measures, yet some say they use gloves during the work.

As regards the disposal it appears that the local recycling sites are used a lot. No one would throw away painter materials in other ways than delivery at these stations.

As regards the marking knowledge almost everybody knows the common danger symbols and the interviewed persons thought that the symbols are very illustrative in an easily understood way. Considering the safety and risk sentences this is an unknown term for most people. This survey has included a limited amount of consumers, and it is hard to conclude anything specific about whether men or women differentiates essentially in their knowledge of painter materials or in their environmental conscience. It is differently with the code numbers. Proportionally a lot, approx. half of the interviewed answered that they know the codes. But when asked more specific only a few knew the meaning of the numbers before and after the hyphen. Still, many answer that a low number is good.

1 Introduction

A lot of the joint sealants that are used professional in the building industry can also be bought in shops, which applies to the “do-it-yourself” people, i.e. building markets, department stores, paint shops and ship’s provisions shops.

This project defines a joint sealant as a product that can be bought by the consumers in the retail business for do-it-yourself-activities in the home, with the purpose to fill up a gap between firm materials, so that a flexible tightening between the materials are done by means of the joint.

Joint sealants can be divided in different ways after hardening mechanism, field of application and chemical composition.

Joint sealants that are sold to the consumers appear only as single-component types. Most often the joint sealant is packed as a cartridge that is to be put in a cartridge feeder. It works by means of a mechanism by a hand-operated push and then the bolt is pushed forward in the cartridge and thereby the joint sealant is dosed through a pointed nozzle. Joint foam is dosed differently, from a pressure tank on which is mounted a nozzle. As propellant gas is typically used dimethyl ether, propane and butane gas. The packaging serves also as a protection of the product against drying out and moisture, to preserve the product’s capability of functioning, and avoid a polymerisation of the mass before use. Finally the outer of the packaging is used to give useful information about the type of the joint sealant, the correct use and sphere of application, the hardening progress and information on danger factors, Code number, etc.

Hardening of the joint sealant is first of all done by means of the moisture from the air. To the oil-based joint sealants the hardening mechanism can be an oxidation of the surface. Often a membrane is formed at the outside, because of the direct contact to the moisture of the air or oxygen. After this a finishing hardening of the joint is happening, as moisture or oxygen diffuses through the joint. The evaporation of joint sealants that contain solvents also influences on the hardening progress. Finally the water dispersing joint sealants, for example on acrylic basis, depend on the evaporation of the aqueous dispersing preparation.

The most commonly used joint sealants are:

- Silicone joint sealants
- Acrylic-based joint sealants
- Polyurethane-based (PUR) joint foam and – masses
- Oil-based joint sealants
- High elastic hybrid joint sealants (Silantermineret polyol(MS-polymeric))

The silicone joint sealants are some of the most used joint sealants. They appear in a lot of qualities, dependent on the use. There are types specifically for wet surroundings. These are usually stabilised with a biocide. Other types are specifically restraining on flames. The silicone joint sealants are built up of

silicon-oxide polymeric chains, which have been substituted with organic radicals; typically methyl or methyl and phenyl.

The process of polymerisation can be very complex, and during the hardening volatiles are formed, which relatively quickly are degassed because of their volatility. Commonly known is splitting of acetic acid from the cross-link remedy methyltriacetoxysilan. In this type tin-based soaps are for example used as accelerators for the cross-link process. This type of silicone joint sealant is usually used when jointing against glass.

But there are also silicone joint sealants, which harden when cleaving off the neutral reacting volatiles. That could be methanol, ethanol or acetone. Splitting off butanon-2-oxim is very common for the neutral hardening silicone joint sealants. In the neutral reacting silicone joint sealants there can also be added titan compounds as catalysts for the cross-link.

It is normal to use trifunctional silanes in the cross-link. These can be volatile, and it is possible to expose in the early steps of the polymerisation process. The silanes combine with the hardening process and are thereby used. There could be added further substances to the joint sealants to regulate the viscosity or cheapen the mass.

Acrylic joint sealants can contain considerable amounts of solvents, but are most commonly on a water-dispersed form. Acrylic compounds have in the monomer form a sharp unpleasant smell. As monomer building stone is normally used ethyl, n-butyl, 2-methoxyethyl- and 2-ethoxyethylacrylate. During the hardening the volatile compounds evaporate with a speed dependent on type, temperature and thickness of the joint. Acrylates are very willing to polymerise and as pure monomers they have to be inhibited so that a momentary polymerisation will not happen.

The water-based types are expected to contain preservatives. There can be added plasticisers, for example diisobutylphahalate, biocides and inorganic substances to fill up. For the water dispersing acrylic types the hardening takes place during evaporation of the water and possible water miscible volatile compounds.

Polyurethane joint foam can be found as single component products for the do-it-yourself purposes. Polyurethane is made from a reaction between difunctional isocyanates and multifunctional polyoles. Mainly used monomers are MDI (diphenylmethan-4.4-diisocyanate. The polyoles can be polyether- or polyester-based types. The reaction mechanism for hardening of PUR, consist of a reaction between isocyanate groups and alcohol groups in polyolen. The reaction can be quite complex since the alcohol groups can have different placements, and since the isocyanates can be either monomers or prepolymers.

In single component PU-joint foam a prepolymerization between diisocyanaten and polyolen has happened, but there is still free diisocyanate present in the product in a certain amount. PU-joint foam hardens up by means of the humidity of the air when urea bridges are produced. Moisture can also function as wind instrument, since carbon dioxide is set free in the hardening process. The products are based on solvents and can contain toluene, xylene and ethyl glycol acetate. There can be added dye and fillers as

talcum, titanium dioxide and ferric oxide. As moisture regulating substance can be added zeolites and hydrogenated ricinus oil as thickening substance.

Hardening takes place in approx. 6-8 hours dependent on moisture, temperature, thickness of the joint, speed of evaporation of the solvents and dispensary.

The oil-based joint sealants are based on a drying oil and polybuten and are used for hidden joints. There can be added nickel and cobalt complexes such as siccatives, which catalyse the oxidative cross-link. As filling compound is used chalk. There can be added ethylene glycol as solvent in quantities of 10-12%. The solvent will evaporate in time dependent on temperature, air change and thickness of the joint.

Joint sealants based on bitumen and rubber, contain considerable amounts of solvents. These elastoplastic joint sealants function as adhesive at the same time, and are used for tightening outdoor, for example of roofs.

There are other elastic joint sealants based on rubber, for instance MS-polymer, which is a silane termined polyol. The MS-polymer is high elastic and is used when jointing fronts and floors. The MS-polymer split of methanol during the hardening and can contain plasticisers of the phthalate type. During use an evaporation of silanes can happen, which mentioned under silicone joint sealants.

2 Method

2.1 Definition

As mentioned in the introduction, we define a joint sealant as a product that can be bought by the consumers in the retail business for do-it-yourself activities in the home both indoor and outdoor. It functions with the purpose of filling up a gap between solid materials, so that an elastic or plastic tightening is established between the materials by means of the joint. Some joint sealants function as adhesives at the same time; that goes for the bitumen-based types.

You can divide the joint sealants into the following main groups:

- Elastic
- Elasto plastic
- Plastic

To the elastic joint sealants belong silicone, polyurethane and MS-polymeric-based types. The acrylic joint sealants and the bitumen-based joint sealants are elastoplastic, and to the plastic joint sealants belongs types based on drying oils.

The elastic types are based on polymers, which are chemically crosslinked in a loose network, and belongs to the group of rubber materials.

The elastoplastic types are similar to the termoplastic elastomers. The crosslink is based on cristalline domaines and not on chemical bonds.

The pure plastic types are similar to modelling clay, but are based on organic polymers without crosslinks.

2.2 Method

The project includes three main phases:

1. Examination of the market for joint sealants for private households and ascertainment of which types of joint sealants, which can be bought in the retail business, and collection of information on the joint sealants. In this phase we try to find out how much the private consumers use of joint sealants and similar products which contain problematic substances. Phase 1 is finished with both screening analyses, as quantitative analyses for content of components that are considered problematic in relation to environment and health.
2. Determination of how much knowledge the private consumers have of the importance of the marking on the products.
3. Implementation of exposure-/migration samples on selected joint sealants both when used and during cure.

2.2.1 Collecting of joint sealants and information on composition

The consumers can buy joint sealants in building markets, paint dealers, supermarkets and ship's provisions shops.

First phase in the project has been to collect joint sealants, which fulfil the criterions for joint sealants as described in section 2.1. The joint sealants have been purchases in different building markets, a paint dealer, a ship's provisions shop, a discount centre and a wholesale society (LIC) to cover the market as good as possible.

The purchased joint sealants are grouped after type/function.

2.2.2 Providing data sheets etc.

For the purchased joint sealants we have collected product information in the form of safety data sheets (also called supplier application guides and product information sheets). The safety data sheets have been found by visiting the producers or importers Internet homepage, or by contacting the supplier or importer by telephone or by e-mail. In some cases we have succeeded the information by contacting the suppliers for supplementary information.

2.2.3 Quantities of joint sealants for private use

Information on the number of joint sealants for private use has been found by contacting Fugebranchens Samarbejds- og Oplysningsråd (FSO).

