4 Assessment of sustainability effects in the context of specific applications

Carrying on from this characterization of nanotechnology and its current manufacturing processes, the process-concurrent assessment approach follows and investigates the sustainability effects of specific applications as compared to existing products and processes, with a focus is on the ecological opportunities and risks. The goal is preparation of environmental profiles in the course of in-depth analysis of selected case study examples.

4.1 Selection of the in-depth case studies

In an initial investigation possible nanotechnology application contexts were considered and qualitatively evaluated. Also studies to life cycle aspects of nanotechnology were analyzed. So far, only a handful of life cycle assessments (LCAs) on nanotechnologies have been completed. A summary of studies of life cycle aspects identified are provided.

Table 8. Overview of studies to life cycle aspects

| Nano-Product | Approach | Tech Benefits | Environmental Benefits | Reference       |
|--------------|----------|---------------|------------------------|-----------------|
| Nano-scale platinum-group metal (PGM) particles in automotive catalysts | Economic Input-Output Life Cycle Assessment (EIO-LCA) | reduced platinum-group metal (PGM) loading levels by 95% | overall reduced environmental impact | Lloyd et al. 2005 |
| Clay-polypropylene nano-composite in light-duty vehicle body panels | Economic Input-Output Life Cycle Assessment (EIO-LCA) |  | overall reduced environmental impact; large energy savings | Lloyd and Lave 2003 |
| carbon nanofiber | Ecobilan | reduced | NA (not com- | Volz and |

48 Scouce: based on Lekas (2005a) and own data
| Application                                                                 | Methodology/Technology                                                                 | Indication of Environmental Benefit                                                                 |
|----------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| (CNF) reinforced polymers                                                 | TEAM software                                                                         | weight, increased structural strength, improved conductivity                                        |
|                                                                            |                                                                                       |pared to traditional carbon fibers)                                                                  |
| Nano-scale platinum-group metal (PGM) particles in automotive catalysts    | Eco-profile following LCA methodology                                                  | reduced platinum-group metal (PGM) loading levels by 50%                                            |
|                                                                            |                                                                                       | overall reduced environmental impact (10-40%)                                                      |
| Photovoltaic, dye photovoltaic cells as compared with multicrystalline     | Eco-profile following LCA methodology                                                  | Steinfeldt et al. 2003                                                                               |
| silicon solar cells                                                        |                                                                                       |                                                                                                     |
|                                                                            | substanve flow analysis                                                                |                                                                                                     |
|                                                                            | Energy assessment                                                                      |                                                                                                     |
| Carbon nanotubes                                                          |                                                                                       |                                                                                                     |
| Energy consumption during nanoparticle production (TiO2, ZrO2)             |                                                                                       |                                                                                                     |
| Anti-reflex glass for solar applications compared with traditional glass  | Not Assessment, only indication of the environmental benefit                           | increased solar transmission 6% higher energy efficiency                                             |
| Printed circuit boards, Organic metal as compared with stannous/lead       |                                                                                       |                                                                                                     |
| Desanilation, Flow-through Capacitor as compared with reversed osmosis and | Not Assessment, only indication of the environmental benefit                           | allows for application of a thinner coating layer with same functionality 10x more resource efficient |
| distillation                                                               |                                                                                       |                                                                                                     |
| Car tire, SiO2, Carbon black                                              | Not Assessment, only indication of the environmental benefit                           | increased energy efficiency very high energy efficiency                                             |
|                                                                            |                                                                                       |                                                                                                     |

Olson 2004 (submitted) Steinfeldt et al. 2003 Steinfeldt et al. 2003 Lekas 2005b Osterwalder et al. 2006 BINE 2002 Omercon o.J. UBA 2006 UBA 2006
Our goal in the selection process was to cover the spectrum of nanotechnological applications (a variety of manufacturing methods and basic nanoscale structures) as broadly as possible and address a diverse selection of research interests. With this in mind, selection of the case studies was made according to the following categories and associated criteria:

1. Type and scope of environmental impact
   - anticipated eco-efficiency potential (high – low)
   - potential for possible risks and/or toxicity (high – low)
2. Extent of market proximity
   - State of development (already on market – still in long-term development)
   - Market relevance (high – low)
   - Potential application spectrum (wide – narrow)
3. Type of innovation
   - Degree of innovation (small – large)
   - Production turnover or volume (high – low)

In selecting the actual application contexts we chose to focus on specific issues/topics. Out of the entire spectrum of nanotechnological applications, four case studies with anticipatable eco-efficiency potential were specifically selected. Integrated technological problem solving innovations were our focus (cf. Kemp 1997, Huber 2004). The possible risks and potential dangers of nanotechnology applications, specifically the issue of nanoparticles, were analyzed and addressed. As a result of these deliberations, five application contexts with corresponding goals for the in-depth case studies were selected. The project results of these case studies follow.
Table 9. Overview of the case studies investigated

| Application context                                      | Goal                                                                                                                                 |
|---------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| Eco-efficient nanocoatings                              | Presentation of the eco-efficiency potential of nanocoatings in the form of a comparative ecological profile (Nanocoating based on sol-gel technology as compared with waterborne, solventborne, and powder coat industrial coatings) |
| Nanotechnological process innovation in styrene production | Presentation of the eco-efficiency potential of nanotechnology in catalytic applications in the form of a comparative ecological profile (Nanotube catalyst as compared with iron oxide–based catalysts) |
| Nanotechnological innovation in the video display field  | Assessment of eco-efficiency potential in video display development by means of a qualitative comparison (Organic LED displays and nanotube field emitter displays as compared with CRT, liquid-crystal, and plasma screens) |
| Nano-applications in the lighting industry              | Presentation of eco-efficiency potential of nano-applications in the lighting industry in the form of a comparative ecological profile (White LED and quantum dots as compared with incandescent lamps and compact fluorescents) |
| Potential risks of nanotechnological applications       | Discussion of possible risks and hazards using titanium dioxide as an example; less a consideration of environmental impact |

4.2 Case study 1: Eco-efficient nanocoatings

4.2.1 Content, goal, and methods of the case study

In the course of this case study the ecological potential of nanotechnology-based coating processes is investigated. As a specific example, we look at a potential process for coating aluminum that utilizes a new nanocoating based on sol-gel technology. Evaluation of the ecological relevance is carried out by means of a comparative life cycle assessment.

The investigation of the ecological aspects are carried out by comparison with other industrial coating systems, specifically waterborne, solventborne, and powder coatings, including associated pre-treatments.
4.2.2 Scope of the investigation

4.2.2.1 Fundamentals of surface coating technologies and their relevance for the environment

The industrial application of self-curing or curable organic compounds to a surface is referred to as a surface coating process. These compounds are applied in very thin layers. By means of a chemical reaction or other physical process, a binding, durable film is created. As part of the surface coating process, one must also consider the pre-treatment of the surface as well as any follow-up treatment. The essential steps in the process are:

- Pretreatment (blasting, grinding/sanding, degreasing, deoxidizing/pickling, phosphating, chromodizing, passivation)
- Application of the surface coating
- Aftertreatment/curing

All liquid coatings share a similar basic make-up that consists of four primary components:

- Binder
- Liquid carrier or solvent
- Coloring agent (organic or inorganic pigments)
- Fillers and additives

Pretreatment

The surface of the component to be coated must be thoroughly cleaned of all grease and dust particles by means of physical or chemical processes. Improvements to corrosion resistance and the later surface coating bond are also part of the pretreatment process. Typical pretreatments include:

- for plain carbon steel: degreasing, pickling, phosphating, passivation
- for aluminum: degreasing, deoxidation, chromodizing or the application of a non-chromated conversion coating based on zirconium, molybdenum, titanium, or silicate

The surfaces of aluminum components generally receive a chromate conversion treatment. Following degreasing and an acid wash the components are placed in a chromate bath. The bath is strongly acidic (pH value 1 to 2) and has as its most important ingredients chromic acid and complex fluorides. As a protection against corrosion, zinc surfaces are also chromated in order to prevent the formation of white rust. In some cases, mechanical processing (for example the sanding of damaged paint areas on a motor vehicle) can also be part of the preparation process. Often an undercoat or primer is applied and serves as a bond between the component material and the surface coating. The undercoating also provides protection...
against corrosion and consists of chromates as well as zinc and lead compounds.

**Chromating**

Until recently, chromate treatment of aluminum was indispensable for the adhesion of a surface coating. With aluminum in particular, exposure to the oxygen in the air quickly causes a thin aluminum oxide coating to form. In order to make possible the adhesion of the surface coating to this oxide layer, the metal parts have always been treated with chromic acid. This reduces the thickness of the existing oxide layer, eliminates other metallic particles, and causes the formation of a new mixed aluminum–chrome oxide layer. The result is a corrosion-resistant aluminum surface and the formation of a protective coating in preparation for the following surface coat application. The chromate conversion process, because of the harmful environmental effect of its chromium compounds, is a significant problem.

The toxicology of the chromium compounds in use is also a problem: Chromic acid is extremely corrosive. The chromate treatment process produces waste water containing chromium(III) and chromium(VI), whose removal requires extensive waste water treatment processing. Substances containing chrome(VI) are considered particularly poisonous and are furthermore carcinogenic. Sludge containing chromium(VI) must be disposed of at expensive hazardous waste disposal sites (Anger 1982; Funk 2003).

As a consequence of the EU end-of-life vehicle directive (2000/53/EG), beginning in 2007 the use of chromium-containing products in the pretreatment of parts to be surface coated will therefore no longer be permitted.

The search for alternative corrosion-resistant coatings for aluminum parts has therefore been underway for sometime. A number of processes, for example, pre-anodizing, are being explored; nonetheless, the corrosion protection these alternatives offer is, so far, not equal to that of chromating.

A coating based on organic-inorganic polymers developed by Nano Tech Coatings GmbH is of particular interest. The use of this surface coating fully obviates the need of chromating or similar pretreatments.

