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Environmental and technical characteristics of conductive adhesives versus soldering

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List of Contents

1 INTRODUCTION **6**

2 TOXICOLOGICAL ASPECTS OF ELECTRICALLY CONDUCTIVE ADHESIVES AS COMPARED TO TIN-LEAD SOLDERING SYSTEMS **8**

2.1 TOXICOLOGICAL ASPECTS IN CONNECTION WITH JOINING TECHNOLOGY 8
2.2 CONDUCTIVE ADHESIVES 8
2.2.1 Polymers 8
2.2.2 Solvents 9
2.2.3 Conductive materials 9
2.2.4 Cleaning agents 10
2.2.5 Evaluation of conductive adhesives 10
2.3 TIN/LEAD SOLDER 11
2.3.1 Lead 11
2.3.2 Tin 11
2.3.3 Silver 11
2.3.4 Flux 11
2.3.5 Solder paste 11
2.3.6 Cleaning agents 11
2.3.7 Evaluation of tin/lead solders 12
2.4 METALS IN THE ENVIRONMENT 12
2.4.1 Silver 12
2.4.2 Lead 12
2.4.3 Tin 13
2.4.4 Evaluation 13
2.5 EVALUATION 13
2.5.1 Working environment considerations 13
2.5.2 Consumer considerations 14
2.5.3 Environment considerations 14
2.6 CONCLUSIONS AND RECOMMENDATIONS 14
2.6.1 Other alternatives 15

3 TEST CASES WITH CONDUCTIVE ADHESIVES **16**

3.1 CASE DESCRIPTIONS 16
3.2 ASSESSMENT OF THE TEST CASES 18

4 SILVER RESOURCE ASPECTS OF SUBSTITUTING TIN/LEAD SOLDERS WITH ELECTRICALLY CONDUCTIVE ADHESIVES **20**

4.1 PRODUCTION, CONSUMPTION AND RESERVES 20
4.1.1 Production of virgin silver 20
4.1.2 Consumption of silver 20
4.1.3 Silver Resources 20
4.1.4 Silver scarcity 21
4.1.5 Prices for silver 21
4.1.6 Trend analysis 22
4.1.7 Production of virgin lead 22
4.1.8 Lead consumption and resources 22
4.1.9 Scarcity of lead 22
4.1.10 Production of virgin tin 22
4.1.11 Tin consumption and resources 23
4.1.12 Scarcity of tin 23
4.2 SUBSTITUTION SCENARIOS 23
4.2.1 Scenario calculations 23
4.3 DISCUSSION 24

5 RECYCLING ANALYSIS **25**

5.1 MATERIAL CONTENTS 25
5.2 RECYCLING PROCESS 25
5.2.1 Collection 25
5.2.2 Dismantling facility 25
5.2.3 Metal recovery - recycling 26
5.3 DIFFERENCES IN MATERIAL VALUE 27
5.4 DIFFERENCES IN ENVIRONMENTAL LOAD 27

6 OCCUPATIONAL HEALTH ASPECTS OF ADHESIVE AND SOLDER TECHNOLOGY 28

6.1 COMPARISON 28
6.2 RECOMMENDATIONS 28
6.2.1 Principles for designing a production line with minimal impact on occupational health. 28
6.3 HANDLING CONDUCTIVE ADHESIVES SAFELY 29

7 LIFE CYCLE ASSESSMENT OF ELECTRICALLY CONDUCTIVE ADHESIVE VS. TRADITIONAL TIN/LEAD SOLDER 31

7.1 GOAL AND SCOPE DEFINITION 31
7.1.1 Products/Alternatives 31
7.1.2 Functional unit 32
7.1.3 Process tree, data quality and limitation of the life cycles 32
7.1.4 Assessment method 35
7.1.5 Irregularities and accidents 36
7.1.6 Capital goods 36
7.1.7 7.1.7 Allocation 36
7.1.8 Critical review 37
7.2 RESULTS – RESOURCES 37
7.2.1 SMT scenario 37
7.2.2 Danfoss scenario 39
7.3 RESULTS - EXTERNAL ENVIRONMENT 41
7.3.1 SMT-scenario (disposal scenario: HW) 41
7.3.2 Danfoss scenario (HW) 44
7.3.3 SMT scenario (TH) 46
7.3.4 Danfoss scenario (TH) 47
7.4 CONCLUSION AND RECOMMENDATIONS 48

8 TEST OF ELECTRICAL CONDUCTIVE ADHESIVES 51

8.1 SURVEY OF ELECTRICAL CONDUCTIVE ADHESIVES TESTED 51
8.2 SURVEY OF TEST SUBSTRATES 51
8.3 SURVEY OF THE MOUNTED COMPONENTS 52
8.3.1 Passive components on each substrate variant 52
8.3.2 Active components on each substrate variants 53
8.4 SURVEY OF THE SAMPLES (ADHESIVE/SUBSTRATE) 53
8.5 SURVEY OF THE MOUNTING PROCESS 53
8.5.1 Stencil printing of adhesives/solder paste 53
8.5.2 Dispensing of adhesives 53
8.6 COMPONENT MOUNTING 53
8.7 CURING / SOLDERING 54
8.8 CLEANING 54
8.9 TEST PLAN 54
8.10 DESCRIPTION OF THE TESTS 55
8.10.1 Adhesion test 55
8.11 CURRENT - TEMPERATURE 57
8.12 DISCUSSION 57
8.13 COMMENTS TO EACH ELECTRICAL CONDUCTIVE ADHESIVE VARIANT 59

9 CONCLUSION 63

10 REFERENCES 66

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1 Introduction

This report covers an overview of the results achieved within the Kamille II project. The project has had the aim of comparing electronics joining technologies based on conductive adhesives and traditional SnPb-solders, respectively. The report describes the environmental aspects of introducing conductive adhesives in electronics manufacture compared with solder. It also contains a technical assessment of 13 adhesive variants by means of laboratory surveys and industrial cases.

The Kamille project aims to describe the environmental aspects of the electronics industry's transition from traditional lead-rich solder to lead-free adhesives for bonding components to printed circuit boards. The project is funded by a grant from the Danish Environmental Protection Agency.

The Kamille II project has been reported in the following working reports:

- Life Cycle Assessment of electrically conductive adhesive versus traditional tin/lead solder, Christensen F M
- Silver resource aspects of substituting tin/lead solders with electrically conductive adhesives, Christensen F M, Jensen A B
- Occupational health aspects of adhesive and solder technology, Christensen F M, Jaroszewski M, Syska J, Cohr K H
- Toxicological aspects of electrically conductive adhesives as compared to tin/lead soldering systems, Cohr K H, Christensen F M
- Recycling analysis of electrical and electronic products assembled with tin/lead solder and electrically conductive adhesives, respectively, Christensen F M
- Comparative testing of electrical conductive adhesives on various substrate platings with different component finishes, Jørgensen T
- Electronic prototype assembly with electrical conductive adhesives, Jørgensen T

Party to the project are Technoconsult (project leader), Danish Toxicology Centre, DELTA Danish Electronics, Light and Acoustics, Danfoss, Grundfos, Bent Hede Elektronik, ElektroMiljø and MEKOPRINT.

The electronics and electrical industries are facing increasing pressure from legislation to remove lead from its products. This is because of the hazards to health during manufacture of the materials and environmental damage caused by their end of life disposal. In order to address adequately the environmental problems associated with the current methods for the treatment and disposal of Waste from Electrical and Electronic Equipment (WEEE), it is considered to introduce measures at Community level that aim, firstly, at the prevention of WEEE, secondly at the reuse, recycling and other forms of such wastes and, thirdly, at minimising the risks and impacts to the environment from the treatment and disposal of WEEE. It is also the aim of this initiative to contribute to the harmonisation of national measures on the management of WEEE in order to ensure the functioning of the internal market. These measures are being proposed in two separate Directives. The first – the draft Directive on WEEE – deals with the management of waste and is based on Article 175 of the Treaty. The second, which seeks to harmonise national measures on the restriction of the use of certain hazardous substances in electrical and electronic equipment, is based on Article 95 of the Treaty.

If the European Commission ratifies the legislation, there will be a major impact on all industries using electronic and electrical components. For producers using/producing solder systems, electronic components and PCB's, this legislation is likely to result in the following changes in their production/assembly systems:

- Switch from the traditional tin/lead solder to a lead free solder or
- Switch from the traditional tin/lead solder to conductive adhesives
- Switch from tin/lead plating on PCBs to a lead free plating

- Switch from tin/lead plated components to lead free plated components
- Modification of the soldering process (temperature, fluxes, etc.)

The present report presents the summary results of the Kamille II project. More detailed project results can be found in the project working reports. This report considers the results of this project and includes the following subjects:

- Toxicological aspects
- Life cycle assessment
- Occupational health aspects
- Silver resource aspects
- Recycling analysis
- Test of 13 conductive adhesives by means of laboratory studies
- 4 industrial case studies

A survey of solder consumption was carried out by means of interviews with the leading suppliers of solder on the Danish market. Interviews were also conducted with a number of major Danish manufacturers of electronic equipment with a view to mapping out the quantities of particular types of solder used for particular processes.

The study has formed the basis for an assessment of the types and quantities of solder used in the following processes: surface mounting, through-hole mounting, Hot Air Solder Levelling, component termination, automated mounting and manual reparation.

Conductive adhesives can replace solder paste in some reflow soldering applications and will also make it possible to eliminate the use of solder for component terminals. The SnPb pre-tinning process, nowadays often employed for the surface treatment of printed circuit boards, can also be replaced by the use of e.g. flash gold. In addition, conductive adhesives will probably be able to replace parts of the lead currently used for wave soldering of through-hole mounted components.

The Danish electronics industry’s consumption of solders is estimated to be approximately 130 tonnes per year, with 4 tonnes being used in reflow soldering, 80 tonnes in wave soldering, 16 tonnes in surface treatment and 30 tonnes in manual mounting and repair using solder wire. On top of this are the 3 tonnes contained in terminals on bought-in components, see [1].

2 Toxicological aspects of electrically conductive adhesives as compared to tin-lead soldering systems

The objectives of the toxicological evaluations were to establish a basis from a health and environmental point of view:

1. For comparison of the different possible conductive adhesives alternatives
2. For comparision of the conductive adhesives with the traditional lead containing solder

2.1 Toxicological aspects in connection with joining technology

In the conventional joining technology of electronic industries tin/lead solder is used. The printed circuit board (PCB) must be cleaned to secure good adhesion (joining). Normally a rosin-containing flux is used. When solder paste is used, the cleaning agents (flux) are integrated in the paste.

In some situations, some conductive adhesives require the PCB to be cleaned to ensure good joining of the electronic components to the PCB. Furthermore, stencils, mixing and dispensing equipment must be cleaned after use in order to remove uncured adhesive. Normally a solvent, e.g. ethanol, isopropanol or butanone is used for these purposes. The same goes for solder joining technology, where e.g. stencils must be cleaned for solder paste, usually with alcohols.

2.2 Conductive adhesives

Thirteen adhesives were included in the study. A fourteenth adhesive was omitted as it contains nickel. In principle, nickel is prohibited on Danish workplaces. Furthermore, nickel is listed on the *List of Undesirable Substances* of the Danish Environmental Protection Agency. The toxicology of conductive adhesives is described in [5].

The thirteen adhesives are based on four types of polymers, i.e. 8 epoxy based products, two of which are two-component; two silicone products, one of which is two-component; two polyester products and one acrylate product. Primarily silver is used as the conductive material. In nine products, silver particles are used, and in 2 products other metal particles, i.e. aluminium or copper, plated with silver are used. In two products, carbon is used. In addition to the adhesive polymers and conductive materials, the adhesives also contain low molecular weight molecules, e.g. epoxides, silanes, amines, solvents, fillers, which act as hardeners, cross-linkers, viscosity regulators etc.

2.2.1 Polymers

In general, *epoxy (one- and two-component) and acrylate products* contain reactive low molecular weight substances. Epoxies and acrylates may cause development of skin allergy. Many epoxy systems use amines, which may be corrosive and may also cause development of skin allergy. In addition to causing allergy, many epoxies are genotoxic and mutagenic. The cured polymer materials are non-toxic.

Silicone products contain low molecular weight silanes, which are irritating or even corrosive, and may have a genotoxic potential. Cross-linking by these small molecules cures silicones. During the curing process, the silanes will release alcohols, normally methanol or ethanol. The polymer materials are non-toxic.

Polyester products are thermosetting or thermoplastic. The thermosetting products may contain cross-linkers. Thermosetting polyesters are cured at elevated temperatures by reaction with low molecular weight cross-linkers, e.g. silanes. These are irritating or even corrosive, and may have a genotoxic potential. During the curing process, the silanes will release alcohols, normally methanol or ethanol. The polymer materials are non-toxic.

2.2.2 Solvents

All the four types of adhesives contain organic solvents, which in general are regarded as irritants and neurotoxic. Most of the solvents will evaporate in the production phase of the electronic equipment. It is evaluated that solvents may cause irritation to eyes and respiratory tract, whereas neurotoxic effects are unlikely to occur due to fairly low exposure concentrations. Exposure in the working environment is relatively easy to control with enclosures and/or exhaust. Minor amounts of high boiling solvents may be left in the final product. This may cause slight nuisance to the consumers during use.

2.2.3 Conductive materials

Silver is the most predominant conductive material either per se or as plating on other metals, e.g. copper or aluminium. Carbon is also used as conductive material. Toxicological profiles for the conductive materials can be found in [5]. The conductive material in the adhesives is not important for choice of adhesives from a working environmental point of view. This is merely a matter of environmental toxicity, cf. the later discussion on metals in the environment.

2.2.3.1 Silver

Silver is highly inert and generally considered to be of low human toxicity. Silver accumulates in the body. Long-term exposure to silver may cause argyria, which is a cosmetic illness. Soluble silver may affect the liver. Mild allergic skin reactions may be seen in rare occasions. Silver is toxic for the environment. Environmental aspects of silver are discussed below.

2.2.3.2 Copper

Copper is an essential element in most organisms and is crucial for the function of many important enzymes in the body. Consequently, the body can regulate uptake and excretion of copper to some extent. Long-term exposure to relatively high doses may affect liver and kidneys slightly, and possibly also the central nervous system. Copper ions are toxic to aquatic organisms, algae and bacteria. The fish toxicity is comparable to that of lead.

2.2.3.3 Aluminium

Aluminium is neurotoxic. However, permanent disturbances of the central nervous system are only seen in persons with chronic kidney deficiencies. Long-term inhalation of relatively high doses of aluminium may cause development of lung fibrosis. Long-term exposure to relatively high doses may affect the central nervous system and cause skeletal disorders. Aluminium is toxic to aquatic organisms. The fish toxicity is comparable to that of lead.

2.2.3.4 Carbon

Carbon is relatively inert and considered to be of low human toxicity. Dust may irritate skin and mucosae in the eyes and the upper respiratory tract. Long-term inhalation of relatively high concentrations may cause development of lung fibrosis. Carbon may adsorb carcinogenic compounds (PAH), but cancer has not been reported in humans or in experimental animals after inhalation or skin exposure. No data on environmental toxicity were found, but it is estimated that the use of carbon in conductive adhesives will have no environmental impact.

2.2.4 Cleaning agents

In connection with conductive adhesive technology, cleaning agents are needed to ensure good conductive joints and to clean stencils, and mixing and dispensing equipment. The common practice is rubbing with alcohols, which is normally sufficient. However, often butanone or the like is used to eliminate rubbing. High concentrations of *alcohols* may cause irritation of eyes and respiratory tract. Often, the commonly used *ethanol* is denatured with mineral spirit. On rare occasions, skin contact with mineral spirit may cause development of skin allergy. *Butanone* irritates skin and the respiratory tract. It has low toxicity, but enhances the toxic effect of other solvents, e.g. the neurotoxic effect caused by *n*-hexane, which may be present in aliphatic hydrocarbon solvents, and the hepatotoxic effect of chlorinated solvents. Butanone is taken up through the skin.

2.2.5 Evaluation of conductive adhesives

2.2.5.1 Working environment

Polyester and silicone adhesives are based on non-toxic polymers and contain only a few more ingredients, including solvent and conductive material. During curing, silicone products will release minor amounts of alcohol *e.g.* methanol or ethanol, which are irritating to the mucosae of eyes and respiratory tract. Inhalation of methanol in very high concentrations may cause damage to the optic nerve and blindness, but these effects will not occur at the concentrations resulting from the emission of methanol from the conductive adhesives. Both types of products may release small amounts of other organic solvents included in the formulation. Uncured silicone adhesives contain low molecular weight silanes, which may irritate the skin on direct contact.

Epoxy-based and acrylate-based adhesives contain low molecular weight reactive molecules, which pose risks for development of skin allergy. This requires additional worker protection. Acrylate-based adhesives contain only a few more ingredients, including solvents and conductive material. Epoxy-based adhesives also contain amines or amides as hardeners, which may cause development of skin allergy.

The conductive adhesives joining technology requires use of solvents as cleaning agents, cf. above, which are irritating to skin and mucosae of eyes and respiratory tract, and may interfere with the toxic action of other substances.

The occupational health risks from the use of electrically conductive adhesives in the electronics production are assessed and discussed in [4].

2.2.5.2 Consumer

From a consumer point of view, the choice of polymer type is not important. Some adhesives may result in minor amounts of high boiling solvents being left in the final product. When they evaporate during use they may cause nuisance to the consumers, i.e. affect the indoor climate especially together with other volatile organic compounds (VOC’s), e.g. from electronics cabinets etc. The emitted amounts of high boiling solvents from conductive adhesives are evaluated to result in very low concentrations.

2.2.5.3 Environment

The polymer part of cured adhesives will have no impact on the environment. Neither will the residual amounts of organic solvents and other ingredients have impact on the environment. It is evaluated that only the metals, i.e. silver, copper and aluminium, in the conductive adhesives may have potential impact on the environment, when electronic equipment is disposed of. In conductive adhesives, copper and aluminium are plated with silver. Consequently, silver will have the highest potential impact on the environment of the three. Furthermore, the additional environmental load of copper and aluminium from the use of conductive adhesives is minimal as compared to the amount of copper and aluminium used elsewhere in electronic equipment, e.g. leads and heat sinks. Silver is discussed later in the section on metals in the environment.

2.3 Tin/lead solder

Traditional tin/lead solder bars contain 63% tin and 37% lead (Sn63Pb37). Flux must be used in order to secure good joining capabilities. A typical flux contains organic solvents (alcohol and/or mineral spirit), rosin and activator for the rosin. Solder paste is a formulation of metals (tin, lead and often small amounts of silver, e.g. Sn62Pb36Ag2), rosin, activator, and organic solvents. The toxicology of materials used in traditional solder is described in [5].

2.3.1 Lead

Lead is a known toxicant to humans and accumulates in the body. Lead is neurotoxic, affects the haemoglobin production, and causes sexual dysfunction and malformation in the foetuses. Furthermore, lead is possibly genotoxic and carcinogenic. Lead is toxic in the environment. Environmental aspects of lead are discussed below.

2.3.2 Tin

Tin in high doses is toxic to humans and accumulates in the body. It may cause symptoms from the nervous system and the gastrointestinal tract. Long-term inhalation of tin (or oxides) may cause stannosis ("tin-lungs"). Tin (salts) is a rare skin sensitiser. Tin is toxic for the environment. Environmental aspects of tin are discussed below.

2.3.3 Silver

Silver is highly inert and generally considered to be of low human toxicity. Silver accumulates in the body. Long-term exposure to silver may cause argyria, which is a cosmetic illness. Soluble silver may affect the liver. Mild allergic skin reactions may be seen in rare occasions. Silver is toxic in the environment. Environmental aspects of silver are discussed below.

2.3.4 Flux

When the flux is heated by applying the hot solder, the rosin may decompose and emit formaldehyde, which is a suspected human carcinogen. Fumes from flux are severely irritating and may cause development of skin and respiratory allergy. Furthermore the solvents evaporate during the process. The solvents are irritating and neurotoxic. Skin contact with flux cause irritation and possibly development of skin allergy.

2.3.5 Solder paste

Heating of solder paste will emit fumes of metals and metal oxides, as well as solvents and decomposing products, like formaldehyde. The hazards will be as for the metals and the flux described above.

2.3.6 Cleaning agents

In connection with solder technology alcohols like ethanol and isopropanol are used to clean *e.g.* stencils. High concentrations of *alcohols* may cause irritation of eyes and respiratory tract. Often, the commonly used *ethanol* is denatured with mineral spirit. On rare occasions, skin contact with mineral spirit may cause development of skin allergy.

2.3.7 Evaluation of tin/lead solders

2.3.7.1 Working environment

During the solder processes fumes of metal and metal oxides may be formed. Vapours and gases may also be emitted to the air in the working environment. These emissions may be inhaled. Especially lead may cause systemic effects, and vapours and gases may irritate the mucosae of eyes and respiratory tract, and possibly cause respiratory diseases with asthma-like symptoms. Skin contact during handling flux and solder paste may irritate the skin and possibly cause development of skin allergy. Repair work implies the risk for inhalation of smoke and vapours from the solder on the PCB's and the solder thread used when mounting the new component on the PCB.