2.2.4 Analyses and monitoring experiments

Parallel to the collection of data sheets and other information on content substances in joint sealants there were made screening analyses of the joint sealants. There have been two rounds of screenings. A preliminary screening and a succeeding one, where the joint sealants have been chosen for screening, on basis of the found information on the joint sealants, and the results of the first screening round.

For the screening analyses there has been used chromatographic and spectroscopic analysis methods and detection techniques. The following analysis methods have been used: Infrared spectroscopy (FTIR), HPLC with UV detection, X-ray analysis and gas chromatography (GC) with flame ionisation detection (FID) and mass spectrometric (MS) detection.

The analyses have included quantitative analyses for substances in the joint sealants selected as a result of the screening analyses. Finally, exposure and monitoring experiments have been carried out on a selection of neutral curing silicone joint sealant and a PU-based joint sealant foam. The purpose of this investigation was to examine which vapours of volatile substances the user will risk to be exposed to.

3 Collection

There have been bought joint sealants from 9 different shops totally. We have tried to buy as many different joint sealants as possible. In each shop the different joint sealants which are comprised in the project have been included, and we have tried to avoid duplicates as far as possible. In some cases we have deliberately bought two cartridges of the same kind because of the analysis work.

There were totally bought 62 joint sealants of which some as mentioned are doublets. From the remaining joint sealants it later turned out that some of the products are identical with other joint sealants from the main producer, but marketed with a different name. Totally we have then collected 54 different joint sealants.

3.1 Register of joint sealants

The collected joint sealants have been registered according to the scheme of the Environmental Protection Agency on bought products.

3.2 Grouping of joint sealant after type

The registered joint sealants were divided into groups after their chemical composition and sphere of application. The groups and the number of the different joint sealants appear from Table 3.1.

Table 3.1 Joint sealants divided after type

Group	Number
Silicone joint sealants	22
Acrylic joint sealants	8
Polyurethane joint foam – and mass	7
Vegetable oil-based joint sealants	3
Bitumen-/rubber-based joint sealants	5
MS-joint sealant	7
Water soluble silicates	2
Totally	54

Totally there were bought 22 different silicone joint sealants. The high number confirms that it is the most frequently occurring joint sealant type in the retail business. A large number of the silicone joint sealants are added sponge and mould restraining agents. We often distinguish between sanitary silicone, universal silicone, glass silicone and building silicone.

There have been bought eight different acrylic joint sealants and seven polyurethane joint sealant foams, when we include a single PU-joint sealant.

The number of vegetable oil-based joint sealants is three, and of the bitumen-based there are five.

There have been bought totally seven joint sealants based on MS-polymer. It seldom appears from the marking on the cartridge itself that it is a joint sealant based on MS-polymer, but it can be seen in the product information sheet.

There have been bought two heat resisting joint sealants, which are based on water soluble silicates.

4 Collecting of data

Information on content substances in the bought joint sealants have been collected from joint sealant suppliers, joint sealant producers or importers and are stated in Table 4.1. Approx. 13 different firms produce the bought joint sealants. Some are doublets, which is why the number varies in the different tables.

Table 4.1 Producers or importers of joint sealants

Producer	Number of joint sealants	Remarks
Bostik	10	Safety data sheets and product info accessible on the Internet
Casco	10	Safety data sheets and product info accessible on the Internet
Danalim	10	Product- og safety data sheets sent per e-mail
Farvemøllen	5	Safety data sheets and product infor sent per e-mail
Harald Nyborg	4	Safety data sheets sent per fax
Alfix	3	Product information on the Internet
Henkel/Loctite	2	Sent information
Sika	2	Supplier information sent per fax
Mira	2	Sent product information and safety data sheet
SuperTex	2	Sent product information and safety data sheet for PU foam
Höganäs	2	Consumer information label on the Internet
Hempel	1	Sent product data sheet
Juliana	1	Safety data sheet sent per fax
Træ-nord	1	Product information and safety data sheet on the Internet
Borup	1	Safety data sheet and product info sent per fax
Icopal	1	Sent page of Icopal-handbook
Totally	57	

There is a difference between the accessibility of information on the joint sealants. Some producers have their safety data sheets and/or the product sheets on the Internet, so they can be copied free. Product sheets are information sheets with information on how and for what the joint sealant can be used, and which precautions that should be taken during use of the product. Safety data sheets, also called 16 point supplier directions, are information for the users of the products built op in 16 points determined by Regulation on substances and materials no. 540 of September 2, 1982 with changes.

Safety data sheets must be available for products, which are sold for commercial use. They give among other things information on the composition, special precautions, demands for education, and danger identification in the presence of danger marks and Risk and Safety sentences (R- and S-sentences).

In most cases safety data sheets have been prepared.

4.1.1 Safety data sheets and information from the packaging

In the following there have been specified for each joint sealant group which information on the content substances that could be concluded from the packaging and the safety data sheets. It is a general fact that the packaging of

the joint sealant, do not by itself give enough information to determine the composition of the joint sealant.

Table 4.2 Silicone joint sealants

Name	No.	Content (from packaging/producer)	Basis
Sanitary silicone	1	Polydimethylsiloxane, fillers, oximsilane (< 2 %). liberates slowly approx. 2 % butanon-2-oxime	Silicone, mould inhibited
Sanitary silicone	2	Polydimethylsiloxane, filling substances, oximsilane (< 2 %). liberates slowly approx. 2 % butanon-2-oxime by cure	Silicone, mould inhibited
Universal silicone	3	Polydimethylsiloxane, inactive filling substance ,etenyltrimethoxysilane, during cure small quantities of methanol, neutral cure are made	Silicone, anti mould treated
Silicone fire joint sealant	5	Dimethylpolysiloxane, methyltrimethoxysilan. During cure methanol, 0.02 % is spilt off	Silicone, fire- and smoke inhibited
Silicone	6, 7*	Polydimethylsiloxane, fillers, processadditives and oximo-silane- cure. During cure a small quantity of butan-2-oxim is liberated. Over 150 °C a small quantity of formaldehyde is formed	Silicone, sponge- and mould dismissive
Silicone	8, 10	Polysiloxane, amorfpheus kieseldioxide, neutral cure	Silicone, sponge- and mould dismissive
Silicone	9	Not specified, neutral cure	Silicone, sponge- and mould dismissive, does not attack metals
Super silicone	22	Polydimethylsiloxane, amorf kieseldioxid, methyl-0,0´,0”-butan-2ontrio-oximesilan (1-5 %w/w). Liberates butanon-2-oxim during cure	Allround, anti mould treated, does not corrode
Glass silicone	25	Is lacking	Silicone, based on acetic acid
Silicone	26	Dodecylbenzol (1-20 %), tributyltinoleate (0.1-0,25 %), oximosilan (1-20 %), siliciumdioxide (1-10 %)	Silicone with neutral cure system
Building silicone for wet environments	27	2-Butanonoxime-formation. Limit value 25 ppm	Alkoxy silicone added fungicid
Do-it-yourself-joint sealant	38	No information required on the substances	Water-based silicone, non-smelling, contain fungicide
Building silicone	40,41	Tetrakis(2-methoxyethyl)ortosilicate, N-(3-(trimethoxysilyl)propyl-1,2ethylendiamin,2-butanon,O,O´;O”(methylsilydyn)trioxim (all < 5 %)	Silicone, neutral cure
Sanitary silicone - new quality	42	Ethenyltrimethoxysilane 1-5 %. Liberates methanol during cure	Silicone with anti mould agents
Silicone	43	Alkyltriacetoxysilanes (< 5 %)	Child-proof silicone, acetic acid hardening
Non-smelling building silicone	44	Oxime-based	Silicone, neutral hardening
Building silicone	45	Has been requested	Silicone, alcohol-based, neutral hardening
Silicone	48	Dearomatised destillates (crude oil), hydrogen treated mean heavy (25-35 %), ethyltriacetoxysilan (1-5 %)	Silicone, smells a bit like acetic acid
Glass silicone	59	Alkyltriacetoxysilaner (< 5 %)	Acetic acid hardening silicone
Building silicone	60	Tetrakis(2-methoxyethyl)ortosilicate , N-(3-(trimethoxysilyl)propyl-1,2ethylendiamin,2-butanon,O,O´;O”(merthylsilydyn)trioxim (all < 5 %)	Silicone, neutral hardening
Sanitary silicone	63	2-butanon,O,O´,O”-(methylsilydyn)trioxime. During cure 2-butanonoxime is liberated (4.1 % max)	Neutral hardening silicone, contain fungicide
Universal silicone	71	Acetoxysilicone	Acetic acid-based silicone

*Supplier changed after finishing the report

Table 4.3 Acrylic joint sealants

Name	No.	Content	Basis
Acrylic joint sealant	11	Calcium-magnesium carbonate, butylacrylat/styren copolymer, water	Water-based acrylic joint sealant for indoor use
Acrylic jointing compound, indoor	12	Single component acrylic dispersion	Water-based acrylic joint sealant for indoor use
Latex mass	16	Acrylic acid ester/acrylonitrile copolymer, calcium-magnesium carbonate, water	Water-based acrylic joint sealant for indoor and outdoor tightening
Acrylic joint sealant	21, 47	Mix of acrylic copolymer emulsion, inorganic fillings and additives	Acrylic joint sealant for indoor and outdoor tightening
Acrylic joint sealant, indoor	23	Acrylic latex	Water-based elastoplastic acrylic joint sealant for indoor jointing
Acrylic painter's joint sealant, indoor	24	Akrylic latex	Water-based elastoplastic acrylic latex for indor use
Acrylic joint sealant	20, 37, 54, 55	Informed by telephone to be acrylic latex-based, diammoniumcarbonate (1-5 %), ethylenglycol 0,5-1 %	Acrylic
Acrylic joint sealant	65	Water-based acrylic joint sealant	Water-based, can be painted, plasto elastic acrylic joint sealant