**The surface coating process**

Industrial surface coatings generally consist of a binder, pigment, solvent and additives. The composition of the binders (resins) determines the properties of the surface coating, including adhesion, mechanical and chemical resistance, sheen, and weather resistance. Pigments and additives are chiefly responsible for properties of color. They may also provide protection from corrosion (for example, zinc dust, red lead oxide) or include
stabilizers for UV protection. Pigments used in undercoatings and primers also serve to cover surface irregularities (filler). Additives are also used to improve application and performance properties. During the drying phase, the solvents become evaporative, volatile substances. Their purpose is to keep the solid components of the coating dissolved or dispersed and to maintain the applicable consistency and working properties of each coating.

**Environmental impact of paint and surface coatings**

A 1995 emissions study looked at the twelve business sectors most important for the application of industrial surface coatings – not including mass production surface coating operations in the automotive industry (Mink & Rzepka 1995). According to the study, 335,000 tons of solvent were being emitted annually. In comparison, the emissions from surface coating operations in automobile production are quite low, perhaps on the order of 30,000 tons annually, corresponding roughly to the emissions from automotive paint repair industry. The paint lines in the automobile industry already demonstrate a very high level of environmental awareness.

If automobile industry figures are included, annual emissions are close to 370,000 tons. This makes up roughly 40% of total solvent emissions or 15% of VOC emissions.

### 4.2.2.2 Specific aspects of the investigation and its scope

The study looked specifically at the surface treatment of light-alloy parts such as those increasingly being employed in automobile manufacturing. The surface treatment of a 1 sqm aluminum automobile part with various clear lacquers served as a functional reference unit.

The system boundaries included the entire life cycle of the coating product, including pretreatment of the surface (see Fig. 13). The individual life cycle stages in this case are:

- Procurement of raw materials
- Manufacture of primary materials (binder, solvent, etc.)
- Manufacture of surface coating
- Surface pretreatment
- Application (surface coating operation)
- Utilization phase
- Disposal/recycling
For the comparative profile, it should be noted that the surface pretreatment processing step could only be dealt with on a qualitative basis due to gaps in the data; the last phase, disposal/recycling, is in every case assumed to be identical and was not considered. The most relevant environmental impact criteria was expected in the surface coating production stages, including manufacture of raw materials, pretreatment, and application, as well as in the utilization stage.

**Fig. 13.** System limits for the comparative life cycle assessment

### 4.2.2.3 Selection of variants

Criteria for the selection of the variants:
- Differentiation by deployment of the basic material forms (binder, etc.)
- Differentiation according to type of surface pretreatment required
- Differentiation according to method of application
For the environmental significance of the surface coating systems being considered, the following influential parameters were ascertained:

- Composition of surface coating
- Required surface pretreatment
- Coating thickness

Using these parameters it was possible to derive four variants that currently reflect the state of the technology. The so-called nanocoating is treated as the fifth variant; however, unlike the other four variants, this has not yet been implemented in automotive production surface coating applications.

**Variant 1 and 2: single- and dual-component clearcoats (conventional clearcoat)**

Among the clearcoat finishes under consideration, the single-component clearcoat (1K CC) has been in use the longest. It therefore brings with it a great deal of working knowledge and a greater degree of development. Dual-component clearcoat (2K CC) is principally used in applications demanding a greater degree of quality and durability. In the automotive branch, both coatings are increasingly being replaced by waterborne and powder coatings, as they are no longer able to do justice to the high standards of the Technical Guidelines on Air Quality Control. The solvent percentage in both coating systems is roughly 50%. Various (synthetic) resins are use as binders in both systems. The percentage of additives, however, is relatively small and consists mainly of flow control agents and light stabilizers.

**Variant 3: Waterborne clearcoat**

Waterborne clearcoat is the most frequently utilized surface coating process in the automotive industry. The amount of solvent used in waterborne clearcoats is higher than in conventional lacquers, but the primary solvent is water (39.8%), which fully evaporates during the drying phase and therefore harmless to the environment. The use of water rather than volatile solvents as the liquid component also makes a difference in primary energy demand: 62.9 MJ/kg lies far below that of the conventional and powder coatings.

**Variant 4: Powder clearcoat**

Unlike all other surface coatings, the powder coat process utilizes no solvents or other liquid carriers and is therefore considered to be particularly safe for the environment. Significant efforts are presently being made to utilize powder coating in more and more application areas. Lack of a liquid carrier also brings with it some disadvantages: For example, dip or immersion application is, of course, impossible.
Variant 5: Nanoparticle clearcoat from the firm NTC

The newly developed nanoparticle coating differs in many respects from conventional coatings. The process is fundamentally different. Like traditional liquid clearcoats it consists of a binder, a liquid carrier, fillers, and additives. The binder, however, does not have the usual organic structure, but is instead a so-called inorganic-organic hybrid polymer. The nanoparticle coating is manufactured by means of the sol-gel process. The sol-gel process has been in existence for a long time, however through increased research and development activities in recent years it has gained in importance. It is viewed as an especially promising field of nanotechnology.

The nanoparticle coating can be applied using customary methods. During the drying phase of the “sol” (the coating in its liquid phase), the particles suspended in it join together to form the so-called “gel.” The material is heated to a temperature of 160°C, the liquid carrier fully evaporates from the layer and the particles bind together to form a stable polymer network (Van Ooij et al. 2002). Significant advantages of this process include: a thinner coating providing the same functionality and the elimination of the chromate pretreatment, which is no longer necessary.

Table 10. Overview of the variants considered

| Composition | Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|-------------|-----------------|-----------------|-------------------------------|-----------------------|-------------------|
| Binder      | 46.7%           | 51.5%           | 41.6%                         | 95%                   | 55%               |
| Additives   | 2.6%            | 3.5%            | 1.4%                          | 4.6%                  | 3%                |
| Liquid carrier | 50.7%        | 45%             | 57%, of which water makes up: 39.8% | 0.4%                  | 42%               |

| Processes utilized | Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|--------------------|-----------------|-----------------|-------------------------------|-----------------------|-------------------|
| Chromating phosphating anodizing | Chrome (VI) or chrome (III) | Chrome (VI) or chrome (III) | Chrome (VI) or chrome (III) | Chrome (VI) or chrome (III) | Mild alkaline rinse |

| Materials utilized (chromating) | Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|---------------------------------|-----------------|-----------------|-------------------------------|-----------------------|-------------------|
| Chrome (VI) or chrome (III) | 10-12           | 10-12           | 10-12                         | 10-12                 | 3                 |

| Surface pretreatment | Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|----------------------|-----------------|-----------------|-------------------------------|-----------------------|-------------------|
| Chrome (VI) or chrome (III) | 10-12           | 10-12           | 10-12                         | 10-12                 | 3                 |

| Coating thickness | Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|-------------------|-----------------|-----------------|-------------------------------|-----------------------|-------------------|
| 35 µm             | 35 µm           | 35 µm           | 35 µm                         | 65 µm                 | 5 µm              |

Source: Harsch and Schuckert (1996) and authors
Primary energy requirement

|        | 87 MJ/kg | 97.7 MJ/kg | 62.9 MJ/kg | 124 MJ/kg |
|--------|----------|------------|------------|-----------|

4.2.2.4 Description of the life cycle stages and base data utilized

The study “Comprehensive Assessment of Powder Coat Technology as Compared to Other Surface Coating Technologies,” by Harsch and Schuckert (1996), provided the base data for further investigation of the life-cycle stages; this study provides a life cycle assessment of the powder coating process as compared to other industrial surface coating technologies.

Production and manufacture of raw materials (surface coating components)

Chromic acid: Chrome ore is the raw material from which chrome(VI)-containing products for chromating are manufactured. South Africa, with between 30% (1992) and 42% (1996) of the market, is the largest worldwide producer of chrome ore, followed by Kazakhstan, Turkey, and India. In 1996, the six largest producers yielded roughly 86% of the approximately 12 million metric tons that were extracted worldwide.

Chrome ore is chiefly used in iron and steel metallurgy to produce stainless steel having special properties. In the chemical industry chrome ore is used to produce numerous compounds for application in diverse areas. Among these, chrome(VI) (chromium trioxide CrO3), used for chromating. In 1993, according to the U.S. Bureau of Mines, roughly 77% of the chrome used in the OECD (Organization for Economic Cooperation and Development) countries was used in metallurgy, 9% in the fireproofing industry, and 14% in the chemical industry. The market segment belonging to the chemical industry – which includes the manufacture of chromic acid – is shrinking due to environmental protection concerns.

Binders

A large number of organic and synthetic resins are utilized in binders for industrial surface coatings. These binder compounds are utilized in various proportions and ratios, as needed, in all industrial surface coatings.
Acrylic resins are synthesized from various primary products
- Epoxy resins are manufactured by means of a condensation process and serve to produce an especially durable and stable surface coating process
- Polyurethane resins are produced from polyether and polyester and have outstanding surface characteristics
- Polyester resins are condensation products resulting from saturated monomers
- Alkyd resins are produced from polyvalent alcohols and polycarboxylic acids
- Melamine resins are synthesized from the source materials melamine and formaldehyde

**Hardeners**
- Isophoron diisocyanate (IPDI)
- Hexamethylene diisocyanate (HDI)
- Phthalic anhydride (PA) with powder coating
- Triglycidylisocyanurate (TGIC)
- Silane in conjunction with nanocoat

An overview of the binders and hardeners in use is given in Table 11.

| Variant 1: 1K CC | Variant 2: 2K CC | Variant 3: Waterborne clearcoat | Variant 4: Powder coat | Variant 5: Nanocoat |
|------------------|------------------|---------------------------------|------------------------|---------------------|
| Proportion of binder and hardener utilized | 46.7% | 51.5% | 41.6% | 95% | 55% |
| Binder utilized | Acrylic, melamin, and polyurethane resin | Acrylic resin | Acrylic, melamin, saturated polyester resin | Acrylic resin | Epoxy resin (proportion: 50%) |
| Hardener utilized | HDI prepolymer | Acid catalyst (PA) | Silane (proportion: 50%) |

Source: Harsch and Schuckert (1996) and authors
Solvent
Organic substances are the most common solvents. Before application they serve to maintain the coating in a liquid state. Following application the solvent evaporates and the coating becomes solid. Commonly used solvents include:
- Diacetone alcohol
- N-Methylpyrrolidone (NMP)
- Aromate
- Butyl acetate
- Butyl diglycol acetate
- N-butanol
- Secondary butyl alcohol (SBA)
- Butyl (poly)glycol

Pigments, fillers, and other additives are also used in very minimal quantities, and were not included in further calculations.