The occupational health risks from the use of traditional tin/lead solder in the electronics production are assessed and discussed in [4].

2.3.7.2 Consumer

As to the use of traditional solder in electronic equipment, it is evaluated that this will cause no nuisance to the consumers.

2.3.7.3 Environment

It is evaluated that only the metals, *i.e.* tin, lead and silver in the traditional solders may have impact on the environment, when electronic equipment is disposed of. The aspects of the metals in the environmental are discussed below.

2.4 Metals in the environment

Conductive adhesives predominantly contain silver as the conductive material, whereas the traditional solder contains tin and lead. The environmental fate and toxicity of these three metals have been evaluated in [5] and in order to compare conductive adhesives and traditional solder with respect to environmental effects of their metal contents.

2.4.1 Silver

Silver will occur in the environment in the oxidation states 0 and +1. In oxidation state +1, silver will form complexes with oxygen, chloride and sulphate. Even though some of these complexes are mobile, they will form stable complexes with humic components in soil. Thus, silver is estimated to be highly immobile in soil. Lowering pH will increase the mobility of silver.

Bioaccumulation of silver is low in the aquatic organisms, but may possibly lead to toxic body burdens. The acute toxicity of silver to freshwater organisms (LC_{50}) is 0.002-0.02 mg/l; the chronic toxicity (NOEC, no observed effect concentration) of silver(+1) is 0.002-0.01 mg/l. Apparently, the acute toxicity to marine organisms is 1-2 orders of magnitude lower than for freshwater organisms; presumably due to the binding of silver ions with chloride ions. A water quality standard for silver ions and soluble silver chloride has been proposed to be 0.0009 mg/l (OECD, 2000). Silver is evaluated to be very toxic for the aquatic environment.

2.4.2 Lead

Lead will occur in the environment in the oxidation state +2. Lead precipitates as sulphides, sulphates, carbonates, hydroxides and chloropyromorphite. Sorption of lead in soil is high compared to other metals, and humic substances immobilise lead in most circumstances. Increasing pH will increase the mobility of lead.
Lead is significantly accumulated in aquatic organisms. The acute toxicity of lead to aquatic organisms (LC_{50}) is 1.5-40 mg/l; the chronic toxicity (NOEC) of lead is less than 0.3 mg/l (EC_{50}, the concentration that inhibits growth in 50% of the organisms). A water

quality standard for lead and lead oxide has been proposed to be 0.0034 mg/l (OECD, 2000). Lead is evaluated to be very toxic for the aquatic environment.

2.4.3 Tin

Tin will occur in the environment in the oxidation state +4. Tin of oxidation state +2 is rapidly oxidised to +4. Oxidation increases with pH above 6. Tin may form compounds like oxides, halides, sulphates, phosphates and carbonates in both oxidation states. The mobility of tin is very low. Tin binds to humic substances, and is immobilised. The mobility of tin is very low and is strongly pH dependent.

No data were available about bioaccumulation of inorganic tin in aquatic organisms. The acute toxicity of tin to aquatic organisms (LC_{50}) is 0.29-50 mg/l; the chronic toxicity (NOEC) of tin(+4) is 0.09-7.8 mg/l. These evaluations are based on the few data that are available. A water quality standard for tin(+4) has been proposed to be 0.02 mg/l (VKI, 2000). Tin is evaluated to be very toxic for the aquatic environment.

2.4.4 Evaluation

Silver, lead and tin are immobile at neutral pH in soil containing natural organic matter, and will be located in such layers. The mobility may increase significantly by changes in pH, microbial activity and presence of other contaminants. All three metals are evaluated as very toxic to aquatic organisms. However, the data indicate that silver is much more acute aquatoxic than lead and tin, which are approximately equally toxic. But the question is, if there is any difference when bioavailability is taken into consideration.

2.5 Evaluation

2.5.1 Working environment considerations

From a working environmental point of view, polyester-based and silicone-based adhesives are to be preferred, because the cured polymers are non-toxic and they contain only a few additional ingredients, including solvent and conductive material. During curing, silicone products will release e.g. methanol or ethanol, which are irritating. Both types of products may release small amounts of other organic solvents included in the formulation. Uncured silicone adhesives contain low molecular weight silanes, which may irritate the skin on direct contact.

Epoxy-based and acrylate-based adhesives contain low molecular weight reactive molecules, which pose risks for development of skin allergy. This requires additional worker protection. Acrylate-based adhesives contain only a few more ingredients, including solvents and conductive material. Epoxy-based adhesives also contain amines or amides as hardeners, which may cause development of skin allergy.

Consequently, from a working environmental point of view, the choice of adhesive should be made according to the following preference:
1. Polyester
2. one-component silicone / two-component silicone
3. acrylate / two-component epoxy / one-component epoxy

During the solder processes fumes of metal and metal oxides may be formed. Vapours and gases may also be emitted to the air in the working environment. These emissions may be inhaled. Especially lead may cause systemic effects, and vapours and gases may irritate the mucosae of eyes and respiratory tract, and possibly cause respiratory diseases with asthma-like symptoms. Skin contact during handling flux and solder paste may irritate the skin and possibly cause development of skin allergy.

Altogether, the intrinsic occupational hazard for the traditional tin/lead solder technology is evaluated to be higher than for the conductive adhesive technology in most cases. The consequence of this is that metal exposure poses a higher hazard solvent exposure.

However, the risk is low for both technologies when adequate preventive measures are taken in the working environment, e.g. enclosures, local exhaust ventilation and personal protection, cf. the report on the occupational health aspects [4]. Amongst the conductive adhesives, epoxy- or acrylate based adhesives pose the largest hazards due to the risk for development of skin allergy.

2.5.2 Consumer considerations

Some conductive adhesives may result in minor amounts of high boiling solvents being left in the final product. When they evaporate during use they may cause nuisance to the consumers in the form of indoor climate problems. The risk is estimated to be low because the emitted amounts are small. The use of traditional solder technology in electronic equipment will cause no nuisance to the consumers.

2.5.3 Environment considerations

From an environmental point of view, the metals used in joining materials, component terminations and printed circuit boards (PCB's) are the critical substances. Cured adhesives will have no impact on the environment other than that of the metals. Uncured waste of acrylate- and epoxy-based adhesives may have some environmental impact until cured.

Silver, lead and tin are evaluated as very toxic to aquatic organisms. However, the data show that silver is much more toxic than lead and tin, which are approximately equally aquatoxic. All three metals are immobile at neutral pH in soil containing natural organic matter, and will be located in such layers. Furthermore, ions of the three metals may precipitate as insoluble salts with inorganic anions. Thus the question is, if there is any difference when bioavailability is taken into consideration. This question is not easily answered, because the mobility of the metals may increase significantly by changes in pH, microbial activity and presence of other contaminants.

Human exposure to the metals through environmental pollution is estimated to be low, because apparently silver, lead and tin are bound firmly to soil components under most conditions. Bioavailable silver may accumulate in aquatic organisms to a low degree and the bioaccumulation of tin is estimated to be low too. Bioavailable lead may accumulate in aquatic organisms in appreciable amounts. Human exposure to the three metals through the food chain is estimated to be low, because of low bioavailability. However, more knowledge about the environmental fate of metals is needed in order to properly assess human exposure via the environment.

The life cycle aspects of conductive adhesives and traditional tin/lead solder was also subject for the Kamille II project (c.f. chapter 7). One interesting result from the life cycle study is that the silver layer on component terminals is thicker for components used together with conductive adhesives. It was estimated that the extra amount of silver on the component terminals represents approximately two times the silver coming from a silver-containing adhesive.

Changing from traditional tin/lead solder technology to conductive adhesive technology will reduce the lead from the environmental load, but only to some extent because lead is used in components too, e.g. as screening material in cathode ray tubes. The environmental tin load will also be reduced. On the other hand, the silver load will increase. This load may be reduced to some extent, if particles of other metals are used, plated with silver, or even omitted if carbon is used as the conductive material instead. But it must be emphasised that the adhesive technology requires additional silver on the component terminals to secure good joining.

2.6 Conclusions and recommendations

From a working environmental point of view, the choice of technology is equivocal. The two technologies impose different hazards, but the occupational risks are minimal when adequate preventive measures are implemented.

For the users of electronic equipment, there might be a little emission of VOC's to the indoor air from electronic equipment manufactured with conductive adhesives. The risk to the consumer is estimated to be very low.

From an environmental point of view, it is a question of release of lead and tin, or silver to the environment, unless carbon is used as the conductive material in the adhesives. All the three metals impose environmental hazards, but the actual risks are not easily evaluated. Both for solder and adhesive, recirculation of electronic equipment may reduce environmental release.

If the choice falls on conductive adhesive technology, one must choose between the alternatives of polymeric and conductive materials. For the thirteen conductive adhesives included in this project the following orders are preferred based on the evaluations of human toxicity, ecotoxicity and environmental fate.

Polymers

1. polyester
2a. one-component silicone
2b. two-component silicone
3a. acrylate
3b. two-component epoxy
3c. one-component epoxy

Conductive materials

1. carbon
2a. silver-plated aluminium
2b. silver-plated copper
3. silver

Consequently, the preferred conductive adhesive would be polyester-based with carbon as conductive material.

The technical properties of the participating electrically conductive adhesives have been tested by Delta [6]. The technical aspects of the adhesives must also be considered when choosing.

2.6.1 Other alternatives

New technologies are under development, i.e. lead-free solder and conductive polymers as well as other polymers in the conductive adhesives.

The most promising lead-free solder for general use is ternary alloys of tin, silver and copper, e.g. Sn95/Ag4/Cu1. A status of this development as of November 1999 may be found in [26]. However, many activities are going on in this area, and may be followed on IPC's lead-free website on the Internet (www.leadfree.org).

Conductive polymers make up another interesting possibility.

Conductive adhesives may also be based on imide-polymers. However, no commercially available adhesives were identified for the project. It is estimated that this type of adhesive will range along with polyester-based adhesives.

3 Test cases with conductive adhesives

The goal of the test cases was to reveal the possibilities and limitations of using electrically conductive adhesive as a replacement for solder. The work was performed in collaboration with four Danish electronic manufacturers: Danfoss A/S, Grundfos A/S, Bent Hede Elektronik A/S, and Mekoprint A/S. Each manufacturer performed a test case with electrical conductive adhesive. Four different substrates and substrate platings were used in the cases:

1) FR-4 substrates with gold over nickel plating
2) Ceramic substrates with thickfilm silver conductors
3) 3D Polycarbonate substrate with depressed copper conductors for chemical nickel and gold plating
4) Polyester substrate with polymer silver conductors.

All mounted components had tin-lead plated terminals. In order to establish a reference the ceramic and FR-4 substrates were also tested with solder. This was not possible for the “low temperature” polycarbonate and polyester substrates since they cannot withstand the high soldering temperatures.

Parallel to the industrial cases DELTA evaluated 13 conductive adhesives on four different substrate platings and with two different component terminal finishes. These results are presented in chapter 8.

The overall result from the cases is that conductive adhesive is not considered to be a general replacement for solder, but conductive adhesives will be used especially on low temperature substrates and possibly where heat transfer is high, i.e. for shielding applications, ceramic substrates, and possibly for low current applications. If conductive adhesives should more generally replace solder a further development of the conductive adhesives will be necessary.

3.1 Case descriptions

The four cases are described in the below table by means of application, motivation, substrates, components, adhesives and various process parameters.

Case I	Case II	Case III	Case IV
Danfoss A/S OEM Manufacturer	Grundfos A/S OEM Manufacturer	Bent Hede Elektronik Electronics subcontractor for PCBs and assembly manufacturing	Mekoprint A/S OEM Manufacturer
Application:			
An electronic thermostat for refrigeration application type ETC. There were manufactured printed circuit boards with conductive adhesive and with solder.	Electronics for pump control.	1) ’Flowerpot’ spear to light-up it the plants needs water. 2) FR-4 Substrate to a levelling instrument.	A two-key switch with light emitting diodes.
Motivation:			
To use electrical conductive adhesive as a solder replacement in the production on the existing production equipment.	As an alternative to solder as conductive adhesive. The substrate is mounted with bare dies and SMD. The dies are mounted with conductive adhesive and the SMD components with solder. As it is preferred to have only one component	Manufacturing and assembly of 3 dimension ’substrates’ in plastic. The demand was a new mounting technology, as solder could not be used due to the high temperature. Further, ’warnings’ from	Is using polyester substrates for keyboard switches. For low temperature polyesters solder could not be used for the component mounting, therefore electrical conductive adhesive was chosen.

	attach process the SMD components were mounted with conductive adhesive as well as the bare dies.	authorities of lead-free electronic production has sharpened the interest of using conductive adhesive.	

Substrate:

a) FR-4 Printed Circuit Board substrate with 0.2 um gold over 4 umNickel b) FR-4 Printed Circuit Board substrate with HAL TinLead Copper layer thickness on both ab. 1 ounce. Dimension: 32 x 57 mm. Thickness: 1.5 mm Double sided with PTH. Smallest conductor width: 0.1 mm Smallest insulation distance: 0.15 mm Solder mask is only applied on the FR-4 substrate with tin lead conductors.	Ceramic Substrate – Alumina, with thickfilm silver conductors. 0.63 mm thickness. Dimension: 1”x2”. 2 layer thickfilm silver conductors seperated by a thickfilm insulating layer. Smallest conductor width: 0.25 mm. Smallest insulation distance: 0.25 mm	a) 3D Moulded polycarbonate substrate. Conductors with < 0.2 um gold over > 4um nickel on 18 um copper plating. The conductors are depressed in the polycarbonate. Dimension: 152 x 40 mm. Inclusive the 62 x 12.5 mm spear. Thickness: 2 mm Smallest conductor width: 0.6 mm. Smallest insulation distance: 0.6 mm b) FR-4 Printed Circuit Board with <0.2 um gold over > 4 um nickel. Copper layer ~35 um. Dimension: 80 x 80 mm, thickness 1.5 mm Smallest conductor width: 0.3 mm. Smallest insulation distance: 0.4 mm. Solder mask is applied on the FR-4 substrate.	Polyester laminate, single sided with two layer screen printed polymer silver conductors separated by an insulation layer. A selective carbon print (on top on silver conductors) for key switch (contact dome). Dimensíon: 59 x 43 mm. (excl. the In/output conductor part) Thickness: 0.3 mm Smallest conductor width : 0.6 mm Smallest insulation distance : 0.5 mm (x,y direction) Smallest insulation distance is estimated to be between the two printed conductor layer. (z-direction). Conductors are protected by a folio glued to the polyester substrate.

Components:

3 diodes, SOT 23 with tin-lead terminal finish. 1 ASIC, SSOP 24, pitch 0.65 mm. With tin-lead terminal finish. 20 resistors size 0603. 1 resistor size 0805. 6 capacitors size 0805. 1 electrolytic capasitor Ø 8mm, height 10 mm. All components with tin-lead terminal finish. 1 ’potentiometer’ leaded with tin-lead terminal finish. The terminal is cut and bended for surface mounting. 1 relay leaded with tin-lead terminal finish. The terminal are cut and bended for surface mounting.	Tantal capacitor, size A (l x w x h, 3.2 x 1.6 x 1.6 mm) Tantal capacitor, size B (l x w x h, 3.5 x 2.8 x 1.9 mm) Capacitor, size 0805. Filter, size 0805. Components with tin-lead or tin terminal finish. Bare dies for wire bonding. 2 glass Melf diodes.	Components for the 3D substrate: 1 diode, 1206 size, with gold terminal finish 1 IC, SOT 14, pitch 1.00 mm with tin-lead terminal finish. Components for the FR-4 substrate are not specified (all with tin-lead finish). Components for the 3D substrate: 4 resistors size 0805. 1 capasitor size 0805. Tantal capacitor, size A (l x w x h, 3.2 x 1.6 x 1.6 mm) All components with tin-lead terminal finish. Components for the FR-4 substrate are not specified.	12 diodes, 1206 size, with gold terminal finish 2 diodes, special chip size, with gold terminal finish.

Conductive adhesive:

Namics XH9626 Solder paste for reference: Sparkle: OZ 2062-221CM5-40-10DMK. SN62/Ag2/Pb36 Solder (for wave solder): Boliden, SnPb for wave solder with Philips RF800 flux	Ablebond 8175A Namics XH9626 Amicon CE3511	Amicon 3504FP and Loctite 3880	EPO-TEK H20F Non conductive adhesive was used to fix the components, as the used conductive adhesive has low adhesion strength. Type and material are not disclosed.

Cleaning materials:

Isopropanol and Ethylmethylketone.	Isopropanol	Isopropanol	Not disclosed.

Process:

Stencil printing: Materials. For solder paste 150 um stainless steel stencil For conductive adhesive, 100 um stainless steel stencil Equipment: DEK 265 GS stencil printer. Dispensing: Needle 0.6 mm Equipment: FUJI GL 5	Stencil printing: 100 um stainles steel stencil Equipment: Automatic stencil printer (MPM UP 2000). Process: Performed by the equipment.	Dispensing: Needle 0.4 mm Equipment: Not disclosed Process: Manual dispensing of the 3D substrate. Automatic dispensing by the equipment of the FR-4 Substrate.	Dispensing: Material: See 3.3 Material. Needle 0.4 mm Equipment: Not disclosed. Automatic equipment Process: 1. dispensing: Non conductive adhesive (To fix the components mechanical to the substrate). 2. dispensing: Conductive adhesive. (To connect the components electrical to the substrate conductors).

Component mounting:

Material: A tweezer for manual component mounting. Gloves. Equipment: FUJI CP IV, FUJI CP IV-3, FUJI IP 1, FUJI QP 242. Hole mounted components were hand mounted with the tweezer.	Material: None. Equipment: Automatic placement Process: The component mounting were perforemed by the equipment (Fuji automatic placement).	Material: None Equipmemt: Automatic SMD placer, Zevatech PM 850.	Not disclosed

Curing:

Equipment: Reflow Soldering: BTU VIP 70, convection. Adhesive Curing: P SELECTA Serie 2000, convection. Wave soldering: SEHO. Reflow profile max. 220 C. Wave solder temperature max. 245 C. Forced cooling after soldering was applied Curing profile max 130 C for 60 min.	Equipment: Process: The adhesive were cured according to manufacturer specification in a Box oven with air circulation.	Equipment: IR-furnace. Process: The adhesive was cured according to manufacturers specification.	Equipment: Furnace Process: The adhesive were cured according to manufacturers specification

Cleaning:

Cleaning was not performed after the solder and the adhesive process.	Cleaning was not performed after the adhesive process	Cleaning was not performed after the adhesive process	Cleaning was not performed after the adhesive process

3.2 Assessment of the test cases

The results from the test cases were:

- electrical conductive adhesive shall be applied on noble metal surfaces, i.e. tin-lead as a substrate or component terminal finish is not recommended, due to oxidation.
- redesign of the footprints on the substrates may be necessary.
- reduction of the openings in the stencil is necessary to reduce the applied amount of electrical conductive adhesive compared to solder.
- the existing production equipment can be used i.e. the stencil printer or the dispenser, the component mounting automate and the furnace. A furnace for adhesive curing is recommended, especially if both adhesive and solder shall be used in the production.
- process optimisation with electrical conductive adhesive is more difficult than with solder, especially due to no self alignment and no contraction of the adhesive.
- curing shall be performed according to manufacturers specification, i.e. the temperature shall be controlled.
- interconnection resistance is higher with electrical conductive adhesives than with solder.

- the adhesion between component/adhesive/substrate seems to be lower for electrical conductive adhesives than for solder, this may not be correct for some SMD (ceramic chip resistors and capacitors) components mounted to thickfilm silver conductors on ceramic substrates. Depending on the electrical conductive adhesives adhesion strength and the component, components shall be mechanical fixed.
- repair may be a problem, as hand mounting of electrical conductive adhesives may give an increased interconnection resistance, and revealed silver flakes may tend to migrate.
- repair is estimated to be much more costly with electrical conductive adhesives than with solder.
- protection against uncured epoxy and epoxy vapour is required. Personal shall be trained to handle epoxy.
- for low temperature substrates there is only one alternative, which is low melting solder containing Indium.
- the price for electrical conductive adhesives is about 5 times higher than for solder.

4 Silver resource aspects of substituting tin/lead solders with electrically conductive adhesives

The aim of the present investigation has been to investigate the possible consequences on silver consumption/demands and thereby scarcity and prices associated with substitution of traditional tin/lead solder with silver containing electrically conductive adhesives.

The first part of the report presents data and descriptions on silver production/mining, consumption, reserves and prices. A few data on lead and tin have been included for comparison.