Table 4.4 PU-joint sealant foam and sealant

Name	No.	Content	Basis
Work joint	39	Propellant: Propane/butane 10–25 %, dimethylether 1-5 % Diphenylmethan-4.4´-diisocyanate 5-10 %	Single component-polyurethane foam (MDI-type)
PU-joint foam	50	Diphenylmethan-4.4´-diisocyanat 45-50 %, polyol 10-25 %, propane 5-15 %, butane5-15 %, dimethylether 1-10 %	Polyurethane plus propellants
Fast Cure Marine Adhesive/sealant	51	Naphta (crude oil), hydro desulhurized heavy 1-2,5 %, 4.4´-methylendiphenyldiisocyanate 0,1-1 %, xylene 1-2.5 %	Polyurethane
Construction joint foam	53**	4.4´-methylendiphenyldiisocyanaet 5-10 %, butan 2.5-10 %,dimethylether 2.5–10 %	Polyurethane plus propellants
Mounting and precision foam	67	Diphenylmethan diisocyanat, isomere and homologous 30-60 %, dimethylether less than 10 %, butan less than 10 %	Polyurethane plus propellants
Precision foam	68	Diphenylmethan diisocyanat, isomers and homologous 30-60 %, dimethylether less than 10 %, butane less than 10 %	Polyurethane plus propellants
PU-foam	70	Diphenylmethan-4,4-diisocyanat 45-50 %, polyol 10-25 %, tris(2-chloro-1-methylethyl)phosphate 5-15 %, propane 5-15 %, butane 5-15 %, dimethylether 1-10 %	Polyurethane and propellant

**Supplier changed after finishing the report

Table 4.5 Oil-based joint sealants

Name	No.	Content	Basis
Jointing compound	15	Vegetable oil, calcium carbonate, magnesium silicate	Plastic, weather resistent, polymere, drying oils
Syntetic joint sealant	35	Vegetable oils and polybutene	Plastic joint sealant based on oils
Plastic joint sealant	58	Single component oil-based, destillates (crude oil), hydrogen treated easy 1-5 % (benzene less than 0.1 %)	Oil-based, plastic butyl joint sealant

Table 4.6 Bitumen-/rubber-based joint sealants

Name	No.	Content	Basis
Jointing compound	52	Bitumen-based	Bitumen, oil, rubber
Roof joint sealant	30	Bitumen 25-50 %, xylener 10–25 %, naphta(crude oil), hydro desulphorized heavy less than 2,5 %	Bitumen, rubber
Roof jointing compound	56, 57	Asphalt bitumen 30-60 %, mineral turpentine 10-30 %, destillates (crude oil), hydrogen treated easy 0-10 %	Rubber-based
Roof glue/roof adhesive	62	Bitumen 30-60 %, White spirit/laknaphta 1-5 % Xylenes 10–30 %	
Roof cement	69	Oxidized bitumen, mineral filliers, mineral fibres and mineral turpentine	Special bitumen with added SBS

Table 4.7 MS-polymer-based joint sealants

Name	No.	Content	Basis
Hybrid joint sealant	13	Silane termined polyether, calcium carbonate, phenol alkylsulfon acid ester, Liberates methanol during cure (< 0.2 %)	MS-polymer
High elastic building joint sealant	14	Silantermineret polyol, kalciumkarbonat, polyetherpolyol. Afspalter methanol ved hærdningen (< 0,2 %)	MS-polymer
High elastic joint sealant	28	Does not contain phthalates	MS-polymer
Marine & Teknik joint sealant	31	Not informed	MS-polymer
Floor joint sealant	32	MS-hybrid polymer, single component	MS-polymer
MS 20 Polymer	46	Non-smelling, neutral, not containing isocyanate	MS-polymer
Danaseal 20	60	MS-hybrid polymer, single component	MS-polymer
Danaseal 40	64	MS-hybrid polymer, single component	MS-polymer

Table 4.8 Silicate-based joint sealants

Name	No.	Content	Basis
Fire joint sealant	4	Polymerised silicate	Silicates
Furnace cement	36	Water soluble silicates, natrium metasilicate 10-25 %	Silicates

4.1.2 Code numbers and danger symbols

Danger marks and Code numbers are marks, which should be applied to certain chemical substances in relation to European and Danish Legislation.

Almost all the bought joint sealants are supplied with Code numbers. Only few of them are obligatory for marking with danger symbols. That is first of all the isocyanate-based joint foam types and joint sealants and the bitumen-based jointing compounds.

Wioth regard to danger symbols, R- and S-sentences information has been avaible either on the packaging or from the safety sheets.

Table 4.9 Codenumbers, danger symbols and R- and S-sentences for silicone joint sealants

Name	No.	Code number	Danger symbols	R- and S-sentences
Sanitary silicone	1, 2	Not stated on the packing	None – It is recommended to use safety gloves	
Universal silicone	3	00-1	None on the cartridge	For the substance Etenyltrimetoxysilan is stated R10, Xn, R 20, Xi, R 38
Silicone brandfugemasse	5	00-1	Out of danger class	
Silicone	6, 7*	00-1	Not obliged for marking, it is informed that during hardening small quantities are formed of a substance that can give eczema	
Silicone	8, 10	00-1	Not obliged for marking	
Silicone	9	00-1	Not obliged for marking	
Super silicone	22	0-1	Not injurious to health	For the substance butanon-2-oxim, which is formed during hardening, is stated Xi, R43
Glass silicone	25	Not stated on the packing: Producer informs that the code is1-1	None	
Silicone	26	0-1	None	
Building silicone for wet environments	27	00-1	None	
Do-it-yourself-joint sealant	38	00-1	Out of danger class	
Building silicone	40, 41	00-1, 0-1	Out of danger class	
Sanitary silicone - new quality	42	00-1	Out of danger class	
Silicone	43	1-1	Out of danger class	
Non-smelling building silicone	44	0-1	None on the cartridge	
Building silicone	45	00-1	None on the cartridge	
Silicone	48	0-1 (on safety data sheet 2-1)	None on the cartridge or on Safety-sheet	
Glass silicone	59	1-1	Out of danger class	
Building silicone	60	00-1,0-1	Out of danger class	
Sanitary silicone	63	0-1	Out of danger class	
Universal silicone	71	00-1	None on the cartridge	

*Supplier changed after finishing the report

Table 4.10 Acrylic joint sealants

Name	No.	Code number	Danger symbols	R- and S-sentences
Acrylic joint sealant	11	00-1	Is not classified as injurious to health	
Acrylic joint sealant	21, 47	00-1	Not obliged for marking	
Acrylic joint sealant	23	00-1	Out of danger class	
Acrylic painter joint	24	00-1	Out of danger class	
Acrylic joint sealant	37, 54, 55	Not stated	None	
Acrylic joint sealant	65	00-1	Out of danger class	

Table 4.11 PU-joint sealant foams and sealant

Name	No.	Code number	Danger symbols	R- and S-sentences
Work joint	39	1-3	Xn, Injurious to health, Fx Extremely inflammable	R 36/37/38-42/43;S 23-24-37-38-45-16-2
PU-joint foam	50	1-3	Xn, Injurious to health, Fx Extremely inflammable	R36/37/38-42/43; S (2)-16-23-26-36/37
Fast Cure Marine Adhesive/sealant	51	Not stated on the cartridge	Xn Injurious to health	R 42; S 23
Construction joint foam	53**	No Code number, only Swedish text on the can	X, flame symbol	R 12-42
Mounting and precision foam	67	1-3	Xn, Injurious to health, Fx Extremely inflammable	R 36/37/38-42/43; S 23-36/37-45-51-2-16-21
Precision foam	68	1-3	Xn, Injurious to health, Fx Extremely inflammable	R 20-36/37/38-42/43; S 23-36/37-45-51-56
PU-foam	70	1-3	Xn, Injurious to health, Fx Extremely inflammable	R 36/37/38-42/43; S 82)-16-23-26-36/37

Table 4.12 Oil-based joint sealants

Name	No.	Code number	Danger symbols	R- and S-sentences
Jointing compound	15	0-1	No danger classification	
Syntetic joint sealant	35	00-1	Out of danger classification	
Plastic joint sealant	58	0-1	No danger classification of the product. Contains 1-5 % destillate, that has the danger symbol Xn	The destillate of 1-5 % has as pure substance R 65, R 66

**Supplier changed after finishing the report

Table 4.13 Bitumen/rubber-based joint sealants

Name	No.	Code number	Danger symbols	R- and S-sentences
Jointing compound	52	2-1	Inflammable	Only received product sheet, no info about it. On cartridge: By consumption, contact doctor and show this cartridge: To be kept out of reach of children
Roof joint sealant	30	3-3	Injurious to health, inflammable	R 10-20/21-38-40; S 24/25-36/37-46-2. NB! R 20/21-40; S 24/25-2-51(R- and S-sentences printed on the cartridge in full text.)
Roof jointing compound	56, 57	2-1	Injurious to health	R 10, R 48/20,65; S 2-46-62-23-24
Roof glue/roof adhesive	62	3-3	Injurious to health, inflammable	R 20-36-danger of cancer when used in longer time, can not be excluded; S 24/25-20/21-29-51 (printed on the cartridge in full text)
Roof cement	69	1-3	Injurious to health	R 48/20-21-40; S 24-2. Printed in full text on the cartridge.