Manufacturing industrial surface coatings

Liquid coating systems
Manufacture of the coating is chiefly a process of mixing together the necessary components. Losses at this stage are minimal and can therefore be ignored. In a premixer the binder, liquid carrier or solvent, pigment, and fillers are mixed together and then ground. Any remaining additives are then added to the mixture in a let-down tank. After filtering, the mixture is packaged.

Powder coat systems
In the manufacture of powder coatings, all ingredients are first carefully weighed out and then fed into an extruder. The mixture is repeatedly powdered in several stages and finally conveyed to a packaging facility. Losses in powder coating manufacture are greater than with liquid coatings and amount to roughly 2–5%.

Nanocoat system
The manufacture of a nanocoating varies not so much in the processes, but rather in the binder that is utilized. As a rule, the binders used in industrial coatings have an organic structure. But inorganic binders are also utilized in certain applications. Their advantage is in their hardness and chemical durability. But because of their serious drawbacks, including difficult ap-
plication and brittleness after hardening, these coating materials do not have an extensive field of application.

In nanotechnology-based coatings, the so-called inorganic-organic hybrid polymers come into application. These new binders are a mixture of organic and inorganic binders and bring together numerous advantages from both types of binder. As the nanocoating cures, the inorganic particles begin to form a glasslike network with cross-linked organic elements.

The fundamental chemical reaction behind the manufacture of nanocoatings is based on the sol-gel process. This process frequently utilizes silicon-organic compounds, the so-called silanes. The synthesis of these binders is achieved by the hydrolysis of alkoxysilane. In this case study, the product Dynasylan® Glymo from Degussa was utilized. This part of the reaction leads to the formation of the inorganic part of the binder.

At the same time the formation of the organic part of the binder takes place. Organic side chains on the silane compounds undergo reaction to organic chains. As this inorganic-organic network forms, the coating hardens.

The finish condition of the coating, however, remains as it was before hardening. The binder is available as a low-viscosity colloidal suspension, whose particles have a diameter of 40–50 nm. The solvent, at this point, contains unreacted silane, silanol, and partially formed polysiloxane. This colloidal system is chemically in the so-called sol state; followed, after application and hardening of the coating, by the gel state. The entire process is therefore referred to as the sol-gel process (Wagner o.J.).

Base data and assumptions: Summary life cycle assessment data from the study by Harsch and Schuckert (1996) provided the base data for the four existing surface coating technologies. Since no quantified data exists for the primary materials in the nanocoating, specifically for the silane that is used, the data from the dual-component coating was also used for the nanocoating and multiplied by a “safety factor” of 1.5. The base data utilized for each 1 kg of applicable coating are provided in the appendix (Table 43).

**Surface pretreatment**

As a rule, before application of the surface coating, steel and aluminum components must receive a series of successive surface treatments to protect against corrosion. This is achieved through the application of a chemical conversion coating. Chromating is the usual corrosion prevention process, particularly for aluminum. The pretreatment occurs by means of a dip or spray process utilizing chrome(VI)-containing products. Aluminum
can also be pretreated using one of the following processes: chemical oxidation, phosphating, or anodic oxidation.

**Chromating**

Chromating forms a conversion coating of complex chromates. The characteristic layer thickness of the resulting protective coating is no more than 0.01 to 10 micrometers. The chromating process itself is quite complex and involved. In automated applications, for example treating the body shell of an automobile, the part being treated often must pass through ten or more in part repetitive baths. At a minimum, it requires the following steps:

- **Solvent cleaning**: Grease, oil, and other contaminants are removed from the surface by means of solvents and other chemical processes.
- **Intermediate rinse**: The solvent and cleaning chemicals are rinsed away with cold or warm water. This step is omitted if only organic solvents were used for cleaning.
- **Activation**: Use of the activator (for example nitrous or sulphuric acid) yields a crystalline layer whose structure is significantly finer.
- **Chromating**
- **Rinse**: The excess chromate and phosphate solutions are rinsed away with deionized water. The water temperature during the chromating process must not exceed 50–60°C.
- **Passivation**: The surface coating is passivated either by spraying or dipping in very dilute chromic or chromic/phosphoric acid solutions.
- **Drying**: The wet treatment is directly followed by a warm-air dry off. To avoid powdery or poorly adherent layers the temperature should not exceed 60°C for yellow or clear chromating or 80–90°C for the green chromate coating (Gersing o.J.).

The conversion coating consists of oxide hydrates of chrome(VI), chrome(III), and aluminum. The surface coating is typically assigned to one of three classes (Jelinek 1997):

- **Class 1**: coating weight 3.2 to 11 g/m²;
  suitable for greatest corrosion resistance even without any further coating
- **Class 2**: coating weight 1.1 to 3.8 g/m²;
  corrosion prevention and pretreatment before application of finish surface coat
- **Class 3**: coating weight < 1 g/m²;
  for decorative purposes only, minimal corrosion protection

The properties – for example layer thickness and corrosion resistance – of the conversion coating produced by the chromate treatment are depend-
ent upon the temperature of the bath, the treatment time, and the solution chemistry of the chromate bath. An overview of the various bath chemistries is given in Table 12.

**Table 12. Typical composition of various chromate baths**

| Composition                        | Quantity (g/l) | pH value | Temperature (°C) | Treatment time (min.) |
|-----------------------------------|----------------|----------|------------------|-----------------------|
| Chromic acid                      | 3 – 7          | 1.2 – 1.8 | 30 – 35          | 2 - 5                 |
| Na (or K) dichromate              | 3 – 6          |          |                  |                       |
| Potassic fluoride                 | 0.5 - 1        |          |                  |                       |
| Chromic acid                      | 3.5 – 4        | 1.5      | 30               | 3                     |
| Sodium dichromate                 | 3 – 3.5        |          |                  |                       |
| sodium fluoride                   | 0.3            |          |                  |                       |
| Chromic acid                      | 5              | 1.8      | 30 – 35          | 2 – 3                 |
| Sodium dichromate                 | 7              |          |                  |                       |
| Sodium fluoride                   | 0.6            |          |                  |                       |
| Ammonium dichromate               | 10 – 350       | < 3      | 30               | 1 - 5                 |
| Hydrogen fluoride                 | 0.25 – 11      |          |                  |                       |

**Phosphating**

Phosphating is commonly used as a pretreatment for steel and iron. But it is an alternative to chromate for the pretreatment of aluminum as well. Treating aluminum with a dilute phosphoric acid solution produces a thin film of aluminum phosphate. Compared to chromating and anodizing, phosphating is certainly more expensive and more complicated, but it results in a more corrosion-resistant surface, which ensures a better bond for surface coatings. Phosphate coatings solutions for aluminum generally have a composition similar to those used for treating steel. The main components include metal hydrogen phosphates, oxidizing agents and complex fluorides (Brock et al. 1998).

**Anodizing**

The anodizing process is comparable in number of baths and complexity to chromating. But it offers significant advantages with respect to environmental impact (chrome-free, fluoride-free). The chrome(VI)- and fluoride-containing solutions used in chromating are replaced by conventional sulphuric acid. This leads to a much higher quality water and waste discharge. Furthermore, the resulting conversion coating is more corrosion-resistant than in the chromate process.

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51 Source: Jelinek (1997)
With nanocoatings no extensive pretreatment is required. Only the very first stage, a mild alkaline rinse, is necessary.

**Table 13.** Comparison of the processes by number of baths

| Baths, number | Chromating                  | Anodizing                  | Pretreatment for nanocoating applications |
|---------------|-----------------------------|----------------------------|------------------------------------------|
| 1             | Mild alkaline degreasing    | Alkaline degreasing        | Mild alkaline rinse                       |
| 2             | Rinse                       | Rinse                      | Rinse                                    |
| 3             | Alkaline etching            | Alkaline etching           |                                          |
| 4             | Rinse                       | Rinse                      |                                          |
| 5             | Rinse                       | Rinse                      |                                          |
| 6             | Pickling/activation         | Pickling/activation        |                                          |
| 7             | Rinse                       | Rinse                      |                                          |
| 8             | Chromating                  | Anodizing                  |                                          |
| 9             | Rinse                       | 2x rinse                    |                                          |
| 10            | Deionized water rinse       | Sealing                    |                                          |

**Table 14.** Environmental advantages and disadvantages of the processes

|                        | Yellow chromating | Anodization | Pretreatment for nanocoatings |
|------------------------|-------------------|-------------|-------------------------------|
| Compound utilized      | Chromic acid (CrO₃) | Sulphuric acid (H₂SO₄) | Mild alkaline cleaner (pH value 8–10) |
| Water Hazard Classification (WGK) Storage | WGK 3 | WGK 1 | WGK 2 |
| Raw material           | Hazardous substance storage, extensive legal and structural requirements - Special instructions for the handling of chromic acid necessary (industrial safety) - Extremely toxic to water organisms - Carcinogenic | Less complicated hazardous substance storage - Special instructions for the handling of sulfuric acid necessary (industrial safety) - Causes severe burns | Simple storage |
| Handling instructions and safety data | | | Health hazard only in the case of inhalation or ingestion |
| Application technique  | Dipping           | Spraying     | Dipping                       | Spraying                            | Dipping | Spraying |
| Effluent volume        | Significantly greater for dip bath technology Can be minimized by selective spraying | Significantly greater for dip bath technology Can be minimized by selective spraying | Significantly greater for dip bath technology Can be minimized by selective spraying |

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52 Source: Funk (2003) and authors
53 Source: Funk (2003) and authors
Base data and assumptions: Because appropriate, quantifiable data for the given pretreatment methods is not available, it is not possible to include this processing step in further environmental impact calculations. However, the comparison already makes clear that nanocoatings offer unique environmental advantages.