The second part outlines different substitution scenarios and calculates their influence on the silver resource situation. Finally, the results are discussed in light of adhesive technology development, recycling possibilities and other precious metal demands connected with substitution of solder with adhesive.

4.1 Production, consumption and reserves

This section presents key figures for evaluation of silver, lead and tin scarcity. For silver, also economic data has been included. The individual metal paragraphs begin with a short description of metal mining/production.

4.1.1 Production of virgin silver

The virgin mining materials most often contain several compounds like lead, copper, zinc, silver or gold.

According to the Silver Institute, Washington, primary silver mine production accounted for just 17% of total silver production in 1997, whereas silver produced as a by-product or co-product of lead, zinc, copper and/or gold mining comprised the remaining 83% [29].

In USA 30% of silver is produced from copper mining.

In Sweden virgin silver is produced from complex mines (20 - 160 g Ag/ton). Silver is extracted from concentrates of copper and lead. Boliden Bergsöe produces *Zn, Cu, Pb, Au, Ag* in mines in Sweden, Spain, Saudi Arabia, Canada and Chile [30].

4.1.2 Consumption of silver

The consumption of silver on the world market is dominated by 37% for industrial use and 27% for photographical use, [31]. The remaining part is used for jewelry, silverware and coinage. Industrial use for electronics and photography is increasing.

Silver consumption for the electronic industry (batteries and electronics) has for 1997 been estimated to 12% of supplies. For non-electronic alloys, solders and for dentistry the estimated consumption was 18% [29].

4.1.3 Silver Resources

Large private and governmental stocks characterize the market for metals - especially for gold and silver -, which balances the difference between production and demand. The variations in stocks also balance prices to a certain extent.

Many silver mines are closed since they cannot profitably produce silver at current market prices [32].

The Silver Institute has recently estimated the total World demand and supply of silver for 1997. The total supply (demand) was 24,477 tonnes and the total production of virgin silver was only 14,532 tonnes (59.4% of demand). Production of silver from recycled scrap was 4,323 tonnes (17.7% of demand). The remaining supply to satisfy the demand was taken from stocks, meaning that stocks has been reduced by 5,622 tonnes, corresponding to 23% of the total supply in 1997 [31].

The silver consumption has outpaced production since 1992, and the balance is being supplied from aboveground stocks. The stocks in coinage are estimated to 60,000 tonnes and private stocks in India alone are estimated to 100,000 tonnes [30].

4.1.4 Silver scarcity

Scarcity of silver can be assessed in different ways. The LCA tool EDIP[1] [33] applies the amount of known global reserves per person as an index. Another way to express scarcity is by estimating the known reserves of silver relative to the annual consumption per year. The scarcity can be expressed as the "Reserves Life Index" (reserves/consumption) – the number of years before all known reserves have been used if the known reserves and the yearly consumption is unchanged in the future.

The reserve base is the part of the identified resources that meet criteria for current and expected mining technology. The known reserves are the part of the reserve base, which can be economically extracted at the time of determination.

Data from various sources are listed in the following table:

Silver scarcity						
Reference	Year	Demand/ Production Per year 1000 tonnes	Known reserves 1000 tonnes	Known reserves per person kg/person	Reserve Base 1000 tonnes	Reserves Life Index Years
EDIP [33]	1990		770	0.15		
Boliden [30]	1998		250			
AMM [29]	1997	16.6 / 11.9				
MCS [34]	1994	13.9				
TSI [31]	1997	24.5 / 14.5	280		420	
Estimated This report	1997	25 / 15-20	280	0.055		14

Based on the above information, the demand is estimated to 25,000 tonnes/year, of which 5,000 tonnes/year is due to recycling. Since stock reductions are not expected to continue in the coming years, it is assumed that stocks are unchanged in the future. Then 20,000 tonnes/year, will be produced from mining of virgin silver. With known reserves of 280,000 tonnes, the "Reserves Life Index" will be 14 years (280 tonnes/20 tonnes per year).

4.1.5 Prices for silver

Silver is a tangible asset, and is recognized as a store of value. Its price can be affected by inflation, changing values of paper currencies, fluctuations in deficits, demands and interest rates, etc. [31]. In recent years, fabrication has greatly outpaced mine production forcing market participants to draw down existing stocks to meet demand.

The annual demand for silver is more than 22,700 tonnes a year (800 million ounces) and the production is 4,300 - 5,700 tonnes (150-200 million ounces) short of that. Since 1990, there has been a cumulative shortfall of more than 28,400 tonnes (1,000 million ounces) [35].

[1] EDIP: Environmental Design of Industrial Products.

Since 1980, the prices have varied considerably from 4 USD to a maximum monthly average of 59 USD an ounce in 1980.

The following table list some key figures:

Silver (TSI [31])	1975	1980	1985	1990	1991	1992	1993	1994	1995	1996	1997	1998
Price in USD per oz a)	4.4	21.0	6.1	4.8	4.1	3.9	4.3	5.3	5.2	5.2	4.9	5,5
Supply in million oz				717	715	730	781	773	774	862	863	
Mine production in mill oz				520	508	483	463	450	483	489	513	
Industrial demand in mill oz				279	272	261	273	285	300	301	326	

a) Annual average price in USD per oz (London Fix)

4.1.6 Trend analysis

It is expected that prices will increase in the coming years due to increasing demands and reduced stockpiles. Stocks have been reduced considerably during more than five years. In the short run production can be increased by re-opening silver mines but this will only take place if prices are increased.

4.1.7 Production of virgin lead

Lead is mostly found in complex veins in combination with zinc. The lead content is approximately half of the zinc content. Lead production is practically always combined with production of zinc and often with production of silver.

Lead is extracted in 3 mines in Sweden (by Boliden) of which The Laisvall Mine is the largest lead mine in Europe [30].

4.1.8 Lead consumption and resources

The lead consumption is approximately 3.4 million tonnes/y. According to Boliden approximately 50% of the world production of lead is due to reused lead.

Collection and reuse is quite easy because lead has only a few areas of applications. 69% of the consumption is used for batteries and the rest is used nearly equally in 3 branches – alloys, chemicals and semi-finished-goods [30].

4.1.9 Scarcity of lead

Lead scarcity						
Reference	Year	Demand/ Production per year 1000 tonnes	Known reserves 1000 tonnes	Known reserves per person kg/person	Reserve base 1000 tonnes	Reserves Life Index Years
EDIP [33]		3,400	70,000	13	120,000	20
World Resources [36]	1992	3,400	70,000		120,000	21
Boliden [30]	1998		100,000			
Estimated This report		3,400	100,000	19		30

4.1.10 Production of virgin tin

Tin is produced from both primary and secondary sources (The Materials Home Page. Tin). The chief source of tin is cassiterite. When heated (with powdered coal) in a reverbarory furnace at 1200 °C, a tin containing slag is formed. By a second melting in a sloping hearth the metallic tin runs off (99% purity). By electro refining greater purity can be obtained.

Primary tin used for tin/lead solder at Boliden is produced in mines in Bolivia, Peru or Thailand. The metals are bought at the London Metal Exchange [37].

4.1.11 Tin consumption and resources

The Western World produces 145,800 tonnes/y of refined tin and 138,800 tonnes/y of tin in concentrates. Western World consumption of refined tin is estimated to 187,000 tonnes/y [38]. China and Russia are major tin producers but data are not verifiable.

About 40% of the world's consumption of tin is as coating material for steel "tin" cans (The Materials Home Page. Tin).

4.1.12 Scarcity of tin

Tin scarcity						
Reference	Year	Demand/ Production per year 1000 tonnes	Known reserves 1000 tonnes	Known reserves per person kg/person	Reserve base 1000 tonnes	Reserves Life Index Years
EDIP [33]		200	5,900	1.1	6,050	27
World Resources [36]	1992	219	5,920		6,050	27
ITRI [38]	1996	187/146				
Estimated This report		200	6,000			30

4.2 Substitution scenarios

This section aims at estimating the increased silver demand for adhesives that will be the result of substitution from tin/lead solder to electrically conductive adhesives. The results will be discussed in the following section.

4.2.1 Scenario calculations

Assumptions:

- The tin/lead soldering market consumes approx. 60,000 tonnes tin/lead solder per year[2]. [39], [40].
- About 1/3 is solder paste or other solder, which in 'the ideal world' could be substituted. A reasonable optimistic estimate on substitution is 20% of this value. That would require that several of the present technical problems (equipment precision placing and component availability) should be solved, see also [7]. Based on the present technology and adhesive performance, a maximum of 5% of the ideal world situation could be expected [7].
- Solder pastes contain 2% (w/w) silver.
- Electrically conductive adhesives contain 80% (w/w) silver.
- On a weight basis, the adhesive demands is estimated to be 1/5 of the solder demand. The difference consists of [7]:
  - Differences in densities. Adhesives have about half the density of solder paste[3].
  - A stencil with about half the thickness can be used when using adhesives.
  - The area necessary for adhesive application is smaller than the area needed for solder

This gives altogether about a factor 5. The factor was almost obtained in the Grundfos case [7], where a thinner stencil was used but where the application area was not reduced. In can also be mentioned that [22] assumed a factor 6,25 in difference in his solder-adhesive comparison.

The demand for silver in adhesives can now be calculated as:

Pb/Sn solder consumption * substitution potential * 1/5 * adhesive silver content

[2] This corresponds to 0.6-0.7% of the world lead consumption and approx. 11% of the world tin production.

[3] [6] has applied prints with adhesive and solder by using the same stencil. He scaled the prints and found a difference of about a factor two.

The substitution will decrease the silver demand in solder paste by:

Pb/Sn solder consumption * substitution potential * solder silver content

The net increase in silver demand is of course the difference between adhesive content and reduced solder content.

Table 4.1 summarises the increased silver demand based on the three scenarios: 'ideal world' (substitution potential 1/3), optimum performance (0,2 * 1/3) and present technology (0,05 * 1/3).

Table 4.1: Increased silver demand

	Subst. potential	Adh. demand	Decr. sold. dem.	Netto increase
Ideal world	1/3 (33%)	3200	400	2800
Optimum performance	0,20 * 1/3 (6.7%)	640	80	560
Present technology	0,05 * 1/3 (1.7%)	160	20	140

4.3 Discussion

If the estimates in Table 4.1 are compared with the yearly silver demand on the world market (about 25.000 tonnes), it can be seen that a widespread substitution would increase the demand by 11%, whereas a presently more realistic substitution would increase the demand by about 0,5%.

As found in the life cycle assessment (chapter 7), the substitution for adhesive will most obviously also increase the silver demands for component termination as Ag/Pd terminated components are highly recommended for adhesives [6]. Though very uncertain, it was assessed that the extra silver demand for component termination was greater than the silver content in adhesive – approx. a factor two [3]. I.e. – if the component estimates reflect reality - that the above estimates should actually be multiplied by a factor three!

A widespread – future - substitution would therefore most obviously increase silver prices – when also comparing to the fact that it is estimated that the silver supply horizon is only about 14 years! However, with the *present technology* level, the increase in silver demand due to adhesive application would most obviously be marginal as compared to other mechanisms affecting silver prices (see discussion in previous paragraph 'prices of silver').

Further, some of the demand can be met by increasing electronics recycling. That would decrease the net consumption of silver resources. More than 90% of silver in electronics can presently be recovered via recycling.

Recycling of electronics is a demand in Denmark (regulated by law) as it is in a number of other European countries. It is expected to be a demand in the entire European Union in the near future. Recycling plant are also found in Japan and the United States. Recycling will therefore become a considerable disposal route for electronics. It is rather uncertain to estimate a realistic global recycling percentage for electronics in the future. However, if it is estimated to be 50%, the above estimated increase in demands should be divided by about a factor two when considering the net resource consumption (draw on resources). Increased recycling would therefore most probably reduce the influence of the increased demand on silver prices.

Further, new adhesives are developed with reduced silver content (e.g. silver plated aluminium or copper) or without silver (e.g. nickel, carbon or perhaps even future 'conductive polymers'), see [5] and [6] for further details. Reduced silver content in adhesives will reduce the possible influence on silver prices, but silver in component termination may still be a potential problem.

Finally, it should be remembered that silver prices might increase due to several other mechanisms (see discussion in previous paragraph 'prices of silver').

5 Recycling analysis

A recycling analysis has been carried out with the aim of identifying differences connected to recycling of electronics assembled with traditional solder and electrically conductive adhesives, respectively. The Danfoss EST (electronic thermostat) was used as a case. It was tried to answer the following questions:

- What are the contents of the two EST subjects?
- Do the recycling processes differ?
- What are the differences in material value?
- What are the differences in environmental load connected to the recycling?

5.1 Material contents

The complete composition of the two EST case subjects was inventoried by contacting the component suppliers. Data were obtained from most suppliers. Data on the remaining 4-5 components were estimated based on data for the other components. Material composition of the PCB's were partly calculated and partly obtained from the suppliers.

Most of the supplier information has been forwarded to Danfoss A/S under confidentiality, why only a total can be presented. Differences are due to:
The surface treatment of the PCB: An eutectic SnPb HAL (Hot Air Levelling) surface and a solder mask (resist) is used when soldering, whereas adhesive requires chemically applied Ni and Au PCB top layers.
The joining material: Solder versus conductive adhesive.
Through-hole components: Two of the through hole components in the soldered version are substituted with SMT components in the adhesive version. NB! Care should be taken not to interpret data on these two components as a general picture of differences between functionally comparable through-hole and SMT components.

Component leading will ideally also differ. Traditional components contain an inner AgPd layer, a Ni-barrier and a SnPb layer on top. Optimum adhesive components only contain a AgPd layer [6]. It was, however, not possible to obtain components with this termination for the test case. Environmental consequences of using different component termination are addressed in the LCA case (Chapter 7).

5.2 Recycling process

5.2.1 Collection

For Danish conditions, end-of-life electronics are collected and forwarded to an electronics dismantling facility.

No differences are expected in relation to collection of electronics joined with solder and adhesive, respectively.

5.2.2 Dismantling facility

Danish dismantling facilities typically conduct a preliminary mechanical separation, where the mounted PCBs are separated from major metal and plastic parts (which are forwarded for recycling). The PCBs are then checked for known problematic components such as mercury batteries and electrolytic capacitors containing polychlorinated biphenyls. Problematic components are removed with a pair of tongs. Elektromiljø A/S carried out a test on the two subjects and did not find any differences in dismantling feasibility.

No differences are expected in relation to dismantling electronics joined with solder and adhesive, respectively.

The PCBs are sent for further resource recovery at abroad recycling facilities.

5.2.3 Metal recovery - recycling

In general, extraction of metals from scrap is a very complex process, because the various types of raw materials used contain a combination of metals and impurities. The processes involve roasting/drying, smelting, converting and refining. After refining of one specific metal, the remaining impurities (sludge) containing several metals are treated in other processes for recovering.

PCB’s may be recovered by different recycling technologies, see e.g. [8]. Elektromiljø A/S has assessed that both subjects would ideally be recycled by the ‘copper process’. The copper process is applied at Boliden Rönnskär, Sweden and will briefly be described as typical for an up to date copper recovery plant.

The Boliden smelter, Rönnskär is one of the largest smelters for electronic scrap. However, the major input to the process is refined copper ore. Other raw materials, incl. electronic scrap consist about 25%.

5.2.3.1 Recovery at Boliden, Rönnskär

The copper process at Boliden is briefly described below. Focus is on metal recovery and especially those metals for which differences are seen between products interconnected with solder and adhesive, respectively.

Electronic scrap (circuit boards from computers, television sets etc.) is inspected to prevent the inclusion of dangerous materials such as mercury and radioactive isotopes. The collectors or dismantling facilities will normally remove electronic components containing dangerous materials before delivery.

The secondary raw materials incl. electronic scrap is flash smelted in a “Kaldo plant”, primarily for recovering the copper. The flash smelting recovers energy from burning the organic materials in the scrap at around 1250 °C.

The melt is transferred to a copper plant for converting, casting and electro-refining. In a converter, sand is added as a slag-former at about 1200 °C for removing iron and zinc. The removed material is further treated and purified in order to give the by-products ‘ironsand’ and ‘zink billets’.

The “white metal” (copper sulphide), formed in the converter, is oxidized (blowing) to 98% pure copper, followed by an injection of liquid ammonia for reducing the level of oxygen. The melt is casted into copper anodes containing 99% copper and 0,5% precious metals.

The copper anodes are electro refined in the copper refinery, using sulphuric acid and copper sulphate as the electrolyte. The sludge in the electrolyte tanks contains precious metal impurities and is forwarded for a separate precious metal plant, where gold, silver, platinum, palladium and selenium are recovered. Boliden has informed that close to 100% palladium and gold is recovered and between 90 and 99% silver. Another by-product from the refinery is a Nickel-fraction, which is treated in a nickel-sulphate plant. The nickel recovery percentage is about 80%.

Tin and lead mainly ends up as dust in gas streams from the Kaldo plant and from the converting. The gas streams are cleaned, capturing the major amount of the tin and lead. This fraction is sent for abroad metal recovery. At present, about 80% may be recovered from an economical point of view.

Metal amounts not recycled end up in waste products, as contaminants in the by-products or leave the plant as emissions.

Very little information is available on these waste streams. However, it is assumed that the far major amount ends up as solid waste products. At present waste materials are stored within the industrial area. A permit from the Swedish National Board of Franchise states that the company shall take measures to store and handle waste material in a manner that prevents nuisance from an environmental point of view via contamination of water, soil or air. The permanent disposal of these waste fractions is currently under investigation. Annually, a public environmental report with full description of the amounts and chemical composition of waste products is sent to the Swedish EPA.

5.3 Differences in material value

Demet Deutche Edelmetall Recycling AG & Co. (Alzenau, Germany) has estimated the following 'recoverable material value' for the two EST subjects:
- Soldered version: approx. 7 DM (German Mark)/kg (about 26,50 DKK/kg)
- Adhesive version: approx. 11 DM/ kg (about 41,50 DKK/kg)
- About 2 DM/kg should be subtracted for processing costs.

The results indicate that considerably more precious metal is used for the adhesive version. Interestingly, differences in component termination are not included in the test case. 'Optimum' component termination for the adhesive alternative (Ag/Pd) would increase the silver and palladium consumption further and result in an even larger difference.

The result should as such only be taken as indicative, as specific print layouts (PCB area, components applied, packing density etc.) may severely affect the metal content and thereby the value. *However, adhesive prints must be assumed in general to contain a higher metal value.*

Elektromiljø A/S has looked at the specific case subject and found that the PCB would not be separated from other thermostat parts (the chassis) due to labour cost at the dismantling facility. Therefore, the entire thermostat would be forwarded for recycling. The chassis parts do not contain precious metals and the value per kg thermostat is therefore much lower than the PCB value per kg. This influences the economic benefit as the recycling process costs to some extent are per kg electronic scrap delivered to the recycling facility.

Finally, it should be noticed that it would require a substantial substitution for adhesive technology before differences in material value becomes economically visible for the dismantlers and other interested parties. If only few 'adhesive PCBs' are present in the PCB scrap fraction, they would physically and economically 'disappear'. Possible adhesive substitution potentials are discussed in [3].

5.4 Differences in environmental load

Different recycling facilities have been contacted in order to inventory differences in environmental loads (energy consumption, emissions and waste generation) from recycling solder and adhesive PCBs. However, except for metal recovery percentages (see previous paragraph 'Metal recovery – recycling'), it has not been possible to obtain data on this issue.

The requested data are not available. It is very difficult to allocate the environmental burdens from the complex recycling processes between the inhomogeneous input materials varying dramatically in composition. Further, an allocation would probably require more detailed measurements than what is presently available.

It can be concluded that it would require a substantial developmental work to map and allocate environmental burdens in a way that would make it possible to differentiate burdens associated with solder and adhesive PCBs, respectively.

6 Occupational health aspects of adhesive and solder technology

The objectives of the occupational health analysis have been to:
1. Compare occupational risk associated with the mounting processes applied when joining electronics with electrically conductive adhesives and tin/lead solders, respectively.
2. Provide recommendations on optimum design of production lines and manual handling when applying adhesives

6.1 Comparison

A detailed analysis for the Danfoss test case can be found in [4]. The conclusion states that it is difficult to judge between the alternatives as exposure data are lacking. However, if proper measures are taken, it is believed that the risk of handling the materials is low for both adhesive and soldering technology.

Another occupational health assessment was carried out at Mekoprint A/S. A comparison with soldering was not possible here as only adhesives are applied. Air measurements had been made here in order to detect possible inhalation exposure connected with adhesive application. Further, an evaluation on skin contact exposure was made. The conclusion – also here – was that proper handling of the adhesives results in a very low occupational risk.

Information on inherent toxic properties of a wide number of adhesives can be found in [5].

6.2 Recommendations

Based on experience from the two occupational health cases, recommendation can be given in relation to design of a production line and to manual handling of conductive adhesives.

6.2.1 Principles for designing a production line with minimal impact on occupational health.

When designing a new production line, a number of occupational health and safety issues have to be taken into consideration.