Table 4.14 MS-polymer-based joint sealants

Name	No.	Code numbers	Danger symbols	R- and S-sentences
Hybrid joint sealant	13	0-1	Is not classified as injurious to health	
High elastic building joint sealant	14	0-1	Is not classified as injurious to health	
High elastic building joint sealant	28	00-1	Out of danger class	
Marine & Teknik joint sealant	31	00-1	Out of danger classification	
Floor joint sealant	32	00-1	Out of danger classification	
MS 20 Polymer	46	00-1	Not obliged for marking	
Danaseal 20	61	00-1	Out of danger classification	
Danaseal 40	64	00-1	Out of danger classification	

Table 4.15 Silicate-based joint sealants

Name	No.	Code numbers	Danger symbols	R- and S-sentences
Fire joint sealant	4	00-1	Out of danger classification	
Furnace cement	36	00-4	Local irritating	R38-41

Isocyanates can give allergic skin irritations and eczema. There are therefore determined rules that you can not work commercially with joint sealants, which contain these substances, unless you have taken a special education. The education can be taken at the semi-skilled schools. The rules are described in:

- The regulation no. 199 of March 26, 1985 from the Ministry of Labour, on epoxy resins and isocyanates etc. which has been changed by regulation no. 779 of October 15, 1999 from the Working Environment Service.

- At-announcement no. 3.01.1 June 1988. Replaces January 1986. Epoxy resins and isocyanates.
- At-guidance C.0.2 January 2001. Secondary postponement for isocyanates.

The bought joint sealant foam types all contain the isocaynate monomer MDI. In these cases it is stated in the safety data sheet that there is demand for special education of persons, who use the joint sealants in relation to their jobs.

The rules about chemical qualities are relevant for joint sealants. According to the rules, when using the joint sealant there must not be a health risk as a result of consumption, inhalation or contact with the skin, mucous membranes or the eyes. Consumption of a large amount of joint sealant must be considered unlikely, because of the consistence of the products. Several producers also print this on their safety data sheets.

We have noted a difference in the safety data sheets considering the amounts of for example MDI and butanon-2-oxime. It is judged that the difference depends on that in cases where the exact content is not known, you have to indicate the amount corresponding to “worst case”. For silicone no. 48 the declaration of contents is unlikely. The producer has been contacted and he has admitted that the information is wrong and that it will be corrected in accordance with the formulary.

5 Knowledge of marking

The Danish Environmental Protection Agency (Danish EPA) has a campaign where the Agency in several projects investigate which chemical substances appear in consumer goods. In this project regarding chemical substances in joint seals the Danish EPA wants to get information regarding the conumers knowledge about the marking of joint sealants and other painter goods.

There has been carried out a questionnaire survey in the building markets Silvan, Daugbjergvej 18, DK-8000 Århus, and in Bauhaus, Anelystparken 16, Tilst, 8381 Mundelstrup. The interviews have been made in the period of October 31, 2002 till November 18, 2002. There have been made interviews in Silvan on the following dates 31/10, 2/11, 4/11 and 7/11 and in Bauhaus the 13/11 and the 18/11.

Totally we have made 50 interviews. The distribution of answers is spread on three age groups and the two sexes, and it is shown in Table 5.1.

Table 5.1 Answers divided in age groups and sexes

Age group	Men	Women	Couples M/W	Answers	Number of persons
18–40 years	8	7	4	19	23
40-65 years	14	7	4	25	29
> 65 years	5		1	6	7
Totally	27	14	9	50	59

The division in age groups has been discussed with Danmarks Statistik. There are no specific rules for grouping in surveys as this one. The division has been made among others to see if there is a difference in the age groups considering finding information on the Internet, and if there is a sex-linked division in relation to personnel protection and environmental conscience.

Only quite few people refused to participate in the interviews with the Danish Technological Institute. As well as the two building markets have shown great kindness, considering the implementation of the interviews in the sections of the shop, where painter's goods were sold.

The questionnaire, which can be found as Appendix A, consists of 28 questions in total. The questionnaire has been made in a way, so the assistant that did the survey, has been able to elaborate the questions to the interviewed consumer. Besides that the interviewed consumer had to answer which age group he/she belonged to.

As the last question, you had to answer if you were professional or amateur in relation to use of the painter's goods. All answered that they use the painter's goods on an amateur basis. A single consumer answered that he was professional in the sense that he bought the joint sealants for use on his place of work.

The questions did not only include joint sealants, but also other painter goods in relation to marking, disposal, etc. The questions that concern amount,

types and sphere of application for joint sealants, are not included in this section, but in the following chapter.

The first questions were treating the consumers' attitude to the information on the packaging of the painter goods, and if this information was sufficient, and if this was not the case, where you would then seek supplementary information. The questions, which are listed in the following, are not quite the same as in the scheme that was used for the interviews. The changes have been made for a better overview, and on the basis of the answers which are the result of the interviews.

As several possible answers exist the number of answers is not necessarely the same for all questions.

5.1 Result of the questionnaire survey

Question 1: Do you read the information on the packing before beginning the work?

Reading of information on the painter goods	Always	Sometimes	When it is a new and not known product	Never
Division of the answers	27	10	12	3

Question 2: Do you read the whole information?

Reading of information	Whole information	The directions for use	Other
Division of the answers	24	19	7

Question 3: Do you sometimes miss information on the packing of the painter goods, or do you find it sufficient?

Information	Always sufficient	Not always sufficient
Division of the answers	31	19

Question 4: Have you ever thought about or tried to find the missing information on another way than the packing?

Other information?	Yes	No	Sometimes
Division of the answers	10	32	4

Question 5: Where do you think you can find supplementary information?

Place for info	Shop personnel	The producer	The Internet	Other
Division of the answers	31	4	14	3

Question 6: Does consideration for the environment matter when you choose type of painter goods?

Consideration for the environment	Yes	Sometimes	No
Division of the answers	28	11	7

Question 7: Do you think the information of the environment is good enough on the painter goods? (Supplementary question 8: Which thouroughly information do you miss?)

Sufficient information of the environment	Yes	No	Do not know	Other
Division of the answers	21	8	12	1

Question 9: Do you know the marking of painter goods with Code numbers (Measure technical working hygiene need for air)?

Knowledge of Code number	Yes	No
Division of the answers	22	28

Question 10/11: If you know the Code numbers, can you explain the meaning of the numbers before or after the hyphen, and do you know which numeral scale that is used?

Meaning of the numbers	Yes	No	Partly
Division of the answers	6	28	14

Question 12 and 13: Do you know the danger classification of chemical products, including painter goods, and can you explain or guess the meaning of these danger symbols?

Danger classificaion	Knows	Does not know	Knows partly
Division of the answers	46	3	1

Question 14: Do you know the R- and S-sentences which are used to inform about the danger of a product and the precautions to take when using the product? (R = risik information, S = safety regulations)

R- and S sentences	Knows	Does not know	Knows partly
Division of the answers	5	42	2

Question 15: If you were in need of more information about the mentioned marking systems (Code numbers and danger codes), where would you seek the information?

Search of info	Shop personnel	The Internet	Other
Division of the answers	36	12	1

Question 16: Do you protect yourself during the painter work?

Protection	Always	Sometimes	Never	Depends on the product
Division of the answers	9	8	1	34

Question 17: Do you follow the information on the packing considering protection of yourself during the work?

Following the information	Always	Sometimes	Never	Depends on the extent of the work
Division of the answers	18	6	4	34

Question 18: How do you clean brushes and auxillary equipment after use?

Cleaning	None	Water (soap)	Solvents	As instructed
Division of the answers	1	31	10	31

Question 19: How do you protect yourself during the cleaning?

Protection	None	Gloves	Other
Division of the answers	22	19	5

Questions 20, 21 and 22: What do you do with the packing when it is empty? What do you do with painter goods, which have not been used entirely, but which have become too old? What do you do with solvents for cleaning after use?

Way of removal	Recycling site station	Municipal solid waste collection	Environment car	Other
Empty packing	23	14	2	2
Old painter goods	42	8	2	1
Solvents	21			19

5.2 Conclusions of the questionnaire survey

It appears from the survey that environmental considerations are of importance when selecting painter goods for far the greater part of the consumers. Most consumers also read the information on the packing about the right use of new types of painter goods they have not tried before and information about cleaning the tools. Besides the packing the personnel of the shop is the most important information source to use if you need advice. The Internet is another information source, but not far as important in the answers. Considering which pages on the net to seek, very few mentions an exact address. Several mentions Google for searching, and say that they would use different words for searching for the information. Few mention the producer, and nobody mentions AT's or MST's homepage.

Those who say they miss information on the environment can not answer exactly what they need. A single consumer said he missed information on disposal after use.