**The surface-coating process (application)**

Following pretreatment, the nano-clearcoat – particularly emphasized in this study – is applied in the same manner as a single-component clearcoat. The main difference to the other coating systems is that only a tenth of the usual coating material is needed. Because the application process for nanocoatings is the same, we will rely heavily on Harsch and Schuckert (1996).

The comparison of the various coating systems by application process is based on design data for new facilities of the same production capacity. The general steps of application are shown in Table 15. From this it can be seen that application generally consists of three steps: Interior, exterior shell, and manual touch-up.
Table 15. Technical stages of clearcoat application\textsuperscript{54}

| 1K CC, 2 K CC, Nanocoating (NC) | Waterborne clearcoat | Powder clearcoat |
|---------------------------------|----------------------|------------------|
| Intermediate dryer | Intermediate dryer | Intermediate dryer |
| Cooling zone | Cooling zone | Cooling zone |
| Air lock | Air lock | Air lock |
| Coating | Coating | Coating |
| Inner body shell | Inner body shell | Inner body shell |
| Robot station | Robot station | Robot station |
| Coating | Coating | Coating |
| Outer body shell | Outer body shell | Outer body shell |
| ESTA station | ESTA station | Tribo station |
| Manual touch-up | Manual touch-up | Manual touch-up |
| Air lock | Air lock | Air lock |
| Infrared predryer | Dryer | Dryer |

The application process is influenced by certain variables that have an influence on quality and quantity of the output. These include formulation of coating, the coating system, energy source, and production capacity. For the purposes of this study average values for these variables were used. The application base data is available in the appendix (Table 44).

Table 16. Modifiable variables and their average characteristics for the various coating systems\textsuperscript{55}

| Coating system | 1K CC | 2K CC | Waterborne clearcoat | Powder coat | Nanocoat |
|----------------|-------|-------|----------------------|-------------|---------|
| Production capacity | 40 body shells per hour | 20 m² | 65 µm | 5 µm |
| Surface area coated | 35 µm | 35 µm | 63.6% | 64.7% | 63.6% |
| Coating thickness | 35 µm | 35 µm | 61.5% | 63.6% | 63.6% |
| Application efficiency | 63.6% | 63.6% | 61.5% | 64.7% | 63.6% |
| Overspray recycling | no | no | no | no | no |
| Qty. (kg/ body shell) | 2.303 | 3.174 | 2.421 | 0.32 |

\textsuperscript{54} Source: Harsch and Schuckert (1996) and authors

\textsuperscript{55} Source: Harsch and Schuckert (1996) and authors
**Use phase, disposal, and recycling**

In the use phase the various environmental impacts of the variants studied – resulting from the various coating quantities applied – are determined. A useful life of 200,000 km was assumed for the automobile. The consumption reduction rule used by Harsch and Schuckert (1996) was likewise utilized.

The so-called consumption reduction rule says that given the weight and consumption of a specific automobile type, a 10% reduction of weight will result in a 2.5–6% reduction in consumption. In the area between 90 and 100% of the original total weight, it is assumed that weight saved and fuel saved are proportional. For the baseline consumption, an automobile type of average fuel consumption was selected from the GEMIS 4.1 database.

It is assumed that the disposal/end-of-life phase will not significantly vary and it is therefore not included in the assessment.

### 4.2.3 Life cycle inventory analysis

In the life cycle inventory analysis, the material and energy relationships between the coating systems being evaluated and the environment are noted, i.e. inputs from the environment and outputs into the environment are recorded. The goal of the life cycle inventory analysis is to establish a data inventory based on functional equivalents for the selected variants.

Since quantitative data for the pretreatment is not available and the disposal/recycling life-cycle stages were not considered, estimates were necessary with the various variants for the coating process, including raw material production, application, and the use phase. The following tables depict the calculated inputs and outputs for the variants studied.

**Table 17.** Quantities utilized for chromating and surface coating operations (g/m² of coated aluminum automobile surface area)\(^{36}\)

|                     | 1 K CC | 2 K CC | Waterborne clearcoat | Powder coat | Nanocoat |
|---------------------|--------|--------|----------------------|-------------|----------|
| Chromating          | 2.50   | 2.50   | 2.50                 | 2.50        | 0.00     |
| Binders / hardeners | 59.99  | 59.30  | 66.02                | 115.00      | 8.80     |
| Additives           | 3.34   | 4.03   | 2.22                 | 5.57        | 0.48     |
| Solvent             | 65.12  | 51.82  | 27.30                | 0.48        | 6.72     |

\(^{36}\) Source: Harsch and Schuckert (1996) and authors’ calculations
### Table 18. Total primary energy consumption (MJ/m² coated aluminum automobile surface area)\(^{57}\)

|                  | 1 K CC | 2 K CC | Waterborne clearcoat | Powder coat | Nanocoat |
|------------------|--------|--------|----------------------|-------------|----------|
| Coating production | 11.175 | 11.250 | 9.982                | 15.010      | 2.345    |
| Application      | 38.225 | 38.305 | 38.605               | 31.970      | 33.600   |
| Use stage        | 7.37   | 7.37   | 7.66                 | 13.87       | 1.02     |
| Total            | 56.769 | 56.925 | 56.248               | 60.849      | 36.961   |

### Table 19. Outputs relative to 1 m² coated aluminum automobile surface area\(^{58}\)

|                  | 1 K CC | 2 K CC | Waterborne clearcoat | Powder coat | Nanocoat |
|------------------|--------|--------|----------------------|-------------|----------|
| Air emissions    |        |        |                      |             |          |
| NM VOC [g]       | 4.835  | 4.722  | 4.323                | 5.780       | 1.590    |
| Methane [g]      | 5.821  | 5.796  | 5.899                | 6.109       | 3.989    |
| NOx [g]          | 5.894  | 5.793  | 5.029                | 5.968       | 3.279    |
| SO\(_2\) [g]     | 2.421  | 2.651  | 2.547                | 2.938       | 1.489    |
| CO [g]           | 10.472 | 10.486 | 10.778               | 18.944      | 1.869    |
| Particulate [mg] | 626.099| 743.811| 598.365              | 548.658     | 484.093  |
| HCl [mg]         | 79.733 | 79.229 | 86.987               | 77.724      | 65.225   |
| HF [mg]          | 27.692 | 27.356 | 29.831               | 24.910      | 23.314   |
| N\(_2\)O [mg]   | 63.868 | 63.875 | 66.396               | 120.205     | 8.812    |
| NH\(_3\) [mg]   | 40.096 | 40.100 | 41.683               | 75.464      | 5.532    |
| Water emissions  |        |        |                      |             |          |
| Discharge water [l] | 198.255| 195.246| 203.430              | 171.742     | 165.012  |
| CSB [g]          | 1.054  | 1.405  | 1.242                | 1.046       | 0.419    |
| TOC [g]          | 0.956  | 1.123  | 1.005                | 0.972       | 0.519    |
| BSB [g]          | 0.240  | 0.171  | 0.232                | 0.270       | 0.054    |
| Solids [g]       | 0.491  | 1.142  | 0.508                | 0.537       | 0.492    |
| HC [mg]          | 14.409 | 12.612 | 10.969               | 17.101      | 3.374    |
| NaCl [g]         | 36.622 | 10.746 | 11.486               | 20.955      | 2.353    |

\(^{57}\) Source: Harsch and Schuckert (1996) and authors’ calculations

\(^{58}\) Source: Harsch and Schuckert (1996) and authors’ calculations
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|                | 5.581 | 5.374 | 5.506 | 32.584 | 3.765 |
|----------------|-------|-------|-------|--------|-------|
| Iron [mg]      |       |       |       |        |       |
| Nickel [mg]    | 0.225 | 0.200 | 0.260 | 0.454  | 0.086 |
| Chromium [mg]  | 0.074 | 0.063 | 0.063 | 0.067  | 0.038 |
| Lead [mg]      | 0.330 | 0.376 | 0.350 | 0.299  | 0.282 |
| Copper [mg]    | 0.044 | 0.035 | 0.038 | 0.044  | 0.021 |
| Cadmium [mg]   | 0.008 | 0.007 | 0.008 | 0.010  | 0.004 |

Waste

|                        |   |       |       |        |       |
|------------------------|---|-------|-------|--------|-------|
| Industrial waste [g]   | 7.964 | 7.087 | 8.227 | 21.806 | 2.928 |
| Household waste [g]    | 2.274 | 1.747 | 2.275 | 2.158  | 0.486 |
| Hazardous waste [g]    | 4.379 | 3.506 | 8.822 | 10.674 | 0.773 |
| Radioactive waste [g]  | 0.227 | 0.230 | 0.221 | 0.345  | 0.104 |

The coating quantities are determined by the surface thickness to be applied. The minimal surface thickness of the nanocoating is the primary reason for the high resource efficiency. In spite of the relatively large amount of solvent, the absolute amount in the nanocoating is minimal as compared to the other variants.

Fig. 14. Coating and chromating quantities (g/m² coated aluminum automobile surface area)\textsuperscript{59}

\textsuperscript{59} Source: authors (base data: authors, Harsch and Schuckert 1996)
The total primary energy consumption is primarily determined by the energy requirement of the application and includes not only the actual coating process but also energy expenditures for drying, etc. The differences here in the variants studied are minimal. The roughly 35% less total primary energy consumption of the nanocoating results is due to reduced quantity of coating material. However, during the use phase, the reduced mass also leads to savings in fuel consumption.

**Fig. 15.** Total primary energy consumption (MJ/m² coated aluminum automobile surface area)\(^{60}\)

With the VOC emissions the advantages of the nanocoating are also quite evident, particularly in the manufacture and use life cycle phases. The VOC emissions of the nanocoating are ca. 65% lower than those of the other variants.

\(^{60}\) Source: authors (base data: authors, Harsch and Schuckert 1996)
Fig. 16. VOC emissions (g/m² coated aluminum automobile surface area)\textsuperscript{61}

The results for the other emissions values in Table 19 are similar. The reduction in waste generation also reflects the environmental advantages of the nanocoating.