First of all, the choice of machinery and the design of the work process should support the establishing of a workplace that is feasible from an ergonomic and a psychological point of view. The machinery should be chosen to avoid noise- or vibration related problems.

These issues will not be discussed any further in this paper. The paper focuses on the possible impact on health and safety caused by the use of adhesives.

The conductive adhesives are dispersions of an appropriate conductor (e.g. silver) in a polymeric binder. The typical one-component binders, which are applied in the conductive adhesives, are epoxy, silicone, polyester and polyimide resins. Silicone and epoxy resins are used in two-component binders as well.

For some applications the use of adhesives will require cleaning of the printed wiring board (PWB) before the adhesive is applied. The recommended cleaning agent will most frequently be an organic solvent such as butanone or ethanol.

The units containing and applying the adhesives must be cleaned regularly using a proper solvent. This solvent will often be identical to the solvent used as a thinner for the adhesive.

For a general hazard and risk assessment of the chemicals, please refer to [5].

Recommendations:

- One-component adhesives should be used whenever possible from a technical point of view. This will render the mixing of two components superfluous and reduce the risk of exposure (skin contact and inhalation). In case a two-component adhesive is to be used, the manual mixture of the adhesives should be avoided by establishing a mechanical mixture unit in the assembly line.
- The adhesives should be bought from the supplier in containers ready for installation in the assembly line if convenient. This will eliminate the risk of exposure (skin contact and inhalation) while decanting the adhesive into other containers. Another possibility would be to decant the adhesive to containers for use in the assembly line in one step and the maybe freeze the containers until they should be used.
- Manual handling of the chemicals should be avoided to the greatest possible extent, e.g. when applying the adhesive, mixing or cleaning the accessories.
    - Cleaning of the PWB should be carried out in a closed automatic cleaning machine. In different industries the problems related to cleaning technology have been solved in ways leaving only few health- and safety related problems. It is recommended to benefit from these experiences.
    - Cleaning of the application part (e.g. a needle) should be done automatically. The cleaning process might be a periodically occurring and integrated part of the production flow.
    - If cleaning is planned as a manual or semi-manual process, proper process ventilation will be required if any organic solvents are used. In addition measures have to be taken to avoid skin contact.
- Most adhesives will cure only or most efficiently by heating. In case the curing process cannot be brought to an end on the automatically line, the PWB’s should be collected in a well ventilated area in order to ensure fresh air in the breathing zone of the people working there.
- It is recommended to establish the possibility for ventilation of the assembly line already when designing since it is difficult to envisage which type of adhesive will be chosen from the technical point of view in due time. Even though a process has been automatized, the possibility for liberation of vapours to the working environment should be avoided. Whether the ventilation has to be process ventilation or a general ventilation of the room depends on the amount and the hazard of chemicals in use.
    - The curing of the adhesive should take place in a ventilated area. Some adhesives will start curing as soon as applied requiring proper ventilation of the assembly line. Special notice has to be taken when silicone based adhesives are chosen, as these may liberate irritating vapours during curing.
    - Any use of organic solvents requires ventilation as well.

The recommendations given adhere to the design- and planning process. Recommendations on how to handle the chemicals safely are given in the following paragraph.

6.3 Handling conductive adhesives safely

Recommendations on how to design a production line with minimal impact on the occupational health and safety was given above. By following these recommendations, the risk connected with working with conductive adhesives will be reduced.

However, a well considered working practice, the proper use of available technical preventive measures and personal protective equipment as well as good hygiene at work are also necessary in order to minimise the actual risk.

As a basic principle, the preventive measures should be prioritised as follows:

1. Designing the assembly line in a way that reduces risk as much as technical possible
2. Establishing technical measures (e.g. ventilation) where needed.
3. Prescribing the use of personal protection equipment.

Personal instruction at the workplace about the actual health hazards arising from the adhesives and other chemicals is a must in order to enable the employees to handle the hazards and to make the right use of the preventive measures offered. Knowledge about the chemicals and their inherent hazards will provide the necessary background for sound handling of the chemicals.

The instruction must include the following:

- Knowledge about the inherent hazards of the chemicals, e.g. whether the chemicals contain sensitising substances, must be available in order to decide how to work with the chemical and to motivate the employees for using the proper preventive measures.
- Skin contact with chemicals must be avoided. It is of utmost importance that gloves are used properly and that the gloves are resistant to the chemicals. Routines on how often to change the gloves and how to handle the gloves must be implemented.
- Inhalation of vapours and dust must be avoided. It is important for the employees to know how to control the efficiency of the ventilation.
- The hygiene at the workplace must be proper in order to avoid the risk for oral uptake of chemicals (e.g. the metals) due to contaminated cloths and contaminated workplaces.

Whenever required by legislation, the employees must receive the mandatory training as well as a general training is recommended.

7 Life cycle assessment of electrically conductive adhesive vs. traditional tin/lead solder

Adhesives have during the latest decades become a potential substitution for lead containing solder in electronics joining. Lead is suspicious from a environmental point of view due to the human toxicological potential of the metal. Adhesives on the other hand contain silver, which is suspicious due to its high ecotoxic potential.

In the first phase of the Kamille project (Kamille I), a qualitative life cycle screening was carried out. The results indicated adhesive to be the better alternative. However, a quantitative assessment was assumed preferable [25]. Other works have been carried out in order to compare adhesive and solder technology. However, [22] did not include the differences in printed circuit board and component terminations, which are necessary when substituting to adhesives and [15] only focused on energy consumption as a parameter.

The aim of the present analysis has been to compare adhesive with solder joining technology in a life cycle perspective by inclusion of all possible differences and by conducting an impact assessment according to the EDIP-methodology [24]. This report only presents some of the LCA. Please consult the working report [2], which contains a careful discussion about limitations as well as the inventory and an energy analysis for full details.

7.1 Goal and scope definition

The overall aim of the LCA is to make an environmental comparison of the electrically conductive adhesive versus the traditional soldering interconnection technologies in a life cycle perspective.

The present analysis is made as environmental documentation in the Kamille project. The intended audience are environmental/LCA specialist; e.g. among authorities, larger companies and consultancies.

It has been aimed at following the main principles in the ISO 14040 standards.

7.1.1 Products/Alternatives

A Danfoss electronic thermostat EST (077F0301) was chosen as a case product. The EST is to be used in a refrigerator.

In the following, ***'EST-sold'*** *refers to the soldered product, whereas* ***'EST-adh'*** *refers to the product interconnected by electrically conductive adhesive.*

In the first run it was aimed at conducting the Danfoss case as representative for state-of-the-art soldering and adhesive technology

However, as pointed out elsewhere in the Kamille project [7], it has not been possible. It has e.g. not been possible to obtain components without PbSn-termination, where AgPd-terminations would have been preferable [6]. Further, the adhesive print and the SMT-stencil in the Danfoss case were not designed to optimise adhesive consumption. During the work it further showed up that the metal amounts estimated for Printed Circuit Board (PCB) surface finish were not representative for the general state-of-the-art.

Another ‘speciality’ of the Danfoss case product is related to the three largest components. In the EST-sold version, these components are mounted by through-hole technology, which include a wave-soldering step. All other components are mounted by SMT (Surface Mount Technology). In the EST-adh alternative, all components (incl. the three largest) are mounted by SMT. Substitution of wave-soldering is an example of an advantage with electrically conductive adhesive technology; that the curing temperature in the SMT/reflow-oven is much lower (and therefore does not harm large/sensitive components) than what is necessary when soldering. However, in most situations, it is assumed that adhesives will be used to simply substitute ‘pure’ SMT soldering.

Altogether, the Danfoss test case showed up not to be representative for the general comparison between technologies

It was therefore decided to model and assess two scenarios - EST-SMT and EST-Danfoss – in which solder and adhesive joining technologies will be compared

EST-SMT scenario
The purpose of this scenario is to model and assess state-of-the-art technology for the most obvious substitution application (SMT). The following assumptions characterises this scenario

- *only SMT is considered*
- *it is assumed that adhesive components are terminated with AgPd*

Important features of this scenario are that:

- *literature data are used to estimate metal amounts used for components termination and PCB surfaces*
- *it is assumed that the adhesive amount by weight contributes 1/5 of the solder paste amount*

EST-Danfoss scenario
The purpose of this scenario is to model and assess the specific Danfoss case. The following assumptions characterises this scenario:

- *Substitution of both SMT and wave soldering with SMT adhesive technology*
- *Component termination is assumed not to differ*

Because of these assumptions, care should be taken in interpreting the results for general purposes

In this scenario the measured adhesive amounts are used.

Disposal will be modelled as recycling, which is required by law in Denmark. It is also believed soon to be demanded in the European Union. Environmental impacts connected to other parts of the life cycle are assumed to be representative for regions with medium to good standards for production and emission handling. The results are therefore altogether assumed to be representative for regions with electronics recycling.

7.1.2 Functional unit

The function to be delivered by the alternatives is:

Possibility for regulation of the temperature in the entire life time of a refrigerator

The two alternatives are assumed not to differ in terms of performance, incl. energy consumption in the use phase and they are both expected to last the entire refrigerator life; i.e. the alternatives can be compared *one to one*.

7.1.3 Process tree, data quality and limitation of the life cycles

A rough presentation of the life cycles for the two alternatives is shown in Figure 7.1 and 7.2.

It is important to notice that the LCA aims at *comparing* the two alternatives. Therefore, identical life cycle phases for the two alternatives will not be considered. For instance, only the thermostat *print* is considered. The remaining parts are excluded. All inventory data are therefore for one print. Further, as described under 'functional unit', it is expected that the performance of the two alternatives in the use phase do not differ. The use phase is therefore excluded.

It was aimed at getting up-to-date on environmental input/outputs (resource consumption, emissions and waste generation) for all included processes. However, it showed up that most data are either non-existing or not available. Quite a few assumptions and estimations have therefore been made during the inventory analysis. Data limitations and general principles used for data collection/estimation in each life cycle phase are discussed below.

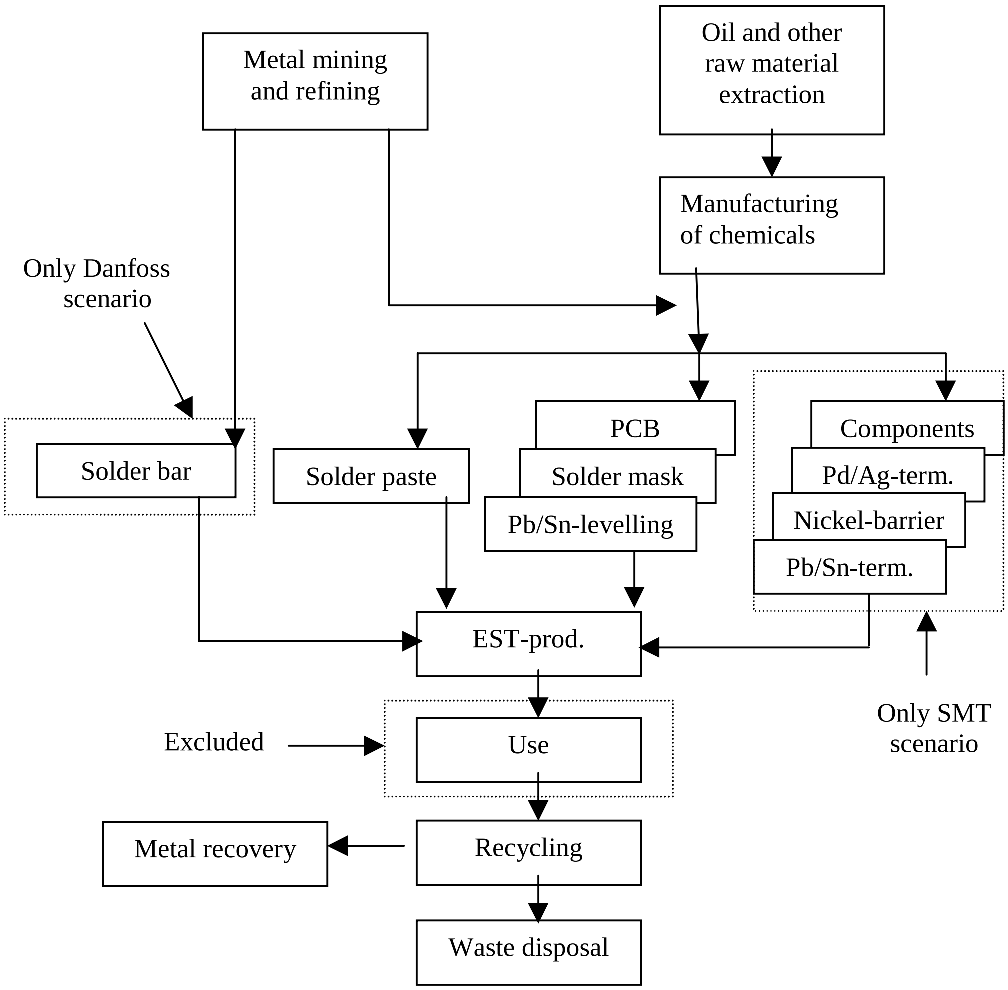

Figure 7.1: Life cycle for EST-sold

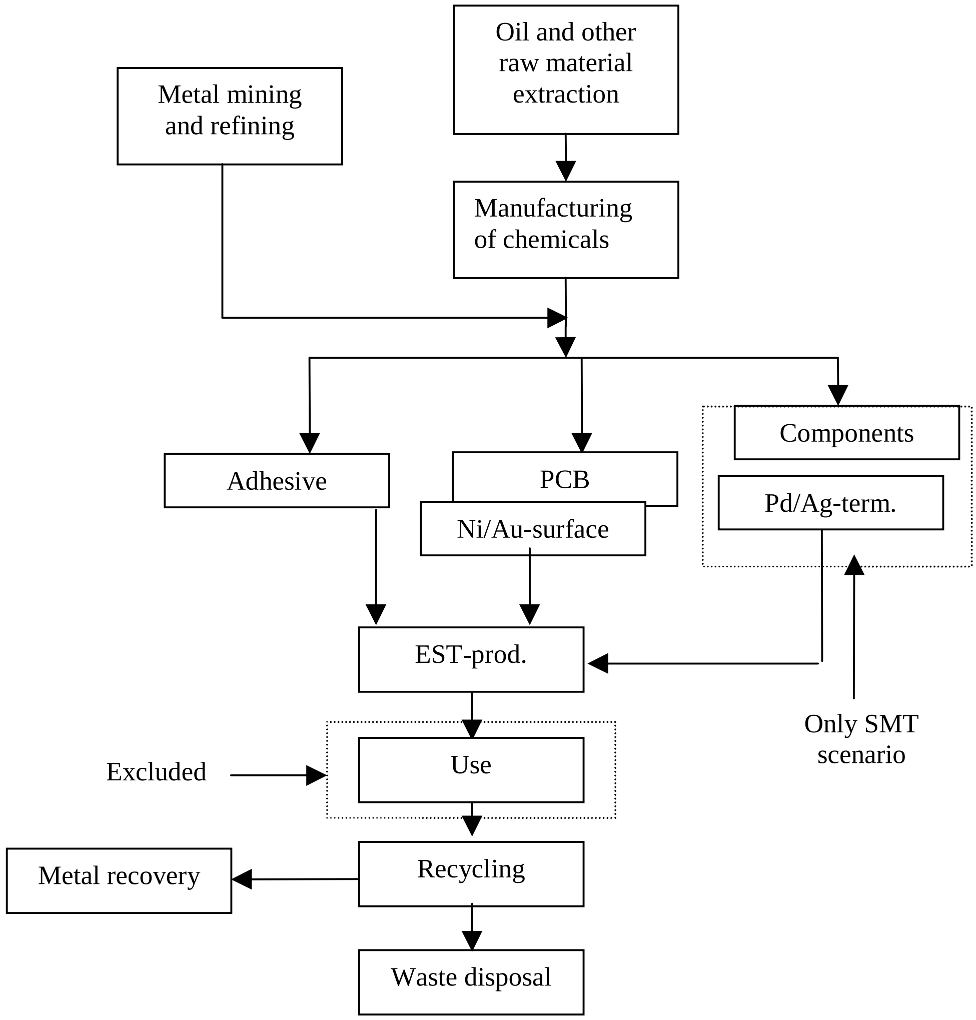

Figure 7.2: Life cycle for EST-adh

7.1.3.1 Printed circuit boards (PCBs)

The same basic substrate, FR-4 (epoxy/fibre glass), has been used for the two products. However, the PCBs differ in terms of surface treatment, where PCB for EST-sold is surface finished with tin/lead Hot Air Levelling (HAL), whereas the EST-adh PCB is finished with a nickel/gold surface applied chemically. EST-sold is further applied with an acrylate solder mask. The surface areas of the PCBs are identical.

7.1.3.2 Components

EST-SMT
It is assumed that traditional components with a top layer PbSn termination are used for EST-sold, whereas it is assumed that adhesive components are terminated with AgPd. Literature data have been used to estimate the amounts used for termination.

EST-Danfoss
Components in the test cases are identical except two – the electrolytic capacitor and the potentiometer. The two components used for the EST-adh are mounted by SMT, whereas the equivalent EST-sold components are "through-hole" mounted requiring an extra wave soldering process step[4].

[4] It might be confusing that *three* through-hole components are mentioned in the goal description but only two here. The third component is the relay, which is the same for the two alternatives. The relay is originally a through-hole component, but the component leads were bended manually to become a 'SMT component' for the adhesive alternative.

Data on material content for the electrolytic capacitor has been supplied to Danfoss, but the data is confidential for others and can therefore not be included in this study, whereas the material composition of the potentiometers are available.

Energy consumption and other environmental input/outputs connected to the actual processing of the components have not been obtained from the suppliers.

As it has only been possible to obtain data for difference in composition for one of the components and because this is not considered representative for substitution of through-hole components for soldering with functionally equivalent SMT components for adhesive application, these differences will not be included.

Two components differ between EST-adh and EST-sold in the Danfoss scenario. The differences may be of importance but are NOT included due to lack of data.

7.1.3.3 Interconnection

Adhesive
The adhesive applied - based on epoxy and silver - is representative for state-of-the-art adhesives.

Solder
Solder paste has been used for SMT mounting and solder bars were used for the wave soldering process. The products applied are considered representative for state-of-the-art.

Metal mining
Extraction of metals is a very complex issue. Usually several metals are mined in the same mine with one metal being the reason why the mine is running. The same metal may in some mines be the major metal and in other mines a by-product. It is therefore not straightforward to allocate environmental burdens from mining to the different metals.

7.1.3.4 Production and use

Data from the Danfoss case is used to emulate the production. The two alternatives are assumed to deliver the same function, incl. having similar energy consumptions and life span (the entire refrigerator life). Environmental input/outputs in the use phase are therefore considered not to differ and have therefore not been included.

7.1.3.5 Disposal

Recycling of electronics is a demand in Denmark (regulated by law) as it is in a number of other European countries. It is expected to be a demand in the entire European Union in the near future.

The disposal phase is therefore modelled as a recycling scenario. A description of the processes can be found in other parts of the Kamille project [9].

7.1.3.6 Transport

Transport is considered not to vary significantly between the two alternatives as their weight and volume are approx. equal.

7.1.4 Assessment method

The EDIP-method [24] is used. EDIP applies the ‘environmental theme’ approach, where inputs/outputs are assessed in relation to their impact on:

- Resource availability
- Global warming
- Acidification
- Nutrient enrichment
- Photochemical ozone formation (photosmog)

- Bulk waste
- Hazardous waste
- Slag and ash
- Human toxicity via air
- Eco-toxicity, acute
- Persistent toxicity (covering human toxicity via water and soil, eco-toxicity via soil and chronic eco-toxicity via water)

Especially for toxicity it should be mentioned that quite a few inventory data are missing. It is assessed that estimation of these would be very uncertain as is the toxicity evaluation method by itself. Toxicity will therefore be discussed qualitatively on top of the quantified values.

Further, some toxicity assessment factors are lacking, which may especially affect the result for the metals. Toxicity factors for lead, nickel and silver (only human toxicity for the latter) can be found in [24]. Ecotoxicity factors for silver have mistakenly not been included, but have been obtained from the authors. Toxocity factors for tin, gold and palladium have not been included as they are assessed considerably less toxic than lead for human toxicity and silver for eco-toxicity.

It has not been possible to obtain specific information on occupational health for processes outside Danfoss. Therefore occupational health has only been included detailed for the production at Danfoss, for which an occupational health assessment has been conducted [4]. Occupational health for other parts of the life cycle will be discussed qualitatively. Only chemical exposures will be considered.

When interpreting the results, it should be remembered that the LCA only includes processes with possible differences between the alternatives. The assessment is therefore conducted for the *difference between adhesive and solder technologies*.