There relatively rarely used protective means, yet a part of the consumers say they use gloves during the work.

Considering disposal it appears that the local recycling sites are used a lot. No one would discard rests of painter goods in other ways than delivery at these stations. A part of the consumers use the collection system for municipal solid waste collection to get rid of empty packing. Considering solvents half of the interviewed persons deliver these at a reuse station. The rest let the solvent evaporate or pour it out. A single person said that he pour it out in the drain.

Most answered that they use water or soap water for cleaning of the brushes. That indicates that the majority use water-based painting for "do-it-yourself" purposes.

Considering marking knowledge almost everybody knows the ordinary danger symbols and the interviewed persons thought that the symbols are very illustrative in an easily understood way. It is different with the Code numbers. Relatively many approx. half of the interviewed persons answered that they know the codes. But when more specific asked, only a few know the meaning of the numbers before and after the hyphen. Yet some answer that a little number is good. Considering safety and risk sentences this is an unknown conception for most people. However when the interviewer gives examples of R- and S- sentences a better recognition was found. This survey included a limited number of consumers, and it is hard to conclude any specific about whether men or women differ substantially in their knowledge of painter goods or in their environmental conscience when buying or using the painter goods. There are proportionally many women in the interviews, which tell that painter work is one of the "do-it-yourself" jobs where both sexes are represented. We can neither conclude anything about the differences between the three age groups, considering their knowledge on marking and environmental considerations. Yet there is a clear tendency that the interviewed persons from the youngest age group would use the Internet as information source far more often than the groups above 40 years.
In total care must be taken regarding the conclusions as only a very litmited amount of consumers have been questioned.

6 Quantities of joint sealants for private use

The quantity of joint sealants for private use has been searched for by contacting Fugebranchens Samarbejds- og Oplysningsråd (FSO). It has not been possible to get exact numbers, but it is expected that the consumption in Denmark is divided equally between private and professional users. This has been presented to a single of the producers, which found the division very likely. It is estimated that the consumers use 3 cartridges per year in average. According to reference 1 the consumption of joint sealants in Denmark was 6000-8000 tons in 1996. When it is hard to get closer to an exact number, it is because the statistics include other painter goods. If the division is equally between the consumers and the professional market, the consumers share amounts to approximately 3000-4000 tons on a yearly basis.

Following supplementary information can be derived from the questionnaire survey, as it has to be noted that the interview has comprised 50 interviews and 59 persons totally.

Question A: Have you within the latest three years bought and used joint sealants?

For this question we have received 27 affirmative answers and 19 negative from the 50 interviews.

For question B: Where it is asked whether it has been for indoor or outdoor use or both, there is obtained the following division:

Area for use	Indoor	Outdoor	Both indoor and outdoor
Division of the answers	15	9	8

For question C about quantities of joint sealants that have been bought within the latest three years, the answers are spread as follows:

Number of cartridges	1	3	10	Over 10
Division of the answers	4	14	5	5

In the rubric “more than 10 cartridges” a single consumer states that the number is 150.

For question D where it is asked which types of joint sealant/foam that was bought, the answers are almost equally divided on acrylic- and silicone joint sealants. In two cases it was polyurethane joint sealant foam.

For question E where it is asked for the purpose the following areas for use are mentioned: windows, doors, floor mouldings, bath, shower, toilet, drain, tiles, aquarium and roof.

Rough estimated there is registered a consumption during three years for the 59 interviewed consumers in the order of 300 cartridges of 300 ml. That

corresponds to 100 cartridges per year or rough estimated two cartridges per year per consumer. That is one cartridge less than FSO estimates, but not essentially different from this. The consumption is however dissimilarly divided on the consumers, when you have in mind that one single of the interviewed persons, bought half of the registered consumption (150 cartridges).

7 Screening analyses

Parallel to the collection of data for the bought joint sealants, we have done screening analyses. This has been performed partly in the form of preliminary screening analyses, partly in the form of new screenings as a follow-up on the collected information, in the form of product information sheets and safety data sheets and the results of the preliminary screening. Both in the screening phase and in the follow-up phase we have used chromatographic and spectroscopic methods, so the results of both phases are treated as one in this chapter.

The selected screening analyses are put together from joint sealant type and information collected from producers or importers.

The infrared spectroscopic (FTIR) characterization of the joint sealants has been made after evaporation of the thinner either in the shape of water or in the shape of organic solvents. By the infrared analysis technique it is possible to get a fingerprint of the joint sealant type itself, and in some cases of added plasticisers.

Moreover there is carried out an analysis of elements by means of screening at X-ray detection after the same pattern as described for the FTIR-analysis. By this analysis the presence of possible heavy metals or other elements of relevance is decided, for example chlorine. The method does not give information on which chemical substances the element appears in.

For the joint sealant types that contain solvents there has been carried out a gas chromatographic screening with flame ionisation detection. Screening of the same samples is besides that done by gas chromatographic/mass spectrometric (GC/MS) technique to determine other volatile components as example plasticisers and monomers.

Selected joint sealant types have been screened for presence of possible formaldehyde added as preservative by a high-pressure fluid chromatographic analysis (HPLC). The analysis is done after extraction and derivation with dinitrophenyl hydrazine reagent.

7.1 Analysis methods

In the following is presented a short description of the used analysis methods.

Detection limits for the different analysis techniques are very dependent on which substances they are targeted for, interfering components and which method that is used. In Table 7.1 is stated the knowledge-based and typical detection limits for the used analyses.

Table 7.1 Knowledge-based detection limits

Substance	Detection limit	Uncertainty % rel.
Organic connections at GC/MS	0.001 W/W %	10
Element analysis by X-ray analyses	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 %	-

7.1.1 FTIR-analysis

The analysis is made with a Nicolet Magna 550 Fourier Transform Infrared spectrometer. The joint sealants have been extracted in approx. 24 hours with dichloromethane, evaporated and mixed with potassium bromide that has been pressed in tablet form and put in the path of rays.

7.1.2 X-ray analysis

The analysis is carried out on a wavelength disperse Phillips PV 2400 instrument. The analysis is made directly on the joint sealant sample without preliminary treatment. For PU-sealant foam there has first been produced a foam of the sample, and for the others there has an evaporation of volatile substances has been carried out. The instrument calculates the compositions of elements of the sample directly. Correction for volatiles has been made in the calculation.

7.1.3 Gas chromatography with FID and mass spectrometric detection

7.1.3.1 Headspace analyses
The principle in the analyses is the following: A part of the joint sealant sample is put in a capped vial with Teflon coated lid and is heated up to 110°C for an hour. After this a gas sample is taken out with a gas-proof spray, which is analysed by capillary gas chromatography combined with FID-detection.

7.1.3.2 Other GC/MS-analyses
The organic-based joint sealants were solved in dichloro methane and the water-based in water followed by a pentane extraction.

7.1.3.3 High pressure fluid chromatographic (HPLC) analysis for formaldehyde
The HPLC-analysis for formaldehyde was carried out on a HP 1100 instrument with diode array detector. The analysis was done after conversion of formaldehyde to a dinitrophenyl hydrazone derivative.

Separation is done on a RP 18 column, 25 cm x 4.6 mm.

As mobile phase, has been used a tetrahydrofurane, acetonitrile and water gradient. Detection wavelength: 360 mm.

The sample preparation was made by extraction with dichloro methane and heptane in proportion 30/70 volume parts after derivation. The extract was washed free from chloride, and the solution was evaporated on a rotation evaporator. The evaporation rest was dissolved in acetonitrile and injected on the chromatograph.

7.2 Analysis results and comments

In the following the results of the different screening analyses are revealed.

7.2.1 Infrared spectroscopic analysis (FTIR)

In the first screening round there has been made a FTIR-analysis on a selection of totally 11 joint sealants. The joint sealants have been selected in such a way that a screening for plasticisers could be conducted. For this reasonmainly acrylic and silicone joint sealants have been screened. Silicones is included as this type is far by mostly used. Further a single PU-based joint sealant type has been analysed.

The FTIR method is especially suitable for determination of which type of plasticisers that have been used. That goes particularly for phthalate plasticisers that have a characteristic carbonyl absorption. When screening for chlorinated paraffins, the method is not very good. The results can be seen in Table 7.2.