Fig. 17. Waste generation (g/m² coated aluminum automobile surface area)\textsuperscript{62}

\textsuperscript{61} Source: authors (base data: authors, Harsch and Schuckert 1996)

\textsuperscript{62} Source: authors (base data: authors, Harsch and Schuckert 1996)
4.2.4 Life cycle impact assessment

To complete a life cycle impact assessment, it is necessary to have access to emissions data to which specific environmental impacts can be allocated. With the data available, it is only constructive to present an analysis for the impact categories greenhouse effect, acidification, and eutrophication.

4.2.4.1 Description of the environmental impacts

Greenhouse effect
The energy in the sunlight that strikes the surface of the earth in the course of the day is stored as thermal energy and then released at night as infrared radiation. A part of this infrared radiation is absorbed by trace gases in the troposphere (0–10 km) and reflected back to earth. This natural greenhouse effect is essential, otherwise the earth's surface would cool to inhospitable below-zero temperatures. The greenhouse effect we speak of as an environmental problem refers to the additional warming of the surface of the earth that is due to the increase in trace gases and the appearance of new greenhouse gases in the troposphere, for example HFCs (fluorocarbons). The most important greenhouse gases are carbon dioxide, methane, ozone, HFCs, and nitrous oxide, which arise to 50% from energy consumption, 20% from the chemistry industry, 15% from agriculture, and another 15% from the destruction of rain forests.

The greenhouse effect covers a wide range of effects that result from the warming of the earth’s atmosphere. Among these are not only the rising mean sea level, but also the increase in extreme climatic weather conditions such as hurricanes, storm floods, catastrophic drought, etc. Changes in the composition and the range of flora and fauna are also already being looked at.

Acidification
Acidification is a collective term referring to several effects. The phenomenon can be primarily traced back to sulfur dioxide and nitrogen oxide emissions from the burning of fossil fuels in power plants and increasingly in motorized transport. In addition, ammonia, hydrogen chloride, and hydrogen fluoride emissions also contribute to acid rain. Sulfur dioxide and nitrogen oxide emissions react with atmospheric oxygen and water to produce sulfuric and nitric acid.

In the life cycle impact assessment, acidification potentials (AP) were generated using coefficients from a study by the Center for Environmental Science (CML) in the Netherlands (Heijungs 1992). Substances that only
contribute to acid rain after oxidation (e.g. ammonia) or hydrolysis (e.g. SO2) are likewise included. In the CML models, only air emissions are considered; water emissions do not enter into the calculations.

**Eutrophication**

Eutrophication describes the spread of chemical nutrients into water bodies. The anthropological contributions of nitrogen compounds (e.g. nitrates) from excessive applications of fertilizers as well as phosphorus compounds (e.g. phosphates) from detergents or agricultural runoff lead to overfertilization of waters. In addition to these two groups of compounds, the COD (chemical oxygen demand) is enlisted as a measure for calculating organic pollutants. A consequence of the excessive nutrient enrichment is the appearance of vast algae growths. Dying algae decompose under a high degree of oxygen consumption and therefore lead to a shortage of oxygen in the water body. Decomposition and decay processes are the result and produce toxic substance such as hydrogen sulfide, which in turn leads to fish die-off. This means that the increased nutrients in our waters will do long-lasting and in part irreparable damage to a fragile ecological structure.

For the life cycle impact assessment the following factors were explored.

**Table 20. Impact factors utilized**

| Air emissions         | Greenhouse potential (GWP 100) | Acidification potentials (AP) | Eutrophication potentials (NP) |
|-----------------------|--------------------------------|------------------------------|-------------------------------|
| Carbon dioxide (CO2)  | 1                              |                              |                               |
| Methane (CH4)         | 21                             |                              |                               |
| Nitric oxide (NOx)    |                                 | 0.70                         | 0.13                          |
| Nitrous oxide (N2O)   | 310                            |                              |                               |
| Sulfur dioxide (SO2)  |                                 | 1.00                         |                               |
| Hydrochloric acid (HCl)|                              | 0.88                         |                               |
| Hydrogen fluoride (HF)|                                 | 1.60                         |                               |
| Ammonia (NH3)         |                                 | 1.88                         |                               |

**4.2.4.2 Quantitative analysis of the life cycle impact assessment**

The greenhouse effect is addressed in the investigation through emissions of carbon dioxide (CO2), methane, (CH4), and nitrous oxide (N2O); in this, the carbon dioxide emissions from the use of fossil fuel energy sources make up the greatest portion. Much as with total primary energy
consumption, the nanocoating comes out roughly 1/3 better than the other coating variants.

Fig. 18. Greenhouse potential (kg/m² coated aluminum automobile surface area)\textsuperscript{63}

The acidification is addressed through emissions of nitrogen oxides, sulfur dioxide, ammonia, hydrochloric acid, and hydrogen fluoride, whereby the last three substances play a lesser role in the scenarios being looked at.

Fig. 19. Acidification potential (g/m² coated aluminum automobile surface area)\textsuperscript{64}

\textsuperscript{63} Source: authors (base data: authors, Harsch and Schuckert 1996)
In addition to the phosphorus compounds in detergents, nitrogen oxide emissions and organic pollutants, which are released due to the chemical oxygen demand (COD), also contribute to eutrophication. In our case nitrogen oxide emissions can primarily be held responsible. In this impact category as well, the nanocoating makes clear its advantage, ranking 40% better than the other variants.

**Fig. 20.** Eutrophication potential (g/m² coated aluminum automobile surface area)

### 4.2.4.3 Qualitative aspects of the impact assessment

A generally accepted quantitative process for representing ecological and human toxicity in a life cycle analysis does not exist. Therefore at this point we take a brief qualitative look at individual substances that demonstrate an impact on ecological and human toxicity. Because of the methods, no local or time-independent evidence could be given in the impact assessment.

Those substances that are of global significance beyond their source of emission should be recorded. Furthermore, substances without an effectivity threshold should be included. The goal should be to minimize or replace such substances to the extent possible.

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64 Source: authors (base data: authors, Harsch and Schuckert 1996)

65 Source: authors (base data: authors, Harsch and Schuckert 1996)
Carbon monoxide (classified as mutagenic) has long been a problem for atmospheric pollution, particularly emissions in the transport sector. The successful reductions in CO achieved through the use of catalysts has made possible a tremendous reduction in emissions, such that the Federal Environment Agency, in a publication on technological options for the reduction of the impact of transport, came to the result that carbon monoxide no longer represents an air quality problem (UBA1999).

4.2.5 Case-study Summary

This case study makes impressively clear that in the area of surface coatings with respect to all emissions and environmental considerations studied that the utilization of nanotechnologically based coatings offers very great eco-efficiency potentials. Beyond this, the further advantages of simplified pretreatment were at least qualitatively shown. The minimal thickness necessary for such coatings leads to greater efficiency in use of resources; advantages in the usage phase can particularly be expected in the transport sector in the course of the trend to lightweight construction. In addition to the automotive industry, this potential would have an even greater effect on the airline and rail industries. A further potential for optimization can be found in the reduction of the solvent quota in nanocoating applications.

4.3 Case study 2: Nanotechnology Innovation in Styrene Production

4.3.1 Contents, goals and methods of the case study

Catalytic processes are among the earliest applications of nanotechnology. In principle, continuing gains in the efficiency and cost-effectiveness of catalytic processes can be achieved through the use of ever-smaller nanoparticles. Our understanding of catalysis is radically changing: the development of catalysts once relied upon empirical methods and values based on experience, but today the application of nanoanalytic methods, such as scanning tunneling microscopy (STM), makes it possible to reveal in detail the mechanisms of catalytic reaction.

In the course of this case study, we will investigate and look at an example of the ecological impact of nanotechnology-based catalytic applica-
tions. As a specific example, we will look at the application of a nanostructured catalyst utilizing nanotubes to the production of styrene. The ecological impact will be evaluated by means of a comparative life cycle assessment (LCA) of the specific processing stages as well as the entire styrene product life cycle. Investigation of the ecological aspects will be made by means of comparisons to existing chemical processes for styrene synthesis.

4.3.2 Scope of the investigation

4.3.2.1 Overview: Catalytic processes and nanotechnology

Catalysts are involved in the production of a great number of articles in everyday use. Catalysts are utilized in refining oil, setting free the energy in batteries and fuel cells, producing medicine and agrochemicals, plastics and paints, and in quite a number of environmental applications, for example the three-way catalytic converter in the automobile.

The generally accepted definition of a catalyst comes from Wilhelm Ostwald, who was awarded the Nobel prize in 1909 for his work on catalysis: “A catalyst is an agent which increases the rate of a chemical reaction without being consumed by it and without altering the final state of the thermodynamic balance of this reaction.”

This definition holds true for all catalysts; they differ in functionality, but not in their effect. There are three different types of catalysts, each with its own distinguishing characteristics:
1. Heterogeneous catalysts
2. Homogeneous catalysts
3. Biocatalysts

Heterogeneous catalysts are those that exist in a different phase than the reactants. In homogeneous catalysis, the catalyst is in the same phase as the reactants. This has the distinct advantage that a greater number of active catalyst molecules are therefore available, whereas in the case of a heterogeneous catalyst, only the surface molecules are active. Biocatalysts, also called enzymes, are the most wide-spread catalysts. Without them life would not be possible, as almost all processes in nature are controlled by biocatalysts.

Catalysis has far-reaching importance for the chemical industries: 90% of all chemical production processes are based on catalysis. More than 80% of the output of the chemical industry is achieved by means of processes that occur in the presence of catalysts. With a world-wide catalyst
market presently estimated at about 12 million dollars (US), the value of the resulting products ranges, according to various estimates, from 1.2 to 6 trillion dollars. The German share of catalyst production on the world market, about 4%, is not commensurate, however, with the significant role the chemical industry plays in the German economy (Herrmann 2000).