7.1.5 Irregularities and accidents

Irregularities and accidents are not included, as these are not assumed to influence the results significantly. This assumption requires that the production volumes are not too small. In that situation, start-up and close-down routines may substantially influence the environmental input/outputs per functional unit.

7.1.6 Capital goods

SMT-scenario
The same equipment can be used for SMT solder and adhesive joining [7]. Capital goods are therefore excluded in this scenario.

Danfoss scenario
The solder alternative requires wave soldering equipment, which the adhesive alternative does not. However, due to the high through-put, environmental impacts from capital good manufacturing is considered negligible and is therefore not included.

7.1.7 7.1.7 Allocation

Raw material phase
Allocation is often implicit in data obtained from raw material suppliers. Except for mining, the allocation principle used is believed to be co-product allocation by mass, where e.g. the APME[5]-data on epoxy production [14] is a good illustration.

As already described, allocation is very difficult when considering mining, as several metals are usually mined at the same location. The data applied are estimated based on literature studies assuming ‘pure’ mining of the considered metal. Palladium, however, is assumed mined in connection with nickel, platinum and rhodium and an allocation based on market prices has been applied.

[5] APME: Association of Plastics Manufacturers in Europe.

Recycling
Recovered metals are subtracted from the inventory by system expansion and reflects thereby an 'avoided production' allocation.

7.1.8 Critical review

A critical review was carried out by Institute for Product Development, Lyngby, Denmark. The first part being a discussion of the goal and scope and data sources and the second a two step review of the final report.

7.2 Results – Resources

The weighting step for resources in the EDIP methodology assesses resources by comparing consumption with known global reserves per world citizen [24]. The unit for this weighting is (milli) Person Reserves (mPR).

7.2.1 SMT scenario

Figure 7.3 shows the resource weighting for the SMT scenario. The figure present *differences* between the alternatives (EST-adh minus EST-sold). E.g. it can be seen that more silver is used in the adhesive alternative. Thus, it does not mean that no silver is used in the solder alternative.

Further, metal columns represent differences in *net consumption*, i.e. overall metal consumption minus metals recovered during recycling.

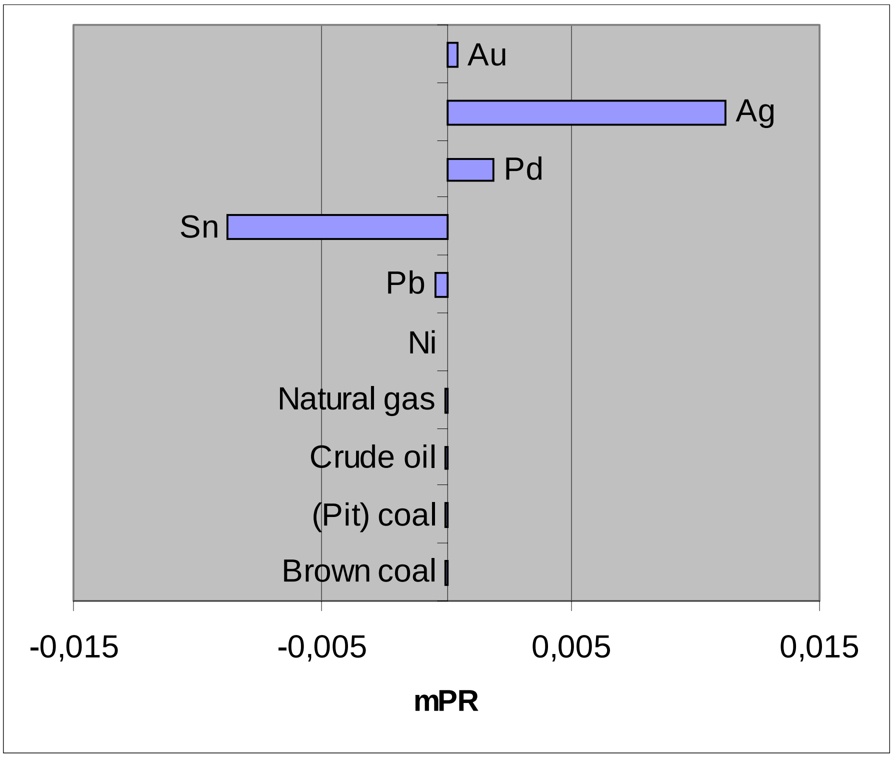

Figure 7.3: Resource weighting (EST-adh minus EST-sold) – SMT scenario

Metal consumption dominates by far as compared to energy resources– by three or more orders of magnitude. The assumption that the energy requirements for metal mining/refining are delivered by oil combustion does therefore not affect the resource evaluation significantly.

The dominating among the metals are silver, tin and palladium. Gold and lead are less important and nickel is negligible.

For silver, about 1/3 of the net consumption is due to the silver loss during production (6-7% loss was estimated for start-up and lost by equipment cleaning), whereas the remaining 2/3 represents loss during recycling. For tin and lead, about 15% of the column heights are the result of solder paste loss (about 5% loss was estimated). Losses during production are considered worst case and would be reduced in case of larger production series.

The figure indicates, the adhesive alternative to be worse (sum of column heights for the adhesive alternative is largest). However, there are several uncertainties connected to the assessment:

- Metal losses during joining material, component and PCB manufacturing have not been included. These losses – if not recycled/recovered – may seriously affect the result. A 10% palladium or gold loss may increase net consumption (and thereby column heights in Figure 7.3) by a factor five. Silver loss during SMT production is included (see above), but a 10% loss during adhesive and component manufacturing would increase the overall net consumption by about 2/3. For tin and lead, a 10% loss would approx. increase the net consumption by 50%. It must be assumed that the 10% are worst case estimates, especially for the costly precious metals.
- EDIP weighing factor for silver. The weighting factors are based on an assumed amount of known global resources. As can be seen in other parts of the Kamille project [3], the estimate on global silver reserves used in EDIP (770.000 tonnnes) differs from other estimates obtained from Boliden (250.000 tonnes) and the Silver Institute (280.000 tonnes). If the alternative values are used, the silver column in Figure 7.3 would be approx. 3 times higher. Tin and lead reserves were also considered but for these metals, the references did not differ significantly from the EDIP value.
- The ‘net consumption’ is heavily depending on the recycling percentages. For silver, the recycling facility has informed that ‘more than 90% are recovered’. A default value of 95% has been used in the calculations. If the right percentage is 99%, the silver column in Figure 7.3 would have been about 1/3 in height, but if the right percentage is 90%, it would be about 60-70% higher. 80% recovery has been assumed for tin and lead - according to the recycling facility. The height of these columns will not change dramatically if this recovery percentage varies within 5%, but a considerably higher recycling percentage would decrease the Sn-column significantly. For palladium and gold, it was stated that close to 100% is recovered. 98% has been used as default. The Pd and gold columns are therefore much likely not underestimated. Possible higher recycling percentages would reduce the column heights. Altogether, especially the precious metals are sensitive towards fluctuations in recovery percentages. However, the major uncertainty is connected to metal recovery efficiency if other recycling facilities were considered, especially if one of the metals is not recovered at all. Altogether, the overall result may be affected in both directions by variations in recycling percentages.
- Joining material consumption. Data on solder paste are measured with high accuracy and therefore assumed accurate within a few percentages, whereas the adhesive consumption is estimated. The estimation is based on the assumption that by weight about 1/5 of the solder paste amount is needed. This is done according to own estimations and information from several other sources. The adhesive consumption is therefore considered pretty reliable (for optimised adhesive technology).
- Metal consumption for component termination. It has been very difficult to get reliable data on metal consumption for component termination. Further, termination amounts differ a lot between component types. The silver consumption for component termination is thus far more uncertain as compared to the silver consumption for adhesive. Further, silver for component termination accounts for about 69% of the silver difference between the alternatives. For palladium, which estimate is also very uncertain, it account for the entire difference. Altogether, it is assumed that the palladium figures (and thereby directly column height) may vary by a factor five. Silver figures may vary by up to a factor three and affect the silver column height by about a factor two. Tin and lead figures for component termination have been estimated based on an assumed distribution between solder material and component termination found in several references. These consumptions are assessed far more reliable than the precious metal consumptions.
- Metal consumption for PCB’s. As can be seen from Figure 7.3 the assessment is far more sensitive to the tin consumption in the soldered alternative than to the gold and

nickel consumption in the adhesive alternative. The tin (and lead) consumption has been estimated based on an assumed distribution between solder material and PCB Hot Air Surface Levelling found in literature references. On average it is therefore considered pretty reliable. Uncertainties in PCB consumption figures are therefore assessed not to affect the overall result considerably. However, for special PCB designs (with a low packaging densities), the tin consumption may be underestimated.

Summary – SMT-scenario - Resources
Consumption of metal resources by far dominate over consumption of energy resources. Especially silver, tin and to some extent palladium are of importance.

Altogether, the results are too imprecise to show a significant difference between the alternatives, though the results indicate a more severe consumption of resources in the adhesive alternative.

The major uncertainties are:
- EDIP weighing factor for silver (may increase weighting factor by about a factor three)
- loss of precious metals in early parts of the life cycle (component, adhesive and PCB manufacturing) may increase net palladium consumption by up to a factor five, silver consumption by about 2/3 and tin consumption by about 50%
- palladium and silver content in component terminations (for Pd the uncertainty and thereby net consumption is assessed to be a factor 5, whereas for silver the uncertainty is assessed to be up to a factor three affected the consumption by about a factor two)
- recovery percentages, especially for silver (may affect silver consumption by about 2/3)
- other recycling technologies than the assumed may dramatically affect the result, especially if one of the metals is not recycled at all

7.2.2 Danfoss scenario

This scenario differs from the SMT scenario with respect to the following parameters:
inclusion of the wave soldering step for EST-sold and the equivalent EST-adh processes
measured/scaled adhesive consumptions is used
component termination is not assumed to differ (SnPb-termination was also used for EST-adh)

The result of the resource assessment can be seen in Figure 7.4.

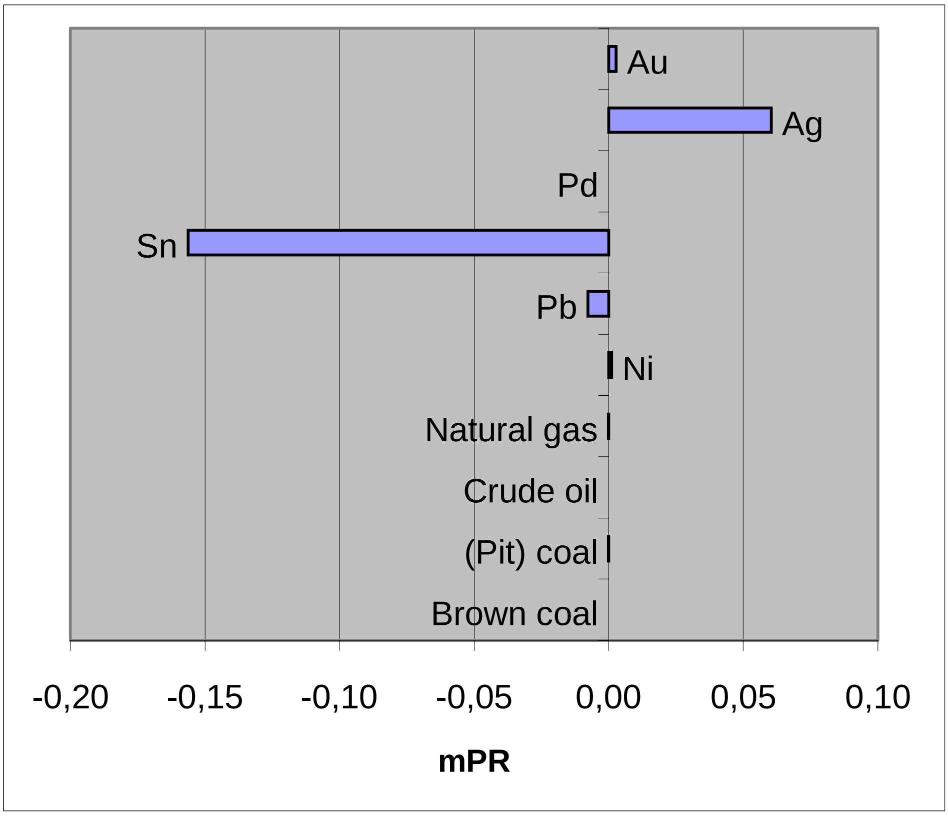

Figure 7.4: Resource weighting (EST-adh minus EST-sold) – Danfoss scenario

As for the SMT scenario, the metals and in particular tin and silver are dominating. For silver, about 45% of the column height is due to losses during manufacturing (the remaining losses during recycling), whereas only about 3% of tin column represent losses during the production phase. The losses may be decreased in case of larger production series.

Based on the figure, the solder alternative seems to be worse.

However, as for the SMT scenario, there are some major uncertainties. Especially the EDIP weighting factor for silver and metal recovery efficiencies (e.g. other recycling facilities) may affect the assessment.

Losses of silver during adhesive manufacturing (assuming 10% loss) would increase the overall silver consumption by about 50% (doubling the part of the silver column which is not represented by loss during production). Losses of tin during PCB and solder manufacturing (assuming 10%) would increase the net consumption by about 50%.

Another uncertainty of importance for this scenario is the metal consumption for Hot Air Levelling PCB surface. The amount, which contributes by 44% of the tin difference, is estimated based on scaling the weight and assumption of layer thickness. The uncertainty is assumed to be in the range of a factor two.

Summary – Danfoss-scenario - Resources
Consumption of metal resources by far dominate over consumption of energy resources. Tin and silver are dominating in between the metals.

Altogether, the results are too imprecise to show a significant difference between the alternatives, though the results indicate a more severe consumption of resources in the solder alternative.

The major uncertainties are:
- EDIP weighing factor for silver (may increase weighting by a factor three)

- Recovery percentages, especially if other recycling technologies (not recycling one or more of the metals) were applied
- Loss of silver and tin in the raw material phase (may worst case increase the net consumption by 50%)

Care should be taken not to generalize the results of the Danfoss scenario, because:
- The adhesive consumption for fastening the relay was very high. That type of component would most obviously not be fastened by adhesive in a 'real production case'. Therefore the adhesive consumption for a substitution of wave soldering with an adhesive process would most obviously result in considerably less adhesive consumption – reducing the silver column in Figure 7.4.
- It is highly questionable whether full scale adhesive production would be carried out with SnPb-terminated components. Application of AgPd-terminated components would increase the consumption of precious metals for the adhesive alternative.
- Differences between through-hole components and equivalent SMT components have not been investigated. This may affect the results considerably.
- The applied PCB may not be representative as the packaging density may vary considerably.

In other parts of the project, it has been assessed whether a severe increase in adhesive application will considerably affect the global silver consumption and thereby potentially silver prices and the scarcity of silver [3].

7.3 Results - External environment

According to EDIP the following environmental parameters have been included:
- Global warming
- Acidification
- Nutrient enrichment
- Photochemical ozone formation (photosmog)
- Bulk waste
- Hazardous waste
- Slag and ash
- Human toxicity via air
- Eco-toxicity, acute
- Persistent toxicity[6]

The following figures will show the weighted results. The weighting principle in EDIP is based on a comparison with politically set target for pollution prevention (see [24] for further explanation). The unit for this weighting is (milli) Person Equivalent Target (mPET).

The weighting method is rather subjective and although, the included environmental impact effects have the same unit, they should not directly be added between effect categories, but can be used as an indication of 'what is big and what is small'.

As pointed out earlier, the assessment methodology for toxicity is rather uncertain and results should therefore be taken with caution.

Disposal of the hazardous waste is modelled by two scenarios. The first scenario assumes the metal waste to be an amount of hazardous waste (named HW = Hazardous waste) and the second assumes that the entire metal content – with time – will leak to the environment surrounding the waste disposal site (named TH = Time Horizon). The "true" situation can be assumed to be somewhere in between these two extremes.

7.3.1 SMT-scenario (disposal scenario: HW)

Figure 7.5 shows the weighted result comparing the two alternatives (EST-adh minus EST-sold).

[6] covering human toxicity via water and soil and eco-toxicity via soil and chronic eco-toxicity via water

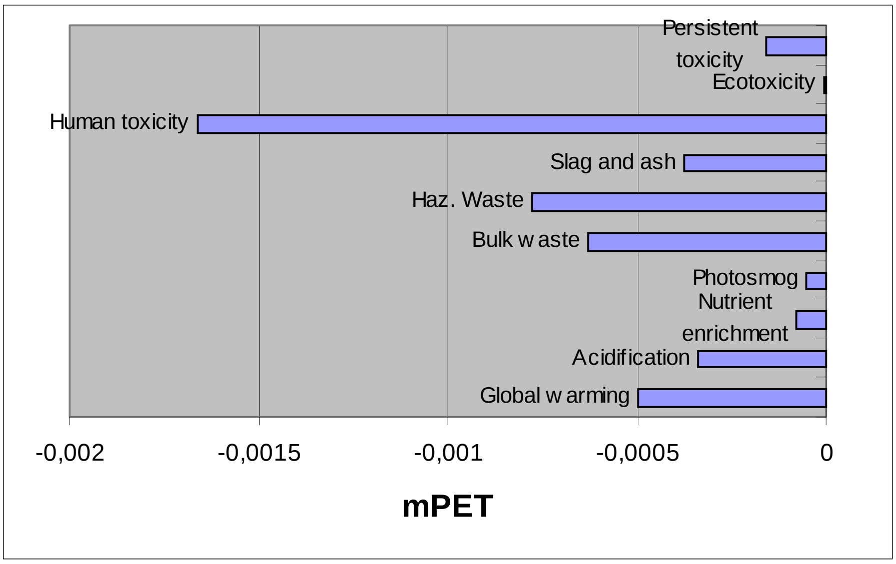

Figure 7.5: Weighted result (EST-adh minus EST-sold) – SMT scenario (HW)

The figure indicates the adhesive alternative to be better for all impact categories. However, the results are uncertain.

Energy related impact categories
Energy consumption is the only (or major contributor) to the impact categories *global warming, acidification, nutrient enrichment, bulk waste as well as slag and ash.* The same interpretation as in the energy analysis (see [2]) can therefore be made for these impact categories, i.e. *differences between the alternatives are not significant.*

Photosmog
Contributions to the effect category 'Photosmog' comes from Volatile Organic Compounds (VOC's) emitted by combustion of fossil fuels or from manufacturing, handling or applying solvents. About 80% of the photosmog column comes from the difference in solvent emission in the production phase. Specific data on solvent emissions in the raw material phase have not been obtained. However, from the APME epoxy data, it can be seen that 5,8 g of hydrocarbons are emitted per kg epoxy. If these are assumed to contribute by an average photosmog potential (POCP=0,3) for solvent, it will only affect the result by 8%. Further, more solvent - and thereby much likely more emissions of solvents in the raw material phase – are used for the solder alternative. *It is therefore assessed that the solder alternative is worse in relation to photosmog formation.*

Hazardous waste
Most of the column representing hazardous waste in the figure results from the recycling step. It is larger for the soldering alternative due to the higher metal consumption in the solder alternative and due to the lower recycling percentages for tin and lead. Data on hazardous waste formation from several of the raw material processes have not been obtained. However, it is assumed to be higher for the solder alternative as larger amounts of materials have been used. *It is therefore assessed that the solder alternative is worse regarding hazardous waste.*

Toxicity
The toxicity parameters are difficult to interpret because there are uncertainties connected to the method. Among others, LCA toxicity potentials does not reflect 'real' but rather 'potential' impact. Whether an estimated impact will really cause harm, very much rely the local environment (background concentration, total emitted amount and sensitivity of the receiving environmental media) to which an emission takes place.

In this LCA case, it has further been very difficult to obtain emission data connected with mining/refining, raw material manufacturing and recycling.

However, if Figure 7.5 is taken as a starting point, it can be shown that emission of the solder paste solvent (for emission purposes modelled as diethylene glycol mono-n-butyl ether) contributes by about 87% and lead emission from mining by about 7% of the difference (i.e. Figure 7.5 column heights) between the alternatives for the impact category ‘human toxicity’. The remaining difference in toxicity comes from energy production.

Due to the relatively low total amounts of solder paste solvent emitted from an SMT-line, it is questionable whether the emission of solder paste solvent will cause an impact. The same consideration can be made for the adhesive solvent. The adhesive solvent (which is confidential) has not been assigned a toxicity factor. Its main toxicity is irritation by inhalation, but with the emission amounts possible it will definitely not be able to cause any harm to humans in the environment surrounding an SMT plant.