Table 7.2 FTIR-results compared with information on data sheet for the screened joint sealants

Name	No.	Content	Basis	FTIR
Fire joint sealant	5	Dimethylpolysiloxane, methyltri-methoxysilane. During cure methanol, 0.02 % is split off	Silicone	The extract consists of silicone. No absorptions from other components
Sanitary silicone	63	2-butanon,O,O´,O"-(methylsilydyn)trioxim. During hardening 2-butanonoxim (4.1 % max) is liberated	Silicone	The extract consists of silicone. No absorptions from other components
Acrylic mass	11	Calcium-/magnesium carbonate, butylacrylate/styrencopolymer, water	Acrylic	The plasticiser is interpreted as a phthalate plasticiser
Acrylic jointing compound, indoor	12	Single component, waterbased acrylic latexmass	Acrylic	The plasticiser is interpreted as a benzoate type
Acrylic joint sealant	21	Mix of acrylic copolymeremulsion, inorganic fillings and additives	Acrylic	The plasticiser is interpreted as a mix of a polyisobutene and an "ester"
Technical advanced polymer joint sealant	54	Acrylic latex-based, diammoniumcarbonate (1-5 %), ethylenglycol 0.5-1 %	The importer informed by telephone that is was to be on acrylic basis	The polymer is interpreted as an acrylic type. Does not contain phthalate. There can only be seen acrylic absorptions.
Hybrid building joint	13	Silane termined polyether, calcium carbonate, phenol alkyl sulfonic acid ester, liberates methanol during cure (less than 0,2 %)	MS-polymer	The plasticiser is interpreted to be a "long chained", possible. Multivalenced alcohol
Building joint	28	Does not contain phthalates	MS-polymer	The plasticiser is interpreted to be a "long chained", possible. Multivalenced alcohol
Marine and technique	31	Not informed	MS-polymer	The plasticiser is interpreted to be a "long chained", possibly a. multivalenced alcohol
Floor joint sealant	32	MS-hybrid polymer, single component	MS polymer	The plasticiser is interpreted to be a "long chained", possible. Multivalenced alcohol
Fast cure Marine Adhesive/sealant and Bedding Compound	51	MS-hybrid polymer, single component	Methylendiphenyldiisocyanate (MDI)	The plasticiser is interpreted to be a phthalate plasticiser

7.2.2 X-ray analysis

In first screening round was made X-ray analysis on 18 joint sealants. The joint sealants were selected across the joint sealant types to give a representative picture. Besides that, there have been made another two X-ray analyses for content of chlorine. All results appear from Table 7.3.

The elements magnesium, silicon and calcium appear in some of the samples in pretty high quantities. This is caused by the presence of inorganic fillers, or that the joint sealants are based on inorganic silicates. In some of the samples were found content of chlorine in percent quantities. These samples are included in the GC/MS-screening for chlorinated paraffins. In some of the samples were found small amounts of tin. The sample where the content was the highest was selected for GC/MS-screening for organo tin substances. There have not been found other heavy metals than cobalt. Cobalt is known as component in siccatives for oxidative curing of vegetable oils.

Table 7.3 Result of X-ray analysis in weight percentages (After Air drying in 24 hours)

Product	ID-no.	Mg	Al	Si	Ca	Ti	Sn	Zn	P	S	Cl	Na	K	Fe	Co	Loss of weight
Silicone joint sealants																
Silicone	8	< 0.001	< 0.001	17	6.3		0.011									1.4
Do-it-yourself-joint sealant	38	< 0.001	< 0.001	22	19		0.012									6.6
Silicone	48	< 0.001	0.016	23	0.001	0.46	0.006									1.9
Acrylic joint sealants																
Latex mass	16	6.6	0.17	0.79	12											4.7
Acrylic joint sealant	21	5.8	< 0.001	0.080	15						2.3					5.7
Acrylic joint sealant	23	5.7	0.20	0.79	10											5.7
Acrylic painter joint	24	6.8	0.20	3.0	11											7.5
Acrylic joint sealant	55	< 0.001	0.05	1.0	0.002	2.0		0.70								16.5
PU-joint foam and mass																
PU-jont foam	50	< 0.001	< 0.001	0.039	< 0.001						4.2					3.1
Fast Cure Marine Adhesive/ sealant	51	< 0.001	< 0.001	0.014	6.6		0.004				2.4					0.8
Precision foam	68	< 0.001	< 0.001	0.082	< 0.001						4.1					-
Vegetable oilbased joint sealants																
Syntetic joint sealant	35	0.15	0.023	0.030	16	1.1			0.0016	0.016	< 0.001			0.029	0.015	0.2
Butimen-rubber-based masses																
Roof joint sealant	30	0.78	2.6	5.8	0.31					1.1						7.1
Jointing compound	52	< 0.001	< 0.001	< 0.001	0.003	0.015				1.5						1.9

Product	ID-no.	Mg	Al	Si	Ca	Ti	Sn	Zn	P	S	Cl	Na	K	Fe	Co	Loss of weight
Roof jointing compound	57	0.06	3.5	4.1	3.3	0.18				2.1						2.1
MS polymer-joint sealant																
Marine Teknik joint sealant	31	0.082	< 0.001	0.48	12		0.093									0.4
Floor joint sealant	32	0.25	< 0.001	0.73	10		0.065									0.4
MS 20 Polymer	46	0.11	0.11	0.99	11		0.12									0.6
Silicate-based joint sealants																
Fire joint sealant	4	< 0.001	4.9	21	0.010							4.1	0.26			3.1
Furnace cement	36	0.11	3.0	34	0.034							3.8				6.9

7.2.3 GC/MS-analyses

The analyses for GC/FID and GC/MS have in the screening phase been made on 14 different types of the collected joint sealants, to screen for volatiles that is solvents, monomers and plasticisers. The results of the screening can be seen in Table 7.4.

Table 7.4 Results of GC/FID compared with information on data sheet for screened joint sealants

Name	No.	Content	Basis	GC/FID	GC/MS
Silicone joint sealant	26	Dodecylbenzole (1-20 %), tributyltinoleate (0.1-0.25 %), oximosilan (1-20 %), silicium dioxide (1-10 %)	Silicone	Iso-propanol, iso-butanol, n-butanol	Silicone substances
Building silicone for wet environments	27	Butanon-2-oxime is liberated	Silicone	Methanol, ethanol, toluene	Silicone substances
Building silicone	44	Safety data sheet has been ordered, but not received	Silicone	Ethanol	Silicone connections
Acrylic joint sealant	11	Calcium-/magnesium carbonate, butylacrylat/styren copolymer, water	Acrylic	Iso-propanol, iso-butanol, n-butanol	Phthalate plasticisers, isomere benzamides
Acrylic joint sealant	65	Water-based acrylic mass	Acrylic	Acetone, n-butanol	Diisononyl-phthalat, xylene
Elastic joint sealant	37	Informed by telephone to be acrylic latex-based, iammonium-carbonate (1-5 %), ethylenglycol 0.5-1 %	Acrylic	Acetone, tert-butanol, ethanol, methanol, n-butanol	A lot not identified components
Joint foam	50	Diphenylmethan-4,4´-diisocyanate 45-50 %, polyol 10-25 %, propane 5-15 %, butane 5-15 %, dimethylether 1-10 %	PU	Propellant	MDI, possibly content of chlorinated paraffins, xylene
Joint foam	53**	4.4´-methylendiphenyldiisocyanate 5-10 %, butane 2.5-10 %, dimethyl ether 2.5–10 %	PU	Propellant	MDI, possibly content of chlorinated paraffins
Joint foam	67	Diphenylmethane diisocyanate, isomeric and homologs 30-60 %, dimethylether less than 10 %, butane less than 10 %	PU	Propellant, acetone, iso-pentane	MDI
Oil-based joint sealant	15	Vegetable oil, calcium carbonate, magnesium silicate	Modified vegetable oil	Propellant	Turpentine-like, heavier hydrocarbons
Syntetic joint sealant	35	Vegetable oils and polybutene	Mod. Vegetable oil	Isomeric C5 hydrocarbond, fuel, buthoxyethanol	Heavier hydrocarbons
Water proof jointing compound	52	Bitumenbased jointing compound	Bitumen, oil, rubber	Toluene	Turpentine-like, xylenes
Elastic bitumen jointing mass	62	Bitumen 30-60 %, White spirit/laknaphta 1-5 % Xylenes 10 – 30 %	Bitumen, art rubber	Acetone, isopropanol	Turpentine-like, xylenes, nonylphenols
MS-jointing mass	46	Non-smelling, neutral, not containing isocyanate	MS-polymer	Propellant, acetone, methanol, buthoxyethanol	Hydrocarbons, two isomeric phthalate-plasticisers

**Supplier changed after finishing the report

7.2.4 Analysers for formaldehyde and lower aldehydes and ketones

There has been made screening for formaldehyde and lower aldehydes and ketones in five selected joint sealants. The silicone types 2, 7 and 9, acrylic joint sealant no. 16 and “do-it-yourself-joint sealant” no. 38. The samples have been chosen, because it is indicated that they have been added anti mould substances, or can be used outdoors, or in wet environments.

The content of the found aldehydes and ketones is very low in the samples. It is in the interval 1-30 mg per kg joint sealant. However there is found a very large content of a compound, which according to the retention time could be butanal. That goes for the samples of silicone no. 2 and 7. The content of the two samples is in the order of 90-100 g per kg corresponding to 9-10%. Since both types are splitting off butanon-2-oxim, the most likely explanation is that it is this component which is the subject. It has later been found out that bunanon-2-oxim give a retention time at HPLC corresponding to butanal. The found quantity is larger than stated by the producer. On the basis of this, it is not possible to give a reason for the difference in the quantity.

As a summing up from the HPLC-analysis, it can be concluded that the anti mould substances, which are used in the examined joint sealants, are not based on formaldehyde or formaldehyde derivates.

8 Quantitative analyses

On the background of the screening analyses and the information that was accessible for the examined joint sealants in the screening phase, there were selected 8 joint sealants and two joint foams for quantitative analysis. It appears from the below tables, which joint sealants and joint sealant foams that were selected for the quantitative analyses, and which substances that have been analysed for, and the found results. The choice has been made in consultation with the Danish Environmental Protection Agency on the basis of the found information and the result of the screening analyses.

8.1 Analysis methods

There has been used the below analysis methods for the quantitative analyses.