Fig. 21. Areas of application for catalysts

Catalysts are among the oldest applications of nanotechnology. The catalytic converter, for example, has been a nanotechnology application from its very beginning. Nanotechnological progress in the development of new catalysts is already being achieved through improvements in the production of nano-scale particles. The reason for this is that the catalytic process is enhanced by these nanoparticles, which have a smaller diameter: catalytic reactions take place on catalytically reactive surfaces and the smaller the diameter, the greater the specific surface area in relation to volume. This yields significant advantages: the size of the catalyst can be reduced while retaining the same reactive surface area; likewise the number of reactive atoms on the surface can be increased for the same given mass. Along with progress in the production of nanoparticles, developments in the field of nanopermeable materials and nanostructured surfaces are also beneficial for catalysis.

This was shown in a study on technological development in catalytic converters for automobiles (Steinfeldt et al. 2003). Increasingly smaller and more homogeneous precious metal particles are being used in catalytic converters for automobiles; the improved catalytic action of these platinum

66 Source: Herrmann (2000)
metal group particles (PGM) relies upon this surface-to-volume-ratio effect. This, along with continual improvements in the thermally stable bonding of these particles in the converter and reductions in the aging process, reduces the amount of PGM required and likewise makes it possible to meet ever stricter international emissions standards. Environmental relief is thus obtained through a reduction of pollutants in automotive exhaust emissions and through the reduced environmental impact achieved by “saving” PGM, the production of which is very expensive. Depending on the type of emission being considered, the eco-efficiency potential ranges from 10 – 40% (Steinfeldt et al. 2003).

Our understanding of catalysis is also changing radically. The development of catalysts once relied solely on empirical methods and experiential values. Nanoanalytical methods such as scanning tunneling microscopy enable us to investigate the mechanisms of catalytic reactions in ever-greater detail and to better understand and model them.

### 4.3.2.2 Focus of the investigation: styrene synthesis

Styrene production is considered to be one of the ten most important petrochemical processes and styrene is one of the most important base chemicals in the chemical industry. Numerous important synthetic polymer materials – the chief one being polystyrene – are made from the monomer styrene. Alongside ethylene and vinylchloride, it is one of the most important monomers.

**Styrene: Economic impact and market data**

Worldwide demand for styrene is estimated to be more than 20 million tons and growing by 5% annually (Rohden 2001). In 20 the styrene industry did face a 1.8% lapse in demand, but by the following year demand had again increased by 5.1% (Childre 2003). An overview of the development of styrene production is provided in Table 21 and Table 22.
Styrene is solely used to produce polymeric products, above all polystyrene. Other possible applications include the styrolacrylnitril copolymer (SAN), terpolymer from acrylnitril, butadiene and styrene (ABS), SBR composition rubbers and unsaturated polyester resins. However, the proportion of polystyrene being used in manufacturing is decreasing. In 1975, 60% the product groups worldwide belonged to polystyrene, but today it is only about 50% (ISEF 2001). As with all other petrochemical derivatives, styrene is very much dependent upon crude oil prices and thus is subject to major price fluctuations.

### Description of styrene production

Styrene is produced in a multi-stage process that can be traced back all the way to the procurement of the raw material. The production of styrene is based on intermediate products obtained from petrochemical resources, and the entire process therefore stretches from the exploration, extraction, and refining of crude oil and gas to the synthesis of styrene in the refinery. Fig. 22 provides an overview of the entire production process.

Naphtha and other petroleum products are produced by atmospheric distillation under normal pressure and temperatures ranging from 350 to 370°C. Subsequently, long-chain saturated hydrocarbons of the naphtha are split by means of steam cracking into low-molecular compounds such as butane (C\(_4\)H\(_{10}\)), benzene (in small amounts), and ethylene (C\(_2\)H\(_4\)) . Ethylene, propene (propylene), butane and other products are likewise obtained from natural gas by cracking. Ethylbenzene is produced catalytically by alkylation of benzene with ethene (using AlCl\(_3\) or silica gel) under press-
sure. It is an aqueous phase ethylation at an ethylene-benzene ratio of about 0.6/1, benzene conversion of 52–55%, temperature of 85–95°C, and atmospheric or slightly greater pressure. Styrene (C₆H₅C₂H₃) is produced from ethylbenzene (C₆H₅C₂H₅) by means of a catalyst. In a further processing step, the styrene is converted by polymerization to polystyrene, thus forming the base material for the production of numerous synthetic materials.

![Diagram of industrial production stages](image)

**Fig. 22.** Stages of industrial production of styrene and further processing for polystyrene

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69 Source: APME (1997)
4.3.3 Scope of investigation and accessibility of data

The scope of this case study is not specifically the entire styrene product life cycle, but rather the stages of processing in the production of styrene. However, it does make reference to the entire styrene product life cycle, i.e. the stages of raw material extraction, pre-production, and production of styrene are looked at in order to be able to assess the eco-efficiency potential within the overall plan. The functional reference quantity for the comparison is 1 kg of styrene. Comprehensive topical data on material and energy flow in the production of styrene are available from the Association of Plastics Manufacturers in Europe (APME). This includes summary life cycle assessment data for the classic production of styrene, i.e. data on all stages, from crude oil and natural gas extraction and processing to the actual production of styrene (APME 1999). Moreover, APME also provides life cycle assessment data on the intermediate products benzene and ethylene. Between these intermediate products and the product styrene are two more stages: the ethylbenzene process and the styrene process, with the consequence that no clear differentiation is possible by means of this database. There are further life cycle assessment data available in the Gabi materials database (Gabi 4 Datenbank 1999b) likewise for the overall styrene production process, but also for the ethylbenzene process (from a production plant in the Netherlands, Gabi 4 Datenbank 1999a). Unfortunately, comparison of all available data sets did not reveal sufficient congruence for the emission data specific to the styrene process. This may be due to differences in calculation procedures or different data sources. Therefore only a differentiated evaluation of the energy consumption in styrene production was possible, as well as specific estimates of individual material flows (heavy metals). No quantified process data is available for the alternative styrene process based on a carbon-nanotube catalyst. However, assumptions about energy consumption can be derived from the description of the technology.

4.3.3.1 Selection of the variants

The production of styrene is a chemical process whose efficiency very much depends on the utilization of suitable catalysts. In contrast to the technologically established use of iron oxide–based catalysts, a newly developed catalyst based on nanostructured carbon tubes, so-called nanotubes, is now available.
Variant 1: Classical styrene synthesis using an iron oxide catalyst

Styrene is synthesized in an industrial process that has been known for roughly 60 years: the dehydrogenation of ethylbenzene. The dehydrogenation of ethylbenzene to produce styrene is a reversible endothermic balance reaction (Lieb & Hildebrand 1982):

\[
C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2 \quad \Delta H^{600^\circ C} = 124.9 \text{ kJ/mol (1)}
\]

The dehydrogenation of ethylbenzene to produce styrene takes place at temperatures of \(600^\circ C\) in an ethylbenzene-water mixture and is assisted by potassium-promoted iron oxide catalysts. Along with this main reaction, other reactions take place; these are listed in the appendix (Fig. 53).

Two technologically different processes are used in the industry; they differ primarily in the way heat for the endothermic reaction is applied (Lieb & Hildebrand 1982; Schoen 2002). In more than 75% of the styrene production plants operating worldwide, dehydrogenation is carried out adiabatically. Multi-stage reactors or a reactor beds in series are used.

a. The adiabatic process developed by Dow Chemical Company:

The necessary heat for the reaction is applied in the form of superheated steam (approx. \(830^\circ C\)), which is added to the ethylbenzene steam before the catalyst. The mass ratio of ethylbenzene to superheated steam is between 1.5:1 and 2:1. The temperature of the reactive mixture as it enters the reactor is approx. \(650^\circ C\) and \(570^\circ C\) as it leaves. The styrene output after this first stage is still relatively low; therefore the reactive mixture is reheated to \(640^\circ C\) in a second (and if required in a third) stage and is dehydrogenated once more. The production capacity of such a plant is presently about 500,000 t/year.
b. The isothermal dehydrogenation process developed by BASF:

In this procedure, a constant temperature is maintained in tubular reactors that are heated by circulating flue gas or molten salt. The feed temperature of the reactive mixture is at about 600°C and can be kept nearly constant during the reaction with the catalyst layer. In this way the amount of superheated steam needed can be kept to about half of that used in the adiabatic process. Newly built dehydrogenation furnaces have a per unit capacity of up to 150,000 t/year.

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70 Source: Denis & Castor (1994)
The addition of steam is an inherent disadvantage of both procedures, as the energy for producing superheated steam can only be minimally recovered. Another weak point is the reversibility of the dehydrogenation process, which inhibits maximum styrene output. The maximum styrene conversion is therefore limited to 40–50% in the first pass, even in modern plants. However, to ensure sufficient selectivity (and as few side reactions as possible), a multi-stage plant brings the conversion rate up to 65–70%. This means that 30–35% of the original ethylbenzene passes by the reactors unprocessed and must be separated and recovered in an energy-consuming procedure.

A purity of more than 99.8% is required to make the styrene usable for subsequent processes such as polymerisation. Separation of ethylbenzene and other byproducts from styrene, a process that relies on the tendency of styrene to polymerize and the 9°C difference in boiling point between styrene and ethylbenzene, is extremely difficult and very cost-intensive.

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71 Source: Denis & Castor (1994)
Aspects of catalyst implementation

The catalyst consists primarily of iron oxides (80%), potassium (10%), and chromium oxide, as well as other selectivity-increasing heavy metal promoters (such as Cr, Ca, Al, V, W or Li). The styrene catalyst is classified as an SLP catalyst (supported liquid phase). These catalysts consist of a porous solid carrier, which can be catalytically inert or active. On the carrier we find the catalytically reactive active components (promoters) in the form of a fused material or in a liquefied state (Hagen 1999).

The potassium-promoted iron oxide catalyst is gradually deactivated by use and must be replaced every two to three years. Considering the vast size of the reactors used in the industrial process, it can be assumed to be an extremely cost-intensive process. Besides the already mentioned causes of deactivation of the catalyst - blocking and coke deposit – another three reasons for gradual failure of the catalyst are given (Maximova 2002):
- Loss or redistribution of the potassium promoters
- Major changes in the oxidation state of the iron oxide
- Physical deterioration of the catalyst

One can give rise to the other and all take place simultaneously; the deactivation of the iron oxide catalyst can therefore be viewed as an extraordinarily complex process.