Several toxic emissions are not included in the inventory data. Toxic emissiones may take place during manufacturing of epoxy, solvents, PCBs, components and joining materials, and during manufacturing of input chemicals for these processes. Toxicity impacts from these phases may severely affect the overall evaluation. However, as most solvents and most reactive polymers (acrylate for the solder PCB) is used in the solder alternative, emission from these productions will most likely increase the human toxic load for the solder alternative more than for the adhesive alternative. Further, because lead is by far the most human toxic of the metals included, air emissions of metals (in the raw material phase and during recycling) will disfavour the solder alternative. *Altogether, the solder alternative must be assumed to be the worse with respect to human toxicity.*

Persistent toxicity is difficult to interpret as it covers several toxic impact categories (see introduction to this section). In Figure 7.5 about 75% of the column height results from Pb air emission during mining. *It is not possible to judge whether emissions not inventoried will favour the one or the other alternative with respect to persistent toxicity.*

Ecotoxicity, can hardly be seen on the figure. However, possible silver emission to water (silver is by far the more ecotoxic metal) will severely affect the ecotoxic load for the adhesive alternative.

A sensitivity analysis was therefore carried out assuming that 1 g of metal is emitted to water for every 1 kg of virgin metal production (assumed for all metals). In that case, the assessment will turn out as depicted in Figure 7.6.

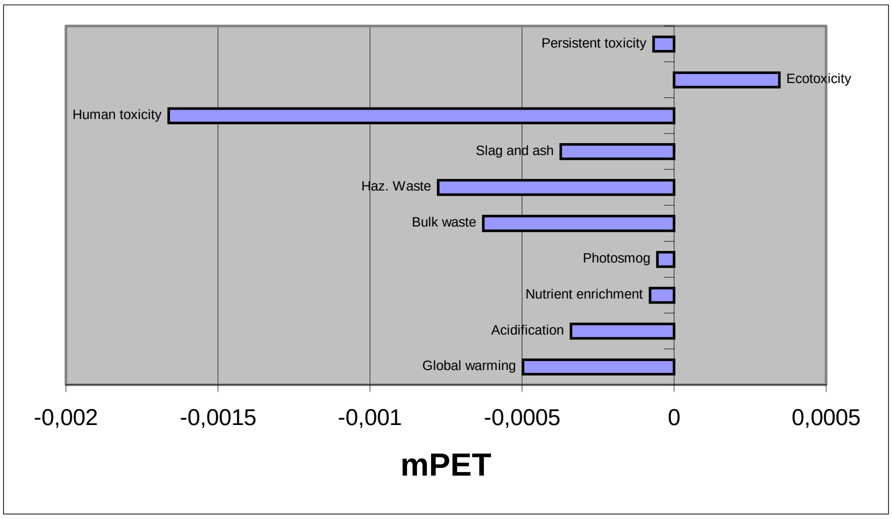

Figure 7.6: Weighted result (EST-adh minus EST-sold) – SMT Scenario (HW) – assuming metal emission to water during metal mining/refining

As can be seen, the silver ecotoxicity (acute water) disfavours the adhesive alternative. Further, it can be seen that the difference in persistent toxicity has now decreased slightly, indicating that chronic toxiocity of silver via water affects this parameter.

Silver emissions may also take place during component and adhesive manufacturing as well as in connection with recycling. That would further disfavour the adhesive alternative.

A sensitivity analysis was also carried out assuming 0,65 g metal air emission per 1 kg metal production (this figures was already included in the lead data). This assumption does not affect the results significantly.

Summary – SMT (HW)-scenario – External environment
The immediate result indicate, the adhesive alternative to be better for the impact categories: global warming, acidification, nutrient enrichment, bulk waste as well as slag and ash. However, as these impact categories heavily or entirely rely on the energy consumption, the result is not significant.

Photosmog formation (due to more emissions of solvents), hazardous waste formation (more recycle waste and more assumed waste in the raw material phase) and probably human toxicity (mainly due to lead emission and to some degree emission of solder paste solvent) are assumed worse for the solder alternative.

Ecotoxicity is assessed worse for the adhesive alternative (due to possible silver emissions to the water environment).

It cannot be judged for which alternative 'Persistent toxicity' is better or worse.

The toxicity aspect will be discussed further in the TH-scenario.

7.3.2 Danfoss scenario (HW)

Figure 7.7 shows the weighted result.

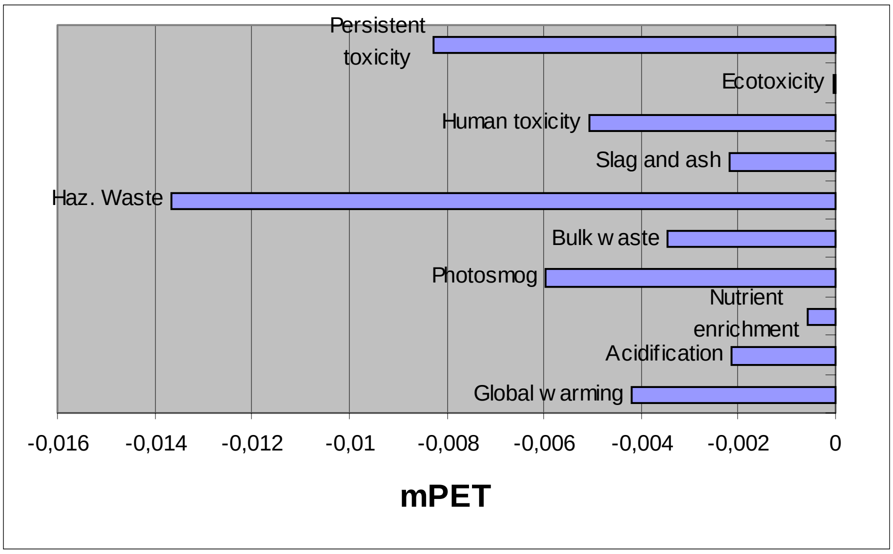

Figure 7.7: Weighted result (EST-adh minus EST-sold) – Danfoss scenario (HW)

The figure indicates, the adhesive alternative to be better for all impact categories.

Energy related impact categories
In this scenario, the impact categories associated with energy consumption; i.e. *global warming, acidification, nutrient enrichment, bulk waste as well as ash and slag, are judged to be significantly better for the adhesive alternative* (see energy analysis in [2]). For metal mining, where the energy system supplying the energy was not known, it has been assumed that the energy is delivered by oil combustion. It could be argued that different energy sources in between the metals would give incompatible emissions (energy supply systems differ to some extent in emissions), but by comparing with the energy analysis, the result must still be assumed to be significant.

Photosmog
For photosmog, the major contributor to the difference is the flux solvent of 2-propanol. *The solder alternative is thus the worse for photosmog formation.*

Hazardous waste
The hazardous waste fraction is even more significant in this scenario as compared to SMT (HW); also here because of the larger consumption and lower recovery percentages for tin and lead. *The solder alternative is thus assessed worse with respect to hazardous waste*.

Toxicity
According to Figure 7.7, human toxicity is worse for the solder alternative. About 30% of the difference is the result of emission of solder paste solvent, about 40% is lead emission form mining, whereas the remaining part results from energy consumption. *Similarly to the SMT (HW) scenario, but even stronger here, human toxicity is assessed to be worse for the solder alternative.*

About 75% of the difference in persistent toxicity results from emission of the flux solvent 2-propanol. Whether this emission will really cause any significant harm in the environment surrounding a production site is highly questionable. *Altogether, as for the SMT (HW) scenario, it is difficult to point out the worse alternative according to persistent toxicity*.

Figure 7.8 represent the situation where water emission of 1 g/kg virgin metal has been assumed.

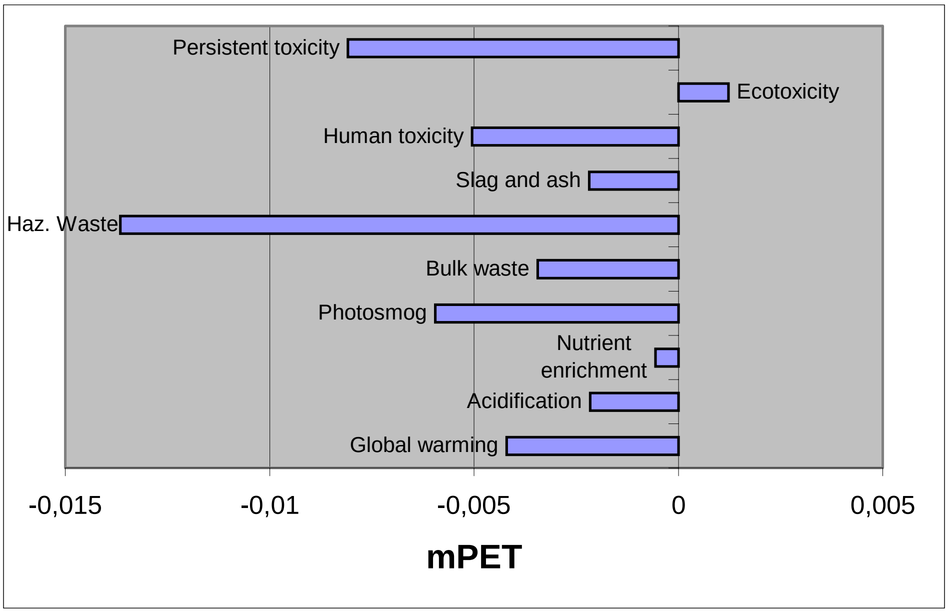

Figure 7.8: Weighted result (EST-adh minus EST-sold) – Danfoss (HW) - assuming silver and lead emission to water during virgin metal manufacturing

As for the SMT (HW) scenario, possible silver emissions to water will turn the ecotoxicity parameter to disfavour the adhesive alternative.

Summary – Danfoss (HW)-scenario – External environment
The Danfoss (HW) scenario shows that the adhesive alternative is the better concerning the energy related impact categories global warming, acidification, nutrient enrichment, bulk waste, as well as slag and ash, and it is also assessed better concerning photosmog (flux solvent emission), hazardous waste (big loss of tin and lead during recycling) and toxicity (mainly due to lead emission, but also due to energy consumption and solder paste solvent emission). It is not clear whether the persistent toxicity parameter is significant, whereas the adhesive alternative becomes worse regarding ecotoxicity, when silver emissions to water may appear during the life cycle.

Care should be taken not to generalize the results of the Danfoss scenario, because:

- It is highly questionable whether full scale adhesive production would be carried out with SnPb-terminated components [7]. Application of AgPd-terminated components would increase the consumption of precious metals for the adhesive alternative.
- Differences between through-hole components and equivalent SMT components have not been investigated. This may affect the results considerably.
- The applied PCB may not be representative as the packaging density may vary considerably.

7.3.3 SMT scenario (TH)

The TH (Time Horizon) disposal scenario models the situation, where it is assumed that the not recovered metals with time will leak to the surrounding environment.

Figure 7.9 shows the weighted result assuming that the metals end up in the soil environment.

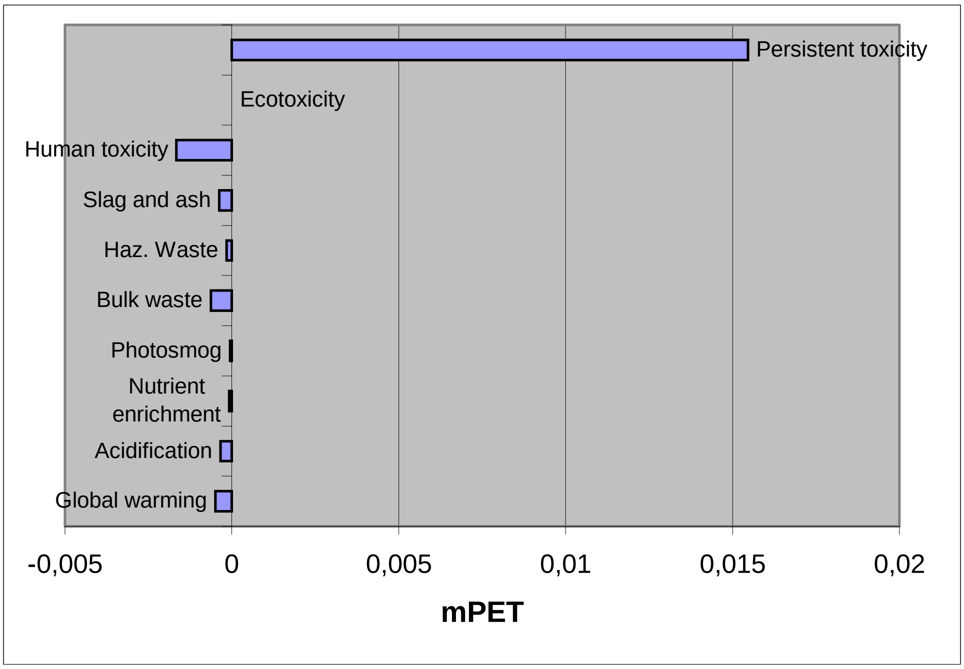

Figure 7.9: Weighted result (EST-adh minus EST-sold) – SMT scenario (TH-soil)
Although care should be taken when comparing in between impact categories, there is no doubt that the impact category 'persistent toxicity' has become dominant.

This is because of the assumed silver eco-toxicity in soil.

Figure 7.10 shows the result where the metals are assumed to end up in the water environment.

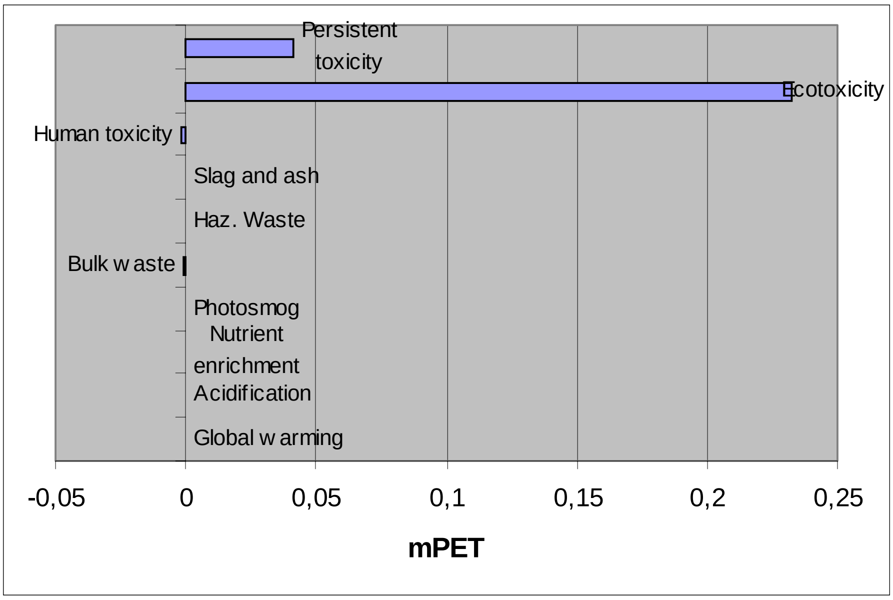

Figure 7.10: Weighted result (EST-adh minus EST-sold) – SMT scenario (TH-water)

Now the ecotoxicity parameter has become the dominant and again it is the silver toxicity that triggers the result.

Persistent toxicity is still high due to the expected chronic toxicity of silver in water. However, when going in more details with the data behind the figure, it can be seen that lead is pulling in the other direction (by about 1/3 of the silver value!) due to the chronic eco-toxicity potential of lead in water.

7.3.4 Danfoss scenario (TH)

Figure 7.11 shows the weighted result when assuming the metals to end in the soil compartment.

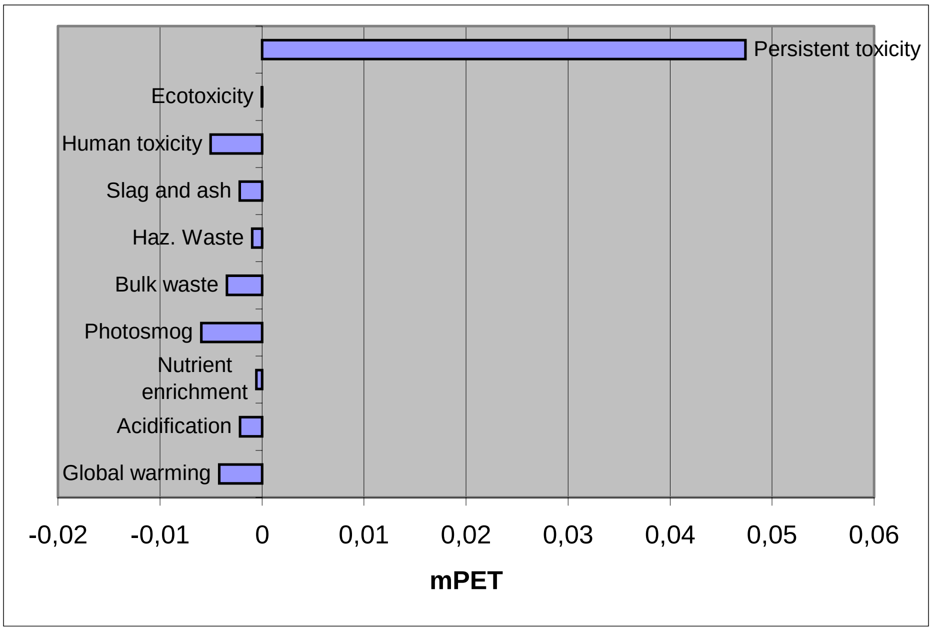

Figure 7.11: Weighted result (EST-adh minus EST-sold) – Danfoss scenario (TH-soil)

As for the SMT scenario, it can be seen that the expected silver eco-toxicity in soil, heavily influence the assessment.

Figure 7.12 shows the weighting by assuming metal leaking to water.

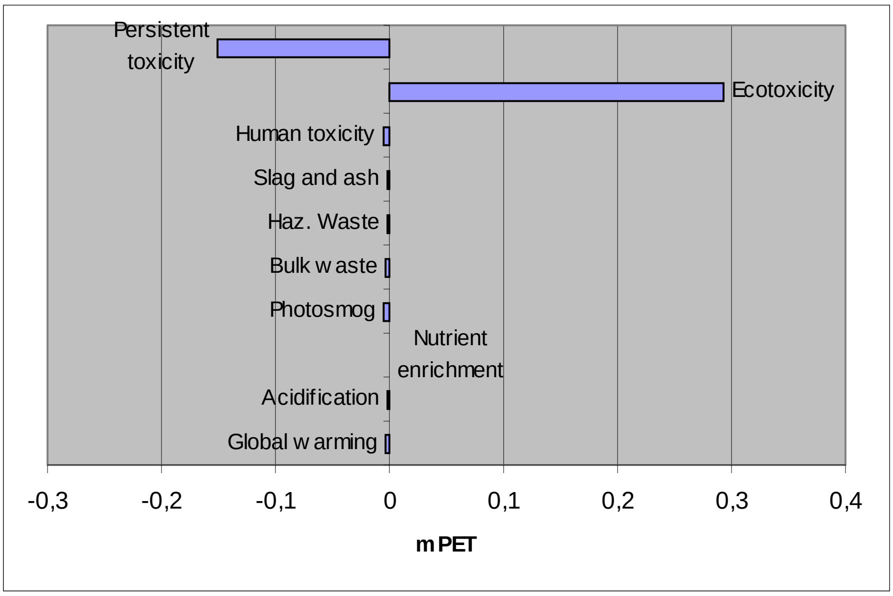

Figure 7.12: Weighted result (EST-adh minus EST-sold) – Danfoss scenario (TH-water)

As compared to the SMT scenario, the relative difference between lead as compared to silver emission has increased (the wave soldering step requires substantial lead amounts and silver content in components is not assumed to differ). Therefore, the persistent toxicity of lead now dominates over silver. Further, when looking into the figures behind the ecotoxicity column, it can be seen that silver contributes by about 1,16 mPET, whereas lead with about 0,90 mPET, i.e. in reality no significant difference. It is however clear that the ecotoxicity parameter is important for both alternatives, if the waste can be assumed to leak to water.

Summary on the SMT and Danfoss scenarios (TH) – external environment
It is clear from the above discussion that the potential risk connected with waste containing silver and lead is substantial as compared to other life cycle impacts. However, actual risk will depend on the bio-availability; i.e. the dose/exposure that can be found in the environment. Among other things (under most conditions), both metals are assumed to be bound firmly in soil layers. However, the environmental fate of the metals is uncertain and no definite conclusion can be drawn here. These issues are discussed in more detail in other parts of the Kamille project [5].

Especially the behaviour of silver is interesting, as silver's eco-toxicity may heavily influence the conclusions. However, with today's knowledge, it is difficult to state, whether silver leaking from (hazardous) waste sites may cause substantial risks. In other parts of the life cycle (e.g. during component and adhesive manufacturing), potential silver emissions (especially to the fresh water environment) may severely affect the result of the LCA.

Occupational health
Only chemical impacts will be considered as other occupational impacts like e.g. noise and physical impacts are estimated not to differ significantly between the alternatives.

No information was obtained about chemical exposures in the life cycle phases outside Danfoss. Considerations about impacts in these phases are therefore qualitative and only an indication of potential impacts can be outlined (see [2]). An occupational health assessment for production of the two alternatives has been carried out at Danfoss. The assessment can be found in chapter 6.