The uncertainty of the performed analyses is less than ± 10 %. The detection limit for the used analysis methods is described under the specific results.

As part of the calibration of the methods of analyses standard materials have been used. Standard materials are chemicals with a known purity or known concentration (preferable p.a. quality).

8.1.1 Analysis method used for quantifying of butanonoxime and organic solvents by GC-FID

0.2-1.5 g sample is weighed out in 50-ml headspace glasses, which are added 2 µl MIBK as internal standard. The glass is heated to 110°C for 60 minutes. 0.2 ml is taken of the headspace glass with a heated needle, and is analysed gas chromatografically at GC/FID. In connection to the quantification there is used standard material for the identified components.

Instrument:	HP 5890
GC-column:	DB-1, 30 m x 0.32 mm id, d_f 3 µm
Injector:	Split/splitless i split-mode 1:25 N_2, temp. 250 °C
Carrier:	He, constant flow: 2 ml/min.
Oven	40 °C in 5 min., 5 °C/min. till 210 °C, stop for 10 min.

8.1.2 Analysis method anvendt for quantifying of plasticisers at GC-FID

3-5 g sample is weighed out and solved in 10 ml dichloromethane containing internal standard o-terphenyle. The solution is analysed gas chromatografically by GC-FID. In connection with the quantification there is used standard material for the identified plasticisers.

Instrument:	Thermo Finnigan GC, Trace 2000
GC-column:	Restek RTX-5 w/integra, 5 + 15 m x 0.25 mm id, d_f 0,25 µm
Injector:	Split/splitless in split-mode 1:20, 2 µl inj., temp. 275°C
Carrier:	He, constant flow: 1 ml/min.
Oven:	80°C in 1 min., 15 °C/min. till 300 °C, hold for 5 min.

8.1.3 Analysis method used for identification and quantification of chlorinated paraffins

2-4 g sample is weighed out and dissolved in 20 ml acetone. The solution is filteredentangled through 0.45 µm mini-uniPrep. The filtrate is then analysed gas chromatographically by respectively GC-MS-NCI and GC-FID. In connection with the quantification there has been used standard material from Fluka Chemica: 25720, Cas. No. [85422-92-0].

According to reference 2 this Cas. No. is synonymous with paraffin oil and hydrocarbon oil, chloro. It is however not specified with regard to short-, medium- or long chain classification. According to Fluka the content of chlorine in the current sample is 60 %.

8.1.3.1 GC-MS-NCI

Instrument:	HP, GC 6890, MS 5973
GC-column:	RTX-5 Silms, 25 m x 0,25 mm id, d_f 0,25 µm
Injector:	Split/splitless in split-mode 1:10, 1 µl inj., temp. 300°C
Carrier:	He, constant pressure: 6 psi
Oven:	40 °C in 1 min., 15 °C/min. till 280 °C, hold for 10 min.

8.1.3.2 GC-FID

Instrument:	HP, GC 5890
GC-column:	CB-Sil 5 CB, 25 m x 0,25 mm id, d_f 0,25 µm
Injector:	Split/splitless in splitless-mode, 1 µl inj., temp. 310 °C
Carrier:	He, constant flow 1 ml/min.
Oven:	40 °C, 20 °C/min. till 300 °C, stop for 15 min.

8.1.4 Analysis method used for quantification of monomeric isocyanates by HPLC

For the analysis of isocyanates there has been used a modified OSHA-method No. 47. Approx. 5 g sample is weighed out and solved in 20 ml DMSO. The monomer is derivated with 1-(2-pyridyl-piperazin). There is made evaporation for dryness and pure solution in mobile phase. The solution is analysed at HPLC with fluorescence detection. In connection with the quantification there is used standard material from Sigma Aldrich: 25,643-9, Cas. No. [101-68-8].

Instrument:	HPLC: PE series 410,
Detector:	Hitachi F 1080, 240 nm Ex. og 370 nm Emi.
Column:	5 µm Hypersil ENV 250 x 4,6 mm
Injector vol:	10 µl
Mobil phase:	40 % acetonitril/60 % ammoniumacetat, pH 6
Flow:	1.4 ml/min.

8.1.5 Analysis method used for quantification of nonylphenoles by GC-MS

3-5 g sample is weighed out and dissolved in 10 ml dichloromethane containing internal standard o-terphenyl. The solution is analysed gas chromatographically by GC-MS. In connection with the quantification there has been used standard material from Sigma Aldrigh: 29,085-8 Cas. No. [104-40-5].

Instrument: HP, GC 5890 series II, MS 5971
GC-column: CP-Sil 5 CB, 25 m x 0.25 mm id, d_f 0.25 µm
Injector: Split/splitless in splitless-mode, 2 µl inj., temp. 275°C
Carrier: He, constant pressure: 11 psi
Oven: 35°C in 1 min., 15°C/min. till 280°C, hold for 18 min.

MS-polymer has been analysed for content of organo tin substances by the method below.

8.1.6 Analysis method used for quantification of selected organo tin connections at GC/MS.

A weighed sample amount (approx. 0.3 g) was extracted with an organic solvent after addition of internal standard.

The extract was derivatised with sodium tetraethylborate and subsequently analysed by capillary gas chromatography combined with mass spectrometry (GC-MS).

Instrument: HP, GC 5890 series II, MS 5972
GC-column: CP-Sil 8 CB, 30 m x 0.25 mm id, d_f 0.50 µm

8.2 Analysis results from the quantitative analysis

The results from the performed analyses are tabulated below.

Table 8.1 Analyses of silicone joint sealants

	No.	Solvents % w/w				Butanon-oxim mg /kg
		Methanol	Ethanol	Hexane	Toluene	
Building silicone for wet environments	27	2.9	1.0	-	-	-
Sanitary silicone	63	-	0.16	0.027	0.020	1,5,3,5;15 *)
Detection limit		0.0001	0.0001	0.0001	0.0001	0.0001

"-" mean less than the detection limit.
*) means three repetitions of the analyses

Table 8.2 Analyses of acrylic joint sealants

Name	No.	Solvents % w/w							Phthalates % w/w	
		Acetone	Iso-propanol	Iso-butanol	n-Butanol	Tert-Butanol	Butyl-acetate	Propylen-glycol	Dibutyl-phthalate	Diisononyl-phthalate
Acrylic joint sealant	11	0.0007	0.0026	0.0014	0.0083	-	-	0.0015	3.2	-
Acrylic joint sealant	65	0.0085	-	-	0.028	0.0019	0.0046	-	-	16
Detection Limit	0.0001	0.0001		0.0001	0.0001	0.0001	0.0001	0.0001	0.01	0.1

"-" mean less than the detection limit.

Table 8.3 Quantitative analysis of PU-joint foam

Name	No.	Solvents	Chlorinated paraffins %-w/w	Phthalates	MDI %-w/w
PU-joint foam	50	-	9.6	-	1.1
Construction joint foam	53**	-	5.3	-	-
Detection limit		0.0001	0.1	0.1	0.002

"-" mean less than the detection limit.
**Supplier changed after finishing the report. Supplier states they no longer sells products containing chloroorganic compounds.

Table 8.4 Analysis of oil-based joint sealant

Name	No.	Propellants % w/w	Organic solvents % w/w
			Turpentine
Jointing compound	15	-	1.9
Detection limit			0.001

Comments: There has not been used any propellant in this product.

Table 8.5 Quantitative analysis of bitumen-/rubber-based joint sealants

Name	No.	Organic solvents % w/w					Nonylphenol substances % w/w
		Iso-propanol	THF	Toluene	Xylenes	Turpen-tine	
Roof glue/roof adhesive	62	0.45	0.19	0.48	17	1.2	8.0
Detection limit		0.0001	0.0001	0.0001	0.0001	0.0001	0.1

Table 8.6 Quantitative analysis of MS-polymer-based joint sealants

Name	No	Organic solvents % w/w			Preservatives % w/w	Plasticisers % w/w	
		Metha-nol	Acetone	Hexan og C_6-isomere	Dibutylltin	Diisodecyl-phthalate	DEHP
Marine and Teknik joint sealant	31				0.05		
MS 20-Polymer	46	3.6	0.087	0.050		32 %	4.2 %
Detection limit		0.0001	0.0001	0.0001		0.1	0.01

The relative uncertainty for the determination of plasticisers is judged to be +/- 15%.

8.3 Estimation of the results

In one of the examined silicone joint sealants was found a content of methanol and ethanol in small quantities of respectively 2.9 and 1% w/w. In the other sample was found small quantities of ethanol, hexane and toluene. In this sample was found very small quantities of butanon-2-oxim (1.5 – 15 ppm). Butanon-2-oxim is liberated during cure, and the found quantities are probably because this process has taken place at very low speed during sampling.

In the two chosen acrylic joint sealants were found respectively dibutyl phthalate and diisononyl phthalate as plasticisers. There were found small traces of alcohol in both samples. In one of the samples there was additionally found butylacetate and in the other propylenglycol. The quantities are very small.

In the two joint sealants, which have been though a quantitative analysis, both samples showed content of chlorinated paraffins. The content is respectively 9.6 and 5.3 % w/w. Only in one sample was found free MDI. The quantity is determined to 1.1 % by HPLC.