Variant 2: Styrene synthesis with carbon nanotube catalyst

By being able to get a nanometer-scale “look” at events taking place during catalytic styrene synthesis, the actual sequences of the styrene synthesis could be recorded by scientists at the Fritz-Haber-Institute of the Max-Planck-Society. New research suggests that the coke layer is constantly present during styrene synthesis, even on the active catalyst surface. The coal gasification and coke formation are in a balanced state. Therefore it is assumed that coke is not simply a black layer that promotes deactivation, but rather that there are different types of coke with different properties (Ketteler 2002).

These investigations suggest that the carbon film that forms contains the real catalytically active species and that the potassium iron oxide film is only necessary for the formation of this active carbon species, i.e. it serves only as a “co-catalyst.” Moreover, it has been demonstrated that various carbon species (carbon black, graphite, “nanobulbs,” and “nanofilaments”) all show excellent activity and output (MPG 2002).

The enterprise Nanoscape AG was founded in 2001 with the goal of technically implementing the results of this fundamental research. Their aim is to develop a new method of technical styrene synthesis using a nanotube-based catalytic process. Following the successful production of styrene on a small-scale, this is now being expanded as part of an EU pro-
ject to a reactor with a 100 g catalytic volume. This will be followed by a correspondingly larger pilot plant.

A new nanostructure catalyst consisting of multi-wall nanotubes will be used. This not only permits increases in styrene output, it also changes the procedure from an energy-intensive endothermic process to a more energy-efficient exothermic process. Additionally the new catalyst makes it possible to run the reaction by adding air instead of water. Moreover, at the same conversion rate selectivity can be increased and the process temperature lowered by 200°C, which significantly lowers the specific expenditure of energy.

![Diagram of process schematic for the oxidative dehydrogenation of ethylbenzene (EB)](image)

**Fig. 25.** Process schematic for the oxidative dehydrogenation of ethylbenzene (EB)\(^{72}\)

a) reactor; b) heat exchanger; c) condenser

The plant schematic makes clear that this process is also characterised by a simpler plant structure as compared to the traditional production of styrene. The advantages of the new styrene production process on the basis of nanotube catalysts and the associated ecological effects can be summarized as follows.

\(^{72}\) Source: Mestl (2004)
Table 23. Advantages of the new styrene synthesis using a carbon nanotube catalyst

| Advantages of the new procedure | Ecological impact |
|--------------------------------|-------------------|
| Change of reaction type from endothermic ($\Delta H_{600°C} = 124.9 \text{ kJ/mol}$) to exothermic ($\Delta H_{400°C} < 0 \text{ kJ/mol}$) | Reduction of the specific energy consumption by (at least) 1.2 MJ/kg styrene assuming $\Delta H = 124.9 \text{ kJ/mol}$, Dependent on the exothermic conditions, which technologically can be kept low; moreover waste heat from the reactor could be used for other processes, such as preheating of reaction gas, heating of tubes, etc. |
| Reduction of the reaction temperature by about 200°C from 600°C to 400°C | Reduction of the specific energy consumption |
| Change of the reactive medium from superheated steam to nitrogen/oxygen or air | Reduction of the specific energy consumption, since production and processing of steam is very energy-intensive; reduction of the plant costs, requirements of reactor construction, heat exchanger (e.g. process water separation is eliminated completely), etc., tube dimensions are reduced due to lower temperature level and different corrosion characteristics of the reactive media |
| Higher selectivity at same conversion rate | Reduction of the specific energy consumption for less distillation and recycling |
| Use of carbon nanotube catalyst | Replacement for heavy metals, no heavy metal contamination |
| Catalyst production | Easier catalyst management (assumption) |
| | Higher (energy) expenditures for the production of the nanotube catalyst are to be expected with the CVD process, knowing that the technical requirements for multi-wall nanotubes cannot be compared to those of single-wall nanotubes. |

Detailed life cycle assessment data for the alternative styrene synthesis are not available. However, on the basis of the description of the technology, the following deduction about the energy consumption for this process will be made in order to assess the energy consumption at this process stage:

73 Source: Mestl (2004) and authors’ own data
1. The change of reaction type results in a reduction of the specific energy consumption by 1.2 MJ/kg styrene.
2. Reduction of the reaction temperature by about 200°C from 600°C to 400°C effects a 25% energy savings.
3. With the change of reaction medium from superheated steam to nitrogen/oxygen or air as well as the higher selectivity at the same conversion rate, a further 5% saving of energy can be assumed.

### 4.3.4 Life cycle inventory analysis

In the life cycle inventory analysis, the material and energy relationships of the various styrene production processes are noted, with a view to possible environmental impacts, i.e. inputs from the environment and outputs into the environment are recorded. The goal of the life cycle inventory analysis is to establish a data inventory based on functional equivalents for the selected variants.

Life cycle assessment data are available in summary form for traditional styrene production. The data encompass all processes, from crude oil and natural gas extraction and processing to styrene production. Intermediate processes as well as energy and transport processes are also included (APME 1999). As an example, gross energy demands are represented in the following. Additional LCA data are available in the appendix (Table 45ff).

**Table 24.** Gross energy demand in MJ for the production of 1 kg styrene

| Fuel type    | Fuel prod’n & delivery energy | Energy content of delevered fuel | Energy use in transport | Feedstock energy | Total energy |
|--------------|-------------------------------|---------------------------------|-------------------------|------------------|-------------|
| Electricity  | 1.36                          | 0.62                            | 0.01                    | <0.01            | 1.98        |
| Oil fuels    | 0.80                          | 12.12                           | 0.26                    | 16.68            | 29.86       |
| Other fuels  | 2.07                          | 19.76                           | 0.05                    | 30.26            | 52.14       |
| Totals       | 4.22                          | 32.50                           | 0.32                    | 46.94            | 83.98       |

**Table 25.** Gross material and fuel demand in MJ for the production of 1 kg styrene

| Fuel type    | Fuel prod’n & delivery energy | Energy content of delevered | Energy use in transport | Feedstock energy | Total energy |
|--------------|-------------------------------|-----------------------------|-------------------------|------------------|-------------|

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74 Source: (APME 1999)
75 Source: (APME 1999)
4.3 Case study 2: Nanotechnology Innovation in Styrene Production

| fuel | Coal | 0.39 | 1.21 | <0.01 | <0.01 | 1.60 |
|------|------|------|------|--------|--------|------|
|      | Oil  | 0.69 | 12.18| 0.27   | 16.68  | 29.82|
|      | Gas  | 2.49 | 23.10| 0.04   | 30.26  | 55.89|
|      | Hydro| 0.04 | 0.03 | <0.01  | -      | 0.07 |
|      | Nuclear| 0.53 | 0.25 | <0.01  | -      | 0.78 |
|      | Lignite| 0.06 | 0.03 | <0.01  | -      | 0.09 |
|      | Wood | -    | -    | <0.01  | <0.01  |      |
|      | Sulphur| -    | <0.01| <0.01  | <0.01  | <0.01|
|      | Biomass| <0.01| <0.01| <0.01  | <0.01  | 0.01 |
|      | Hydrogen| <0.01| 0.04 | <0.01  | -      | 0.04 |
|      | Recovered| -   | -4.34| <0.01  | -      | -4.34|
|      | Unspecified| 0.01| <0.01| <0.01  | -      | 0.01 |
|      | Peat | <0.01| <0.01| <0.01  | -      | <0.01|
|      | Total| 4.22 | 32.50| 0.32   | 46.94  | 83.98|

For further discussion there arises the question as to what portion of these material and energy flows and/or the associated total environmental impact is to be attributed to the styrene process under investigation.

As already discussed, using the available data it is only possible to make a precise differentiation with respect to the energy requirements of styrene production. This reveals that the feedstock proportion, i.e. the energy content of the material, makes up the greatest share (56%) with respect to the gross energy demand. The direct energy demand for styrene production makes up 44% of the gross energy demand at 37.04 MJ/kg.

Table 26. Energy demand in MJ for the production of 1 kg styrene and/or intermediate products

|                  | Benzene production, APME | Ethylene production, APME | Styrene production, APME data | Styrene production, APME data | Styrene production, Gabi data |
|------------------|--------------------------|---------------------------|-------------------------------|-------------------------------|-------------------------------|
| Feedstock        | 45.54                    | 47.73                     | 46.94                         | 46.94                         | 46.94                         |
| Raw material extraction | 2.83                    | 3.08                      | 4.22                          | 4.22                          | 4.22                          |
| Transport       | 0.21                     | 0.12                      | 0.32                          | 0.32                          | 0.32                          |
| Production      | 19.14                    | 16.10                     | 32.50                         | 17.62                         | 26.45                         |
| Part of ethylbenzene + styrene | 14.88                   |                           |                               |                               |                               |

Source: (APME 1999; Gabi 4 Datenbank 1999b; Gabi 4 Datenbank 1999a), authors’ calculations
part of the styrene process requires about 6.4 MJ/kg of the 37.04 MJ/kg. This corresponds with a 17% share of the energy demand for styrene production. This share is influenced by the higher efficiency of the alternative styrene production process.

| Potential savings in energy | Traditional styrene synthesis | Alternative styrene synthesis |
|----------------------------|--------------------------------|------------------------------|
| Change of reaction type    | - 1.20 MJ/kg                  |                              |
| Reduction of reaction temperature | - 1.59 MJ/kg            |                              |
| Change of reaction medium, higher selectivity at the same conversion rate | - 0.32 MJ/kg               |                              |
| Energy demand              | 6.36 MJ/kg                    | 3.25 MJ/kg                   |

The alternative process based on a nanotube catalyst already yields at this stage a potential energy saving of almost 50%.
With respect to the total energy requirement for styrene production, this would result in an 8–9% increase in energy efficiency.

Another advantage of the alternative styrene production process is the replacement of heavy metals, which would otherwise be present in the catalyst. Heavy metal emissions into water from styrene production would be reduced by about 75%.