7.4 Conclusion and Recommendations

Based on the present LCA, it cannot be judged whether adhesive technology is better or worse than solder technology. The available data on material consumption and emissions during the life cycle are too uncertain. Further, in relation to toxicity, which is a crucial impact category in this assessment, too little is known about the actual environmental fate of metals leaking to the environment from waste steams.

More specific conclusions may be drawn in relation to some of the impact categories. These are described below along with description of the major uncertainties.

Resources
The assessment showed that the weighted metal values and especially silver, tin and palladium consumption dominates consumption of energy resources by several orders of magnitude.

However, it has not been possible to judge between the alternatives, because of the following major uncertainties:

- evaluation of the scarcity of silver (different references vary by a factor three)
- consumption of silver and palladium in component termination for adhesives is very uncertain
- uncertainty about recovery percentages during recycling – especially application of different recycling technologies than the one considered, may heavily affect the result
- metal losses during manufacturing processes have not been included, but may to some extent affect the evaluation

A very interesting finding was that the component termination may account for a larger difference in silver consumption than the adhesive itself.

External environment
Toxicity is assessed to be the potentially major impact category concerning external environment.

It has major influence on the result how big metal emissions to the environment are and how the environmental fate of metals in hazardous wastes is assessed. Especially, the inherent ecotoxicity of silver is crucial. However, the knowledge of silvers behaviour in the environment is at the moment too weak to really quantify the risks connected to (hazardous) waste disposal of silver containing waste. Also the fate of lead affects the assessment.

For both the SMT and Danfoss scenarios, it is assessed that the solder alternative potentially is the worse in relation to human toxicity and the adhesive alternative potentially in relation to exotoxicity. Human toxicity is mainly affected by lead emissions and possibly to some extent by solder paste solvent emission during production and ecotoxicity mainly by silver emissions.

Both for the SMT and Danfoss scenarios, photosmog and hazardous waste generation are assessed worse for the solder alternative. For the Danfoss alternative especially because of substitution of the flux solvent emission during wave soldering.

For the energy related impact categories (global warming, nutrient enrichment, acidification, bulk waste as well as ash and slag generation), it is not possible to judge between the alternatives with the available data for the SMT scenario. For the Danfoss scenario, the solder alternative is assessed significantly worse due to the energy requirement for the wave soldering process.

Finally, it should be stressed that care should be taken not to overinterpret results from the Danfoss scenario, mainly because it has a pretty special print layout and differences in components are not considered.

Occupational health
An occupational health assessment at Danfoss showed that both alternatives can be produced with potential low risk, if proper care is taken. For other parts of the life cycle, it has not been possible to judge which alternative is preferable based on the available information.

Recommendations
The study has lead to the following recommendations in relation to manufacturing and emission handling:

- Use components with as little silver and palladium termination as possible
- Optimise adhesive consumption (for SMT about 1/5 as compared to solder paste amount)
- Assure high recovery percentages for the metals during recycling and reduce losses during manufacturing operations
- Assure proper treatment of hazardous wastes
- During production: avoid skin contact with solder paste, flux and adhesives and avoid inhalation of solvent vapours and lead fumes (see also more specific guideline in other parts of the project [4])

8 Test of electrical conductive adhesives

The present test is a quality assessment of 13 electrical conductive adhesives from ten different manufacturers. The variants include adhesives based on epoxy and silicone with silver or carbon particles. Further adhesives with silver on aluminium particles and silver on copper particles were included. The adhesives have been tested on four different substrates; ceramic and polyester substrates with silver conductors and FR-4 substrates with gold over nickel and tin lead conductors. The components attached to the substrates had silver palladium and tin-lead finish on the terminals.

The test programme included environmental testing of the component to substrate connection. A lead-free solder paste was tested as a reference.

The interconnection resistance was tested before and after all environmental exposures, and the shear strength was tested initially and after the final exposure.

8.1 Survey of electrical conductive adhesives tested

The tested electrical conductive adhesives are shown in *table 8.1 (*The information is from the manufacturer's datasheet).

- 6 electrical conductive adhesive variants, nos.1, 2, 3, 4, 5 and 6, are epoxy with silver particles, all 1-component except for variant no. 6 which is a 2-component adhesive.
- 1 variant, no. 7, is 'thermoplastic' 1-component electrical conductive adhesive with silver.
- 1 variant, no. 8, is 'thermoset' 1-component electrical conductive adhesive with silver.
- 3 electrical conductive adhesive variants, nos. 9, 10, and 11, are silicone, variant no. 9 is a 2-component adhesive with silver, variant no.10 is a 2-component adhesive with silver-plated aluminium particles and variant no. 11 is a 1-component adhesive with silver-plated copper particles.
- Two 1-component variants have carbon particles, one with epoxy, variant no. 12 and one with 'polymer', variant no. 13.
- No further specification was found for the thermoset, the thermoplastic, and the polymer variants, variant nos. 7, 8, and 13 respectively.
- Variant no. 14 is a lead-free solder paste (Sn / 3.8 Ag / 0.7 Cu), and is tested as a reference.

8.2 Survey of test substrates

Four different substrate types were included in the investigation:

1. Alumina (thickfilm) substrate with thickfilm silver conductors (Manufactured by Grundfos A/S)
2. Polyester substrate with polymer silver (Ag) conductors (Manufactured by Mekoprint A/S)
3. FR-4 printed circuit board with gold over nickel (Au/Ni) finish, on copper conductors (Manufactured by Bent Hede Elektronik A/S)
4. FR-4 printed circuit board with tin lead (Sn/Pb) finish, on copper conductors (Manufactured by Bent Hede Elektronik A/S)

The same layout was used for all four substrate types.

Description of the different test pattern is given in section 8.10.

TABLE 8.1 List of adhesive variants.

No.	Manufacturer	Type/ Material	1 / 2-comp.	Conductive particles	Storage/ shelf life	Pot life	Curing	Tg °C	Best suited application
1	Emerson & Cuming	Amicon CE 3511/ Epoxy	1	Silver	-18 to –25°C/6 months	18 to 25°C/ >2 weeks	100°C/1 h 120°C/45 min. 150°C 20 min.		Dispensing
2	Ablestik Electronic	Ablebond 8175A/ Epoxy	1	Silver	-10°C/6 months -40°C/1 year		150°C/3 min.	80	
3	Namics	XH9626/ Epoxy	1	Silver	-20°C/>3 months	Min. 15 days	150°C/30 min. 180°C/10 min.	120	Stencil or screen printing
4	Loctite Corporation	3880/ Epoxy	1	Silver	-20°C to 0°C		95°C/45 min. 125°C/10 min. 150°C/6 min. 175°C/3 min.	64	
5	Loctite Corporation	3882/ Epoxy	1	Silver	-40°C/1 year	25°C/3 h	25°C/24 h 65°C/2 h 110°C/1 h 150°C/15 min.	-10	
6	Epoxy Technology	Epo-Tek H20F/ Epoxy	2	Silver	Room temp./1 year	4 days	100°C/1 h 120°C/20 min. 150°C/10 min	<20	Screen printing
7	Multicore	M-4030-SR/ Thermo-plastic	1	Silver	25°C/6 months		35°C/min. up to 175°C/15 min.		Dispensing and screen/ Stencil printing
8	Acheson	Electrodag SMD 10/ Thermoset	1	Silver	-15 to –20°C/6 months		120°C/1.5 h		Dispensing
9	Wacker Chemie GmbH	Semicosil 970 EC/ Silicone	2	Silver	5 to 30°C/6 months	>6 h	150°C/30 min.		
10	Tecknit	72-00236/ Silicone	2	Ag on Al	9 months	25°C/4 h	Room temp./168 h		
11	Tecknit	72-00151/ Silicone	1	Ag on Cu	9 months	25 min.	Room temp./168 h		
12	Creative Materials Inc.	106-22/ Epoxy	1	Carbon	25°C/1 month -10°C/1 year		150°C/15-30 min.		
13	Creative Materials Inc.	107-25/ Polymer	1	Carbon	25°C/6 months -10°C/1 year		Room temp. plus 175°C/5-10 min.		
14	*Multicore-SOLDER*	*96SCMX39 AGS88.5/ SnAgCu*	-		*5-10°C/6 months*		*Compare with datasheet*		*Ag 3.8 / Cu 0.7*

8.3 Survey of the mounted components

Three different passive components and two different active components were mounted on the test substrates.

8.3.1 Passive components on each substrate variant

0603 0-Ω chip resistors for contact resistance measurements:

- 23 resistors with Sn/Pb terminal finish (21 for the ceramic substrate)
- 23 resistors with Ag/Pd terminal finish (21 for the ceramic substrate)

Distance between terminals: Sn/Pb 0.95 mm and Ag/Pd 1.10 mm.

1206 0-Ω resistors for the shear test:

- 16 resistors with Sn/Pb terminal finish, shear test was performed on 7 resistors initially and 7 resistors after the final environmental exposure.

- 16 resistors with Ag/Pd terminal finish, shear test was performed on 7 resistors initially and 7 resistors after the final environmental exposure.

Distance between terminals: Sn/Pb 2.45 mm and Ag/Pd 2.50 mm.

3 surface mount electrolyte capacitors with tin lead finish, for shear test.

8.3.2 Active components on each substrate variants

- samples LQFP, 44 leads Plastic low profile quad flat package (Pitch: 0.8 mm, with smallest insulation distance of 0.45 mm between terminals. Terminal plating: Sn/Pb).
- 4 samples SO 28 Plastic small outline with 2 times 14 leads (Pitch: 1.27 mm, with smallest insulation distance of 0.80 mm between terminals. Terminal plating: Sn/Pb).

Both types for visual inspection of the interconnections between the leads and the substrate finish, flow-out or reduced insulation distance, short circuit and colour change.

8.4 Survey of the samples (adhesive/substrate)

Table 8.2 shows on what substrate, the electrical conductive adhesive variants have been tested.
- 3 variants and the solder reference were tested on ceramic substrate.
- 5 variants were tested on polyester substrate.
- 8 variants and the solder reference were tested on FR-4 with gold over nickel finish.
- 8 variants and the solder reference were tested on FR-4 with tin lead finish.

These gives 24 electrical conductive adhesive/substrate samples and 3 solder reference samples.
Passive and active components were mounted on each of the 24 + 3 test samples.
The solder reference variant no. 14 was not tested on the polyester substrate, as the polyester could not withstand the solder temperature. Therefore, there is no reference for the polyester substrate.
Variant no. 2, Ablebond, and variant no. 3, Namics, were tested on ceramic and both FR-4 substrates, and variant no. 4, Loctite (3880), was tested on polyester and both FR-4 substrates. The other variants were either tested on the ceramic, the polyester or on the 2 FR-4 substrates.

8.5 Survey of the mounting process

The mounting process was done in the same way for all variants although variants, which were not suitable for stencil printing due to low viscosity, were dispensed.

8.5.1 Stencil printing of adhesives/solder paste

A manual stencil printer with stainless steel squeegees (100 μm stencil) was used for contact printing (i.e. the stencil is placed on the substrate during the process). The electrical conductive adhesives/solder paste was applied on the stencil and with the squeegee. The electrical conductive adhesive/solder paste was screened by hand through the opens in the stencil. The opens in the stencil in percentage of the footprint were 100%.

8.5.2 Dispensing of adhesives

A KEPRO 210B dispenser with 0.4 mm needle (1.7 bar pressure) was used. The electrical conductive adhesives were applied onto the test boards with a handheld dispenser activated by a footswitch.

8.6 Component mounting

The components were mounted by means of a KEPRO 210B vacuum tweezer. All components were mounted in the electrical conductive adhesive/solder paste by the handheld vacuum tweezer. Due to the hand-mounting, the mounting force could not be identical from component to component, which may give greater variations in the contact resistance measurements and the shear test for each variant as if the components were machine mounted. The printing, dispensing, and the mounting procedure were performed by the same person for all the variants.

8.7 Curing / soldering

A box oven with air circulation was used for the curing. All variants were cured just after the mounting process, according to the manufacturer's cure times (compare with table 8.1).

8.8 Cleaning

Cleaning was made by means of 2-propanol Acetone and compressed air. The screen and squeegee were wiped off with 2-propanol followed by Acetone applied on absorption paper. Finally, the opens in the stencil were blown clean with compressed air. The cleanliness of the stencil was inspected in microscope after each cleaning process to assure that no forcing materials are present before applying a new variant on the stencil.

8.9 Test plan

The test plan is shown on Figure 8.1.

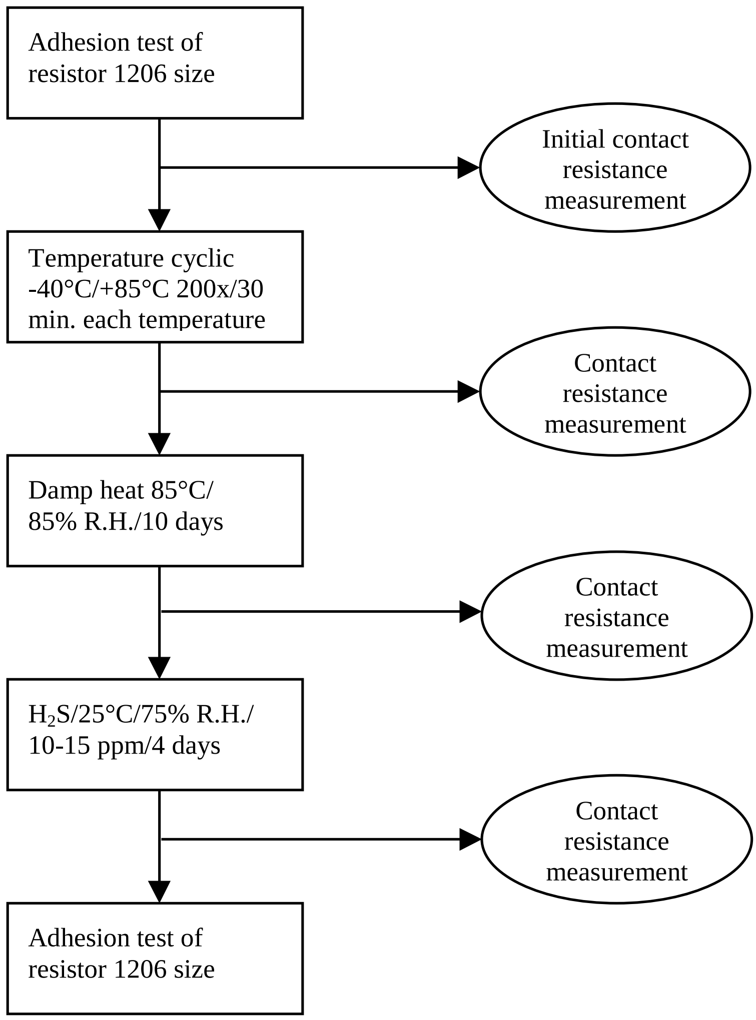

Figure 8.1 KAMILLE test plan.

8.10 Description of the tests

8.10.1 Adhesion test

The intention was to make the adhesion test with a mandrel; this test however requires a hole beneath the component in order to push the mandrel through. This is unlikely to perform on production boards (substrates). Therefore the values from a mandrel test will be stand-alone values. To be able to compare the adhesion test performed in this project to what is possible on production boards, it was decided to perform the adhesion test as a shear strength test.

Adhesion test was performed as a shear strength test, like MIL-STD 883C method 2019.2 of 1206 resistors with both Ag/Pd and Sn/Pb component finish.

Seven resistors of each terminal finish were shear tested initially and after the H_2S exposure.

The test substrate layout is shown on Figure 8.2 with letters related to each test pattern described below.

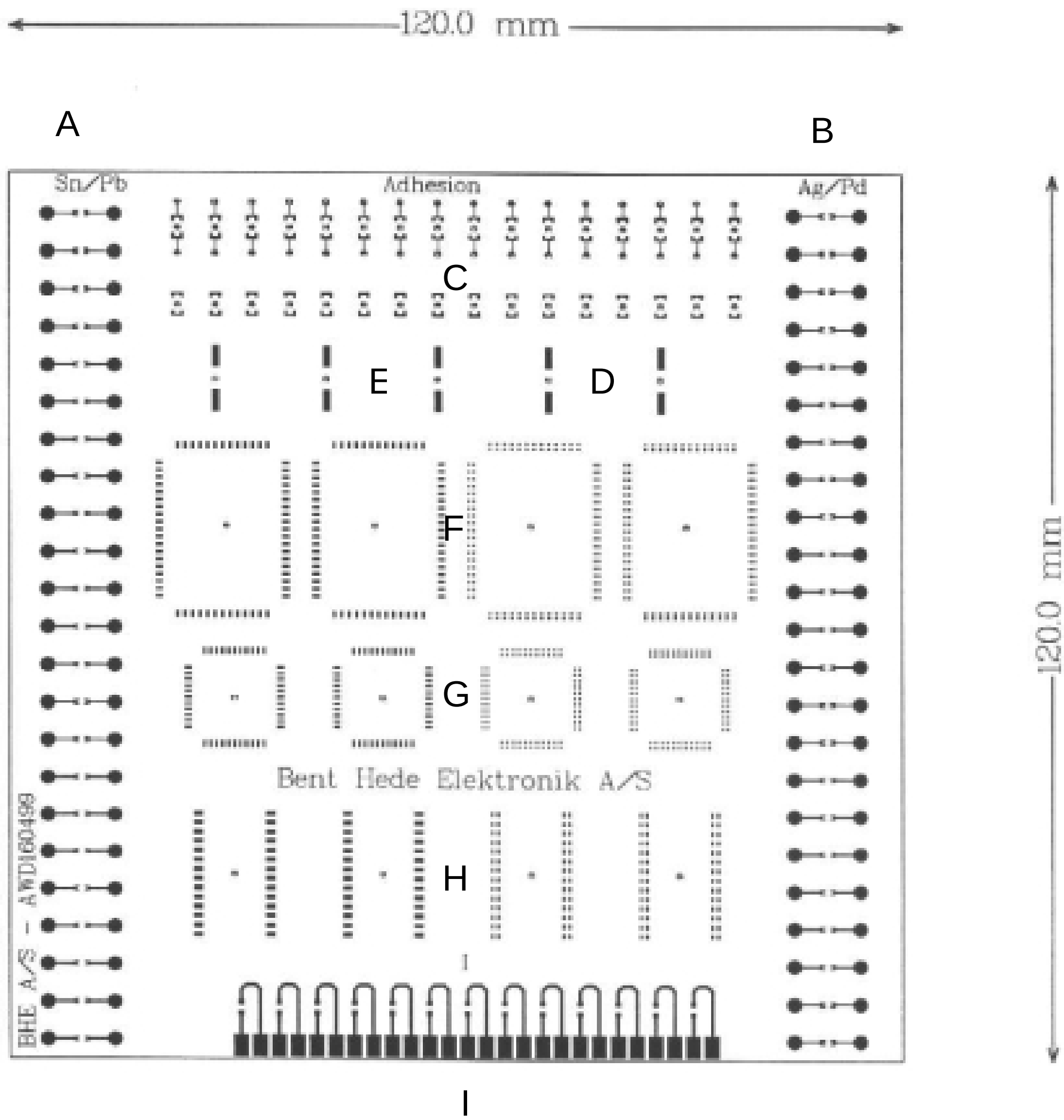

Figure 8.2 Test patterns on test substrate.

Test pattern A: Left side of the substrate
Mounting of 23 0-Ω 0603 resistors with tin lead on nickel barrier finish for 4terminal contact resistance measurement.

Measurement through 1) Substrate conductor – 2) Adhesive – 3) Component terminal – 4) Component – 5) Component terminal – 6) Adhesive – 7) Substrate conductor, where the resistance of the substrate conductor, component terminal, component, and interface between component terminal and component are assumed to be constant throughout the test programme leaving the adhesive and its interface to the substrate and to the component terminal to vary.

Test pattern B: Right side of the substrate
Mounting of 23 0-Ω 0603 resistors with silver palladium finish for 4-terminal contact resistance measurement.
Measurement through 1) Substrate conductor – 2) Adhesive – 3) Component terminal – 4) Component – 5) Component terminal – 6) Adhesive – 7) Substrate conductor, where the resistance of the substrate conductor, component terminal, component and interface between component terminal and component are assumed to be constant throughout the test programme leaving the adhesive and its interface to the substrate and to the component terminal to vary.

Test pattern C: Middle/top of the substrate
Mounting of 16 0-Ω 1206 resistors with silver palladium finish and 16 0-Ω 1206 resistors with tin/lead on nickel barrier finish for shear test initially and after final the environmental exposure.
The footprint could not be used for shear test of soldered components, as there was no space for a solder meniscus on the footprint.

Test pattern D: Footprint for surface mounting of 3 electrolyte capacitors (from the Danfoss A/S case)
The electrical conductive adhesive/solder joint was visually inspected initially and after test exposure for degradation, colour change, cracks, etc.