There has not been found content of solvents in the samples. However, there has been found content of propellants, but it has not been possible by the used analysis method to make a quantification of the content of propellants (volatile hydrocarbons and dimethylether).

In the examined oil-based joint sealant there has been found a content of 1.9 % turpentine. In the bitumen/rubber-based sample there has been found xylen as main component of solvents (17 % w/w). The quantity of turpentine is 1.2 %. There has been found a large content of nonylphenol substances (8% w/w).

In the two examined samples of MS polymer-based joint sealants there has been found dibutyltin as preservative (0.05 % w/w) in one sample, and in the other a content of respectively diisodecyl phthalate and diethyl hexyl phthalate in quantities of 32 % and 4.2 %. The mentioned value for dibutyltin is a guiding value, as the found concentration in the extract is beyond the calibration area and the recovery is not known.

It was agreed that the silicate-based joint sealant “Furnace cement” was supplementary analysed for possible content of solvents. There was found extremely low concentrations of acetone (0.0025 %) and toluene (0.0004 %). All percentages are weight-based.

9 Exposure and monitoring experiments

9.1 Plan for experiments

9.1.1 Exposure and monitoring experiments

PU-joint sealant foam no. 50 and sanitary silicone no. 63 figure in the performed exposure experiments.

For PU foam there is searched for liberation of MDI.

For the silicone there is searched for butanon oxim and solvents.

Exposure times 15 minutes, 1 hour, 5 hours and 24 hours. Temperatures: 20°C and 30°C for the joint sealer foam. There has to be taken care that there is water in the glass without direct contact to the joint sealant. For three of the experiments the relative humidity in the experiments is adjusted by using saturated potassium bromide in the glasses. For the joint sealant both measurements happens at 20°C, but with respectively KBr and pure water. KBr gives 58 % relative moisture. There is balance by letting the glass be standing for 24 hours before exposure.

The joint sealant is weighed out and is applied to an object glass in a thickness of 0.5-1 cm. The application was performed in such a way that there is not direct contact between the joint and the water/KBr-solution.

The joint sealant foam is dosed in the same way on an object glass, which has been weighed in advance, so the mass can be found subsequently.

There has been measured during a period of 10 minutes in the monitoring experiments, which corresponds, to a typical working situation.

There was used 100 ml Duran-glass with Teflon membrane screw cap for the experiment. There was added 10 ml tap water/saturated KBr-solution. The examined subjects were applied to an object glass and immediately put in the sample glass. The sample quantity was 0.5-1.5 g/glass. There was taken measurements for respectively MDI for PU-joint foam no. 50, and butanonoxim and organic solvents for sanitary silicone no. 63, after respectively 15 min, 1 hour, 5 hours and 24 hours.

The experiment with PU-joint foam no. 50 was done at respectively 20°C and 30°C with 100 % relative atmospheric humidity. There was taken 20 ml headspace on MDI-filters.

The person that did the test was first equipped with 4 pieces calibrated SKC-pumps. Around the breathing zone was placed 4 different sorbent materials for collection of possible organic volatiles.

The measurements were taken in climate room at 23°C and a relative atmospheric humidity of 49 %. The examined subjects were put on a glass plate with an emptying of the joint cartridge of 10 min. for each joint cartridge.

9.2 Used analysis metods

9.2.1 Analysis method used for quantification of butanon-2-oxim and organic solvents by GC-FID

0.2 ml of headspace is taken with a heated syringe, and is analysed gas chromatographically by GC-FID. In connection to the quantification there has been used standard material for the single components.

Instrument:	HP 5890
GC-column:	DB-1, 30 m x 0,32 mm id, d_f 3 µm
Injector:	Split/splitless in split-mode 1:20, 2 µl inj., temp. 275°C
Carrier:	He, constant flow: 1ml/min
Oven:	40 °C in 5 min., 5°C/min. till 210°C, hold for 10 min.

9.2.2 Analysis method used for quantification of butanonoxim by HPLC

Butanonoxim is derived with DNPH-reagent. The derivative is shaken with dichloromethane/hexane solution. There is made evaporation to dryness and redissolution in mobile phase. The solution is analysed by HPLC with UV-detection. For the quantification there has been used standard material from Acros: 202-496-6, Cas. No. [96-29-7].

Instrument:	HP: 1100 series
Detector:	UV, 360 nm.
Column	LiChrosorb RP 18
Injector vol:	20 µl
Mobil phase:	MilliQ-water, Acetonitrile and tetrahydrofurane
Flow:	1.5 ml/min.

9.2.3 Analysis method used for quantification of monomere isocyanates by HPLC

For the analysis there has been used a modified OSHA-method No. 47. The monomer is derived with 1-(2-pyridyl-piperazin). There is made evaporation for dryness and pure solution in mobile phase. The solution is analysed by HPLC with fluorescence detection. For the quantification there has been used standard material from Sigma Alsrich: 25,643-9, Cas. No. [101-68-8].

Instrument:	HPLC: PE series 410,
Detector:	Hitachi F 1080, 240 nm Ex. and 370 nm Emi.
Column:	5 µm Hypersil ENV
Injector vol:	10 µl
Mobil phase:	40 % acetonitrile/60 % ammoniumacetate, pH 6
Flow:	1.4 ml/min.

9.3 Experimental results

9.3.1 Results of exposure examinations

The results from the performed analyses on sanitary silicone no. 63 appear from below two tables. The shown results are given in area units, which is an expression for the development of the concentrations during the examination period.

100 % relative moisture and 20 ºC		
Time	Toluene	Butanonoxime
15 min.	17	92
1 hour	23	108
5 hours	25	65
24 hours	26	34

58 % relative moisture and 20 ºC		
Time	Toluene	Butanonoxime
15 min.	24	172
1 hour	26	172
5 hours	25	111
24 hours	23	78

The exposure experiments for the examined sanitary silicone joint sealant show a constant but low level of toluene in the sample during both examination conditions. Both at 58% relative moisture and at 100% moisture a concentration change of butanon-2-oxim occurs. In both cases the highest quantity (decided from the area of the top) is measured after an hour's pause.

The quantitative analysis of sanitets silicone gives an amount of toluene in the sample corresponding to 0,020 % w/w. The highest amount of butanon-2-oxime is 4 – 7 times higher in the exposure experiments, when the peak area are used for the quantification.

If one assume that the total amount of toluene in sanitets silicone is liberated in the Duran bottle (air volume 90 ml) and that 1 g of joint sealant is used in average in the experiment one can calculate that the concentration of toluene in the air is 2 mg/l, and that the amount of butanon- 2- oxime maximum will be 8-14 mg/l.

In the exposure experiment for the PU-foam there was not demonstrated MDI in measurable quantities on the MDI filters.

9.3.2 Resultats of the monitoring experiments

The collected air volumes and used sorbent materials are shown in Table 9.1:

Table 9.1 Collected air volumines and used sorbent materials

Sorbent	Flow speed l/min.	Sampling time min.	Sampling volume L
XAD-2	0.286	14	4.0
Coal tubes	0.283	12	3.4
DNPH-tubes	1.63	15	24.4
MDI-filter	2.00	12	24.0

It has been chosen to monitor butanon-2-oxim on 3 different sorbent materials, as no standard method exists for this component in connection to indoor climate measurements. The monitoring of MDI was done on a 1-(2-pyridyl-piperazine) primed 37 mm glass fibre strainer.

On the examined MDI-strainer was not found content of the monomer MDI. Since the detection limit for the method is 0.02 µg/strainer, this gives an average air concentration less than 1 µg/m^3 during the sampling period.

Of the three other sorbent materials the examined PNPH-tube showed a content of butononoxim corresponding to 108 µg/tube. This corresponds to an average air concentration during the sampling period of 4.4 mg/m^3.

There has not been found content of organic solvents on the examined coal tube. With a detection limit of 2 µg/coal tube this gives an average air concentration of less than 0.5 mg/m^3 during the sampling period.

9.4 Estimation of the results

It must be stated that there has not been found solvents or MDI in measurable concentrations in the monitoring experiments, during the 10 minutes period that has been monitored. A period of 10 minutes must be regarded as a suitable time, when you consider your own experiences with jointing. There has been found butanon-2-oxim in the monitoring experiment in an average air concentration of less than 0.5 mg/m^3.

For comparison the limiting value for butanone (CAS nr. 78-93-93) and butanol are respectively 145 mg/m3 and150 mg/m3 (Arbejdstilsynets vejledning C.0.1., October 2002: Grænseværdier for stoffer og materialer). For butanon-2-oxime one propose a limiting value corresponding to 90 mg/m3. Incomparison with these limiting values the meanair concentration of butanon-2-oxime must be judged to be very low..

10 References

Reports

ref 1: Problematic substances in building goods, SBI-meddelelse 122 - Statens byggeforskningsinstitut, 1999

Ref. 2: Chloric paraffins in Denmark, Miljøprojekt nr. 248 (1994)

Ref 3: The list of unwanted substances from the Environmental Protection Agency, Orientering fra Miljøstyrelsen Nr. 9, 2000

Documentation foundation

Map 1:

Safety datasheets and product information sheets from suppliers of joint sealants. The suppliers appear from the documentation material

Summary scheme of purchases

Scheme of the bought-in goods

Map 2:

Analyse reports

Questionnaire master

Answered questionnaires

Appendix A: Master of the questionnaire (inserted in the report at the back)