Test pattern E: Footprint for 4 SOT319-1, Plastic quad flat package (QFP44)
Pitch: 1.0 mm.
The component was not available from the vendor. The printing on the footprint was visually inspected for printing quality, short circuit, degradation, colour change, cracks, etc.

Test pattern F: Footprint for 4 SOT389-1, low profile quad flat package (LQFP44)
Pitch: 0.8 mm.
The electrical conductive adhesive/solder joint was visually inspected initially and after test exposure for short circuit, degradation, colour change, cracks, etc.

Test pattern G: Footprint for 4 SOT136-1, plastic small outline package (SO28)
Pitch: 1.27 mm.
The electrical conductive adhesive/solder joint was visually inspected initially and after test exposure, for short circuit, degradation, colour change, cracks, etc.

Test pattern H: Middle/bottom of the substrate
Electrical conductive adhesive/solder paste was printed on and between the footprint making a short circuit with the adhesive/solder paste.
5 of the short circuit pattern was 4-terminal contact resistance measured before and after each environmental exposures.
After the final contact resistance measurements one of the short circuit pattern was current/temperature tested.

Test pattern for insulation resistance/silver migration
Insulation resistance / silver migration of electrical conductive adhesives has been investigated in a previous report [27]. The result from this report stated that: No migration or indication of migration could be identified using microscope up to 100x enlargement.

This was in general the result for all adhesive variants. The no-migration result was confirmed by the insulation resistance measurements.

The no-migration results are, however, valid as long as the adhesive media encapsulates the silver particles.

Migration of the silver conductors on both the ceramics and the polyester substrate is beyond this project and has therefore not been investigated.

An investigation of silver migration of min. 10 μm electroplated silver on copper conductors is found in [28].

8.11 Current - temperature

The results after the current/temperature test are shown in table 8.2.

To have adhesive joint heated up to 105°C in equipment will not be suitable for most applications, and will reduce the reliability of the whole equipment if not cooled. Therefore, the electrical conductive adhesives must be used with low currents and cannot be recommended for power use without cooling.

In table 8.2 it is seen that highest current values are found for the ceramic substrates, this was expected due to the temperature coefficient of ceramic substrates.

TABLE 8.2 Current – temperature measurement of the electrical conductive adhesive as a short circuit.

Var. no.	Name	Type	Substrate	40°C	85°C	105°C	Comments
1	Amicon	EC3511	Ceramic	0.6	1		Burned open at 1 amp.
2	Ablebond	8175A	Ceramic FR-4/Au FR-4/Sn	1.7 1.3 1.1	3 2.1 2	3.5 2.4	Burned open at 2 amp.
3	Namics	XH9626	Ceramic FR-4/Au FR-4/Sn	2.2 1.55 1	3.5 2.7 1.5	4 3 1.8	
4	Loctite	3880	Polyester FR-4/Au FR-4/Sn	x 1 0.58	x 1.55 1	X 1.7	Burned open at 1 amp.
5	Loctite	3882	Polyester	x	x	X	
6	Epo-Tek	H20F	Polyester	x	x	X	
7	Multicore	M4030SR	FR-4/Au FR-4/Sn	1.1 1.4	1.8 2	2 2.3	
8	Acheson	SMD10	FR-4/Au FR-4/Sn	1.6 1.1	2.8 1.6	3.3 1.8	
9	Wacker	970EC	FR-4/Au FR-4/Sn				Too high resistor value Too high resistor value
10	Tecknit	72-00236	FR-4/Au FR-4/Sn				Too high resistor value Too high resistor value
11	Tecknit	72-00151	Polyester	x	x	X	
12	Creative	106-22	FR-4/Au FR-4/Sn				Too high resistor value Too high resistor value
13	Creative	107-25	Polyester	x	x	X	

The figures are in Amps.

8.12 Discussion

A very important parameter seems to be the component mounting pressure. A too high mounting pressure will tend the adhesive to flow-out, which may result in short circuit after the curing. On the other hand a too low mounting pressure may cause very high contact resistance of the interconnection.

Therefore, process optimising with electrical conductive adhesive may be a hard task.

The stencil printing was performed by hand as contact print with a stainless steel stencil. This may not be the most optimum process for large-scale production.

The use of snap-off printing with a polymer stencil or screen may give better printing results (recommended by Loctite). This has not been tested in this investigation, but should be considered.

Some flow-outs of the adhesives have been observed. This flow-out can be avoided by process optimising, either by reducing the stencil thickness or the printing area on the footprint. Reducing the stencil thickness will, however, result in a faster worn down of the stencil. Reducing the opens in the stencil may be a problem for the fine pitch components due to the distribution of the conductive particles in the adhesive during the printing process. With a sufficiently stirred adhesive with sufficiently small conductive particles this should not be a problem.

Regarding solder paste, it is even more important that the viscosity of the adhesives is constant over time and from lot to lot, as the self-alignment and the contraction effect are not present for the electrical conductive adhesives like it is for solder paste. The environmental humidity, which is an important parameter for solder paste, may not be as critical for the electrical conductive adhesive. This has, however, not been investigated. For the adhesive it is important that the adhesive will not create skin, especially from the printing process to the mounting process.

The visual inspection after the H_2S exposure has shown a colour change for all electrical conductive adhesives with silver and for the silver palladium component terminals. The colour has become dark or black; this is what could be expected for silver in hydrogen sulphide environment. This colour change may be expected over time for silver, as hydrogene sulphide is in the atmosphere.

Contact resistance for a component to substrate interconnection may depend on the circuit. Normally low contact resistance is required, but for components with relatively high input impedance (LCD display) a high resistance may be accepted.

Comparing the contact resistance values from the short circuit pattern with the values from the component mounted pattern, there is, in general, seen a somewhat lower standard deviation for the short circuit pattern.

It was assumed that this was due to the handmounting process, however if hand-mounting has caused the relative high standard deviation, handmounting of components in electrical conductive adhesives may be a serious problem. As a result of this, prototypes or engineering models with electrical conductive adhesives may first be manufactured after optimising the mounting process.

Single measured contact resistance and samples with no failure throughout the test sequence were observed.

The high standard deviation can therefore also be assumed to be due to an inhomogeneous distribution of the conductive particles in the adhesive after the curing process or due to different oxidation degrees of the surfaces to be glued.

The mounting process is assumed as follows: When the component is pressed into the adhesive the conductive particles will be pressed down as well, and stay there due to the gravity. This may result in less conductive particles on the top of the joint where the component is attached which may result in higher contact resistance. A high conductive particle density will of course minimise this effect.

The 2 kg and above limit for the shear strength test is estimated as an acceptable shear strength value for a 1206 chip resistor. The shear strength test is, as the contact resistance possible dependent on the hand-mounting process, and it will also be a question of mounting force contra flow-out of the adhesive.

In order to avoid the effect of shear strength of the electrical conductive adhesive, the components can be glued to the substrate with a non-conductive adhesive with high shear strength force value. This may, however, add an extra process to the production flow, if a dispenser for 2 adhesives is not used simultaneously.

The initial minimum shear force value may be due to the hand-mounting process, but may indicate that process optimising is necessary for a variant with minimum shear strength value below 2 kg.

For both contact resistance and shear strength the thickness of the adhesive joint is important, and the process optimising shall be related to this. Normally, a thin joint is preferred.

The curing time is important as well, if the manufacturer gives minimum times for the curing, due to the total processing time, and insufficient curing can result, this may give at higher contact resistance and a lower shear strength values.

Initially, the contact resistance was very high for some of the variants, but after the temperature cycling the contact resistance had decreased to 'normal'.

Due to the possibility of silver migration, it may be necessary to conformal coat circuits connected with electrical conductive adhesives. The reaction between a electrical conductive adhesive and a conformal coating must be reliability tested before production.

For the current/temperature test it shall be noted that the highest current values were found on the ceramic substrates, which was expected due to the temperature coefficient of the ceramic substrate. Power circuits with components connected with electrical conductive adhesives on FR-4 are not recommended, without cooling.

8.13 Comments to each electrical conductive adhesive variant

Comments to each electrical conductive adhesive variant are given below.
The conclusion below does not compare the actual measured contact resistance values, but only the increase of contact resistance from the initial value. This may give some variants a bad assessment even if the contact resistance is lower as a variant which have shown good results.

Variant no. 1, Amino CE 3511, tested on ceramic substrate with silver conductors
The adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were acceptable. However, it is seen from the calculated mean value that for the tin lead finish the resistance has been lower and the standard deviation higher compared to silver palladium finish.
Shear strength values were acceptable for both component finishes.

Variant no. 2, Ablebond 8175A, tested on ceramic substrate with silver conductors and FR-4 substrate with gold over nickel conductors and tin lead conductors
For the ceramic substrate the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were acceptable after temperature cycling but not after the humidity and H_2S exposure. A greater fall in contact resistance was measured after temperature cycling for both 0603 resistor types.
For the FR-4 substrate with gold over nickel plating the adhesive has shown good results after all environmental exposure as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.

For the FR-4 substrate with tin lead plating the adhesive has shown acceptable results after all environmental exposure as used as a short circuit. To connect 0603 resistors with silver palladium and with tin lead finish the results were not acceptable.
Shear strength values were acceptable for both component finishes on ceramic and FR-4 substrate with gold over nickel finish. Other values were unacceptable.

Variant no. 3, Namics XH9626, tested on ceramic substrate with silver conductors and FR-4 substrate with gold over nickel conductors and tin lead conductors
For the ceramic substrate the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with gold over nickel plating the adhesive has shown good results after all environmental exposure as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with tin lead plating the adhesive has shown acceptable results after all environmental exposures as used as a short circuit. To connect 0603 resistors with silver palladium and with tin lead finish the results were unacceptable.
Shear strength values were acceptable for both component finishes on all substrate types.

Variant no. 4, Loctite 3880, tested on polyester substrate with silver conductors and FR-4 substrate with gold over nickel conductors and tin lead conductors.
For the polyester substrate the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with gold over nickel plating the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with tin lead plating the adhesive has shown unacceptable results after all environmental exposure as used as a short circuit and to connect 0603 resistors with silver palladium and with tin lead finish.
Shear strength values were acceptable for both component finishes on FR-4 substrate with gold over nickel finish and with tin lead finish. Shear strength values on polyester substrate were unacceptable.

Variant no. 5, Loctite 3882, tested on polyester substrate with silver conductors
The adhesive has shown good results after all environmental exposures to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable.
When used as a short circuit the results were only acceptable after temperature cycling.
Shear strength values were acceptable for Ag/Pd component finish on polyester substrate but for Sn/Pb components finish the values were unacceptable.

Variant no. 6, Epo-Tek H20F, tested on polyester substrate with silver conductors
The adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were acceptable, H_2S may increase the contact resistance when components with tin lead finish are used.
Shear strength values were unacceptable for both component finishes on polyester substrate.

Variant no. 7, Multicore M-4030-SR, tested on FR-4 substrate with gold over nickel conductors and tin lead conductors
For the FR-4 substrate with gold over nickel plating the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were acceptable with the same resistance values as for the components with silver palladium finish.
For the FR-4 substrate with tin lead plating the adhesive has shown acceptable results after all environmental exposures as used as a short circuit tin lead it and to connect 0603 resistors with silver palladium. To connect components with tin lead finish the results were

unacceptable compared with the initial value. However, the contact resistance values were a factor 3 higher than the solder reference initially and a factor 6 higher than the solder reference after the exposures, which may be accepted for some applications.
Shear strength values were acceptable for both component finishes on FR-4 substrate with gold over nickel finish and with tin lead finish.

Variant no. 8, Acheson Electrodag SMD10, tested on FR-4 substrate with gold over nickel conductors and tin lead conductors
For the FR-4 substrate with gold plating the adhesive has shown good results after all environmental exposures as used as a short circuit and acceptable results to connect 0603 resistors with silver palladium finish. To connect 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with tin lead plating the adhesive has shown acceptable results after all environmental exposures as used as a short circuit. Connecting 0603 resistors with silver palladium has not been tested due to an assembly failure. To connect components with tin lead finish the results were unacceptable.
Shear strength values were acceptable for both component finish on FR-4 substrate with gold over nickel finish and for Sn/Pb component finish on FR-4 substrate with tin lead finish. Other values were unacceptable.

Variant no. 9, Wacker Semicosil 970EC, tested on FR-4 substrate with gold over nickel conductors and tin lead conductors
For the FR-4 substrate with gold plating the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit to connect 0603 resistors with silver palladium finish and to connect 0603 resistor with tin lead finish.
For the FR-4 substrate with tin lead plating the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit, connecting 0603 resistors with silver palladium, and to connect components with tin lead finish.
Shear strength values were unacceptable for both component finishees on FR-4 substrate with gold over nickel finish and with tin lead finish.

Variant no. 10, Tecknit 72-00236, tested on FR-4 substrate with gold over nickel conductors and tin lead conductors
For the FR-4 substrate with gold over nickel plating the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit, to connect 0603 resistors with silver palladium finish and to connect 0603 resistor with tin lead finish.
For the FR-4 substrate with tin lead plating the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit, connecting 0603 resistors with silver palladium, and to connect components with tin lead finish.
Shear strength values were unacceptable for both component finishes on FR-4 substrate with gold over nickel finish and with tin lead finish.

Variant no.11, Tecknit 72-00151, tested on polyester substrate with silver conductor
In general, the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium and tin lead finish. Process optimisation may prove the results for connecting components with silver palladium finish, as good results were found for 8 out of 23 measurements.
Shear strength values were unacceptable for both component finishes on polyester substrate.

Variant no. 12, Creative 106-22, tested on FR-4 substrate with gold over nickel conductors and tin lead conductors
For the FR-4 substrate with gold plating the adhesive has shown good results after all environmental exposures as used as a short circuit and to connect 0603 resistors with silver palladium finish. The measured contact resistance values were however relatively high, possibly due to the fact that the conductive material is carbon. To connect 0603 resistor with tin lead finish the results were unacceptable.
For the FR-4 substrate with tin lead plating the adhesive has shown unacceptable results after all environmental exposures as used as a short circuit, connecting 0603 resistors with silver palladium finish and with tin lead finish.
Shear strength values were acceptable for both component finishes on ceramic and FR-4 substrate with gold over nickel finish and with tin lead finish.

Variant no. 13, Tecknit 107-25, tested on polyester substrate with silver conductors
The adhesive has shown acceptable results after all environmental exposure as used as a short circuit and to connect 0603 resistors with silver palladium finish. To connect the 0603 resistor with tin lead finish the results were unacceptable. H_2S may increase the contact resistance when components with tin lead finish are used. The resistance value for the adhesive used as a short circuit was high compared with the other variants used on polyester substrate.
Shear strength values were unacceptable for both component finishes on polyester substrate.

Variant no. 14, Multicore 96SCMX39AGS88.5 Sn/Ag/Cu lead-free solder, tested on ceramic substrate with silver conductors and FR-4 substrate with gold over nickel conductors and tin lead conductors
All results were good.

9 Conclusion

It is estimated that electrically conductive adhesives will not be a drop-in replacement for solder, but be used in niche applications like low temperature substrates and possibly where heat transfer is high, i.e. for shielding applications, ceramic substrates, and possibly for low current applications. A further development of the electrically conductive adhesives and process technology may be necessary if electrically conductive adhesives should more widely replace solder.

The overall result of the evaluation is that the reliability of the adhesives is very dependent on the substrate and the component plating. The silicone variants showed unacceptable interconnection resistance and the variants with carbon showed high interconnection resistance. In general, adhesives applied on tin-lead substrates or to tin-lead component terminals showed increased interconnection resistance.

The shear strength showed acceptable values for most of the variants especially when mounted on the ceramic substrate and on the FR-4 substrate with gold over nickel plating. However, the silicone variants have shown very low shear strength values on all substrates.

The overall results from the contact resistance measurement showed that the silicone variants were unacceptable for either the short circuit or mounting of chip resistors. The variants with carbon particles have relatively high contact resistance, and will only be suitable for components with high input impedance. The silver-filled epoxy, thermoplastic and thermoset variants showed good results when used with silver palladium component finish mounted on gold and silver conductors. Tin lead-plating is not compatible with the adhesives, as high contact resistance values were measured. However, one variant, the thermoplastic, showed reasonable contact resistance values when tested with tin-lead platings.

The overall results from the shear strength test have shown that when the adhesive is bonded to tin lead surfaces the fraction will be between the adhesive and the tin lead. When the bonding material is gold, silver or silver palladium the separation will be in the adhesive joint. All variants tested on the ceramic substrate showed very high shear strength force value. The variants tested on the polyester substrate has low shear strength value, except for one epoxy variant connecting to silver-palladium finish.

The variants tested on the two different FR-4 substrates have for the two silicone adhesives shown unacceptable results. The shear strength value for all other variants was acceptable when tested on the substrate with gold finish. When tested on the substrate with tin lead finish one of these variants has unacceptable shear strength values, while the other variants (except one with the same values on both substrate finishes) have lower values on the tin lead substrate.

From an environmental point of view, it is a question of release of lead and tin, or silver to the environment, unless carbon is used as the conductive material in the adhesives. All the three metals impose environmental hazards, but the actual risks are not easily evaluated. Both for solder and adhesive, recirculation of electronic equipment will reduce environmental release.

Based on the Life Cycle Assessment, it cannot be judged whether adhesive technology is better or worse than solder technology. The available data on material consumption and emissions during the life cycle are too uncertain. Further, in relation to toxicity, which is a crucial impact category in this assessment, too little is known about the actual environmental fate of metals leaking to the environment from waste steams.

The study has lead to the following recommendations in relation to manufacturing and emission handling:

- Use components with as little silver and palladium termination as possible
- Optimise adhesive consumption (for SMT about 1/5 as compared to solder paste amount)
- Assure high recovery percentages for the metals during recycling and reduce losses during manufacturing operations
- Assure proper treatment of hazardous wastes

From a working environmental point of view, the choice of technology is equivocal. The two technologies impose different hazards (the potential hazard impact of solder is slightly higher), but the occupational risks are minimal when adequate preventive measures are implemented.

A well considered working practice, the proper use of available technical preventive measures and personal protective equipment as well as good hygiene at work all reduce the actual risk. As a basic principle, the preventive measures should be prioritised as follows:
- Designing the assembly line in a way that reduces risk as much as technical possible (avoid skin contact with solder paste, flux and adhesives and avoid inhalation of solvent vapours and lead fumes)
- Establishing technical measures (e.g. ventilation) where needed.
- Prescribing the use of personal protection equipment.

From a working environmental point of view, the choice of adhesive resin should be made according to the following preference:
- Polyester
- one-component silicone / two-component silicone
- acrylate / two-component epoxy / one-component epoxy

From an environmental point of view, the choise of adhesive conductor should be made according to the following preference:
1. Carbon
2a. Silver-plated aluminium
2b. Silver-plated copper
3. Silver

From a technical point of view the adhesive systems should be selected with due respect to the below criteria:
- electrical conductive adhesive shall be applied on noble metal surfaces, i.e. tin-lead as a substrate or component terminal finish is not recommended, due to oxidation.
- redesign of the footprints on the substrates may be necessary.
- reduction of the opens in the stencil is necessary to reduce the applied amount of electrical conductive adhesive compared to solder.
- the existing production equipment can be used i.e. the stencil printer or the dispenser, the component mounting automate and the furnace. A furnace for adhesive curing is recommended, especially if both adhesive and solder shall be used in the production.
- process optimisation with electrical conductive adhesive is more difficult than with solder, especially due to no self alignment and no contraction of the adhesive.
- curing shall be performed according to manufacturers specification, i.e. the temperature shall be controlled.
- interconnection resistance is higher with electrical conductive adhesive than with solder.
- the adhesion between component/adhesive/substrate seems to be lower for electrical conductive adhesive than for solder, this may not be correct for some SMD (ceramic chip resistors and capacitors) components mounted to thickfilm silver conductors on ceramic substrate. Depending on the electrical conductive adhesives adhesion strength and the component, components shall be mechanical fixed.
- repair may be a problem, as hand mounting in electrical conductive adhesive may give an increased interconnection resistance, and revealed silver flakes may tend to migrate.
- repair is estimated to be much more costly with electrical conductive adhesives than with solder.
- protection against uncured epoxy and epoxy vapour is required. Personal shall be trained to handle epoxy.

- for low temperature substrates there is only one alternative, which is low melting solder containing Indium.
- the price for electrical conductive adhesives is about 5 times higher than for solder.

A widespread substitution of solder with silver based adhesives would increase the silver demand by approximately 11%. However, with today's technology the demand will increase with less than 1%. The substitution for adhesive will most obviously also increase the silver demands for component termination as Ag/Pd terminated components are highly recommended for adhesives.

A widespread - future - substitution would therefore most obviously increase silver prices - when also comparing to the fact that it is estimated that the silver supply horizon is only about 14 years! However, with the *present technology* level, the increase in silver demand due to adhesive application would most obviously be marginal as compared to other mechanisms affecting silver prices.

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