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77 Source: authors (database: authors’, APME 1999; Gabi 4 Datenbank 1999b; Gabi 4 Datenbank 1999a)
However, in real-world applications care must also be taken with the new nanotube catalysis method to minimize to the extent possible emissions of carbon nanotubes. The nanotubes should be firmly bonded to the carrier structure of the catalyst so as to avoid “tear off” of the nanotubes from the carrier surface. Moreover nanotube emissions should be minimized by means of sealed-plant technology. A discussion of possible risks and hazards associated with nanotube emissions takes place in the specific case study with a focus on risk potential.

### 4.3.5 Life cycle impact assessment

For the life cycle impact assessment, it is necessary to have access to emissions data which can be associated with specific environmental impacts. Inasmuch as the available data only allowed for a reasonable calculation of the energy demand, no additional impact assessment was possible.

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*Source: authors (database: authors’, Gabi 4 Datenbank 1999b; Gabi 4 Datenbank 1999a)*
4.3.6 Impediments to the introduction of nanotechnology to the marketplace

In the context of this case study it makes sense to discuss the subject of impediments to the launch of nanotechnology. It is not necessarily a given, that new nanotechnological processes, for example for styrene synthesis, that demonstrate environmental as well as economical advantages will succeed in the market place.

Within the context of this study, a more indepth interview was conducted to look at the market implementation of this nanotechnological solution. From the results it is clear that a number of styrene producers who have been introduced to this process do not deny its potential advantages. Since it is a procedure which so far has only been realized on a laboratory scale, upscaling up to a larger-sized plant is necessary to prove the economic feasibility of the nanotechnological process. This requires considerable investment in further development, with all the risks that such development entails. The financing for this is not yet settled.

At the same time, we find plant manufacturers and operators using the traditional processes who do not plan any re-investment and who point to their already extensive experience with the existing technology. In the end, it is these sunk costs or unrecoverable past expenditures (already invested capital as well as plant production experience) of the facility operators that may finally prevent implementation of the new process.

4.3.7 Case-study Summary

In the course of this case study, we will investigate and look at an example of the ecological impact of nanotechnology-based catalytic applications. Use of a nanostructured catalyst based on nanotubes for the chemical process of styrene synthesis serves as a specific example.

Implementation of the new catalyst would greatly increase energy efficiency (by almost 50%) at the process level. This improvement in efficiency results from two specific effects: first, it is possible to replace the former endothermic reaction with an exothermic one; second, the reaction temperature can be lowered considerably, the reaction medium altered, and the plant power input minimized. With regard to the overall styrene production life cycle, this would mean an increase in efficiency of about 8–9%. Furthermore, the new catalysis would make possible considerable reductions in heavy metal emissions during the product life cycle. Investigations into potential risks associated with the utilization of nanotubes must continue and be accounted for in facilities planning.
4.4 Case study 3: Nano-innovations in displays

4.4.1 Contents, goals, and methods

The display market is a dynamic and immensely growing market due to the importance of display screens in the fields of information and communication technology. The present sales volume of 26.5 billion dollars in 2005 is expected to reach 49.6 billion dollars in 2005 (Euroforum 2003). Other sources even assume growth to 100 billion dollars in 2005 (Mounier 2002).

Several different display technologies are competing in the market. In the past decade, display technology research and development has intensified with respect to the application of nanomaterials. Formerly CRT displays were the most common in use. These are increasingly being squeezed out of the market by new display technologies. The new display technologies offer many advantages: improved technical specifications (e.g., reduced radiation emissions) and easier handling (e.g., smaller size and less weight). So far, only a slightly weaker performance in some respects (visual angle, brightness, etc.) and, above all, a higher price have kept the new technology from spreading even faster.

In the course of the case study, a comparative investigation of conventional and nanotechnology-based display technologies in the form of a life cycle assessment profile was carried out. Possible eco-efficiency potentials were quantified to the extent possible.

4.4.2 Scope of the investigation

4.4.2.1 Subjects of the investigation

The detailed investigations in this case study are limited to the following display technologies:
- Cathode-ray tube – CRT
- Liquid-crystal display – LCD
- Organic light-emitting display – OLED
- Plasma display panel – PDP
- Carbon nanotube-based field-emitter display – CNT FED

The CRT, the conventional and currently most widely used display technology, and the likewise well-established LCD face two new
nanotechnological rivals: the OLED and the CNT FED. These are still primarily in research and development, but some product applications using OLEDs are already on the market. Plasma displays are already available commercially in various configurations and are being promoted as the best solution for large displays and information read-outs. In exactly this segment of the market, FEDs are said to have great potential; comparisons are thus made to plasma technology.

**Variant 1: the cathode-ray tube (CRT)**
The cathode-ray tube is the oldest and best known facility for generating moving images. A CRT monitor consists of a vacuum-filled (10^-6 to 10^-7 torr) glass bulb plus a heated cathode (voltage about 25 kV), also known as the hot cathode or electron gun (Abrams et al. 2003). When heated, the electrons of the negatively charged cathode begin to oscillate and are then emitted from it. Between the cathode and the anode exists an accelerating potential of several kV. Due to this voltage difference, the electrons are accelerated in the direction of the anode and generate a point of light when they strike a phosphor coating on the side of the glass vessel (Tannas 1985). Color is generated by three individual electron beams, which strike differently endowed phosphor layers through a hole or a slotted mask, thus generating red, green, and blue light. The grid regulates the intensity of the electron beam and thus the brightness of the resulting light spot and is controlled by the video brightness signal. The electron beam passes through an electromagnetic field (the deflection yoke) and is thus able to reach every point of the screen. By means of a focusing as well as magnetic coils and a shadow (slot) mask, the electron beam is concentrated and directed to a corresponding pixel (see Lohmann 1997; Blankenbach 1999; and others).
Due to their construction, CRTs are very heavy as compared to other display technologies, require a lot of space, and are characterized by high energy consumption. Image quality is also negatively affected by screen burn-in, which occurs when a fixed image is displayed over a longer period of time. The advantage they offer over other display technologies is their considerably lower price.

**Variant 2: the liquid-crystal display (LCD)**

Liquid-crystal displays are passive, i.e., transmissive, displays requiring a light source placed behind the screen. The crystals function like a valve, either allowing light to pass or blocking it. This function is based on the anisotropic properties of liquid crystals. Their liquid crystalline aggregate state combines the molecular orientation in the solid, crystalline phase with the mobility of the liquid state.

A liquid-crystal display consists of a system of two glass plates with a metallized lattice of conductors; positioned between them are the liquid crystals. In addition, a polarizer filter is positioned in front of and behind the glass plates, respectively, such that their orientation is crossed. If a light beam is sent through the first polarizer, only one polarization component remains. Unless a voltage is applied, the light is then rotated in its plane of polarization by the liquid crystal and thus can pass through the second polarizer filter, resulting in a bright pixel. When a voltage is applied, the light is no longer refracted and cannot pass through the second polarizer filter.
filter; a dark pixel is the result (see Chalamala 2000; Theis 2000; Lueder 2001; and others). There have been a number of different developments: passive-matrix, active-matrix LCD (AMLCD), twisted-nematic LCD (TN LCD), ferro-electric liquid crystal (FLCD), and others (Nocula & Olbrich 2003), which are not discussed in this study.

![Schematic of a liquid-crystal display](image)

**Fig. 29.** Schematic of a liquid-crystal display\(^{79}\)

The greatest advantage of LCD technology is the relatively small size of the displays and their low energy consumption (see Nocula & Olbrich 2003 and others).

**Variant 3: the plasma display (PDP)**

PDP – plasma display panels – consist of a system with two glass plates, each with a metallized lattice of conductors; between them is a mixture of inert gases such as argon or neon. An electric field is created at the cross-over points by applying a voltage to the grid of conductors. This field raises the gas atoms to a higher energy level. When returning to the original level, the absorbed energy is emitted in the form of photons.

Each pixel is directly generated “on site” by its own light source. A large pixel matrix is situated between the flat glass panels. Each pixel consists of three cells, each filled with inert gas. As a rule, neon and xenon are the main components; some manufacturers also add helium. The amount of gas used is very small and the pressure is also minimal. The three cells each have their own wall coating which consists of different phosphor

\(^{79}\) Source: Merck KGaA Darmstadt (2000)
mixtures. Charged electrons create tiny gas explosions which cause short-term changes of the aggregate state from gas to plasma. The resulting ultraviolet radiation generates – depending on the coating of the rear and lateral sides of the cell – red, green and blue light via the phosphors. This phosphorescent light is visible as a pixel through the front panel. The process of light generation is similar to that of the fluorescent tube, but on a much smaller scale, with the result that the energy efficiency of the discharge is only about six percent (Jüstel et al. 2000).

Its advantages include outstanding image quality (fully distortion and flicker-free, high resolution), a wide viewing angle, and immunity from electromagnetic interference (Blankenbach 1999). Disadvantages of PDP technology include, above all, high energy consumption, weight, and difficulties in achieving high brightness and strong contrast at the same time (see Deschamps 2000 and others).

**Variant 4: the OLED**

OLEDs (organic light-emitting diodes) differ from the usual LED displays through the use of organic emitter materials. The principle functionality of an OLED, like the inorganic LED, is based on injection electroluminescence. Positive and negative charge carriers, which are injected at the respective electrodes, are brought to radiative recombination in an emitting layer. A DC voltage of only a few volts is sufficient for injection electro-luminescence. A significant advantage of OLEDs is their independence from the substrate material (Scott et al. 2000; Steuber 2000).

Organic light-emitting diodes were invented by C. W. Tang and S. A. Van Slyke (1987) of Kodak, who were the first to discover that organic semiconductors of the p- and n-type could be combined – in a way similar to the formation of p-n-transitions in crystalline semiconductors – to make diodes. Moreover, the polymers generate light by recombination of holes and electrons in a very efficient manner, similar to gallium-arsenide and III-V semiconductors. In contrast to the manufacture of III-V LEDs, where crystalline perfection is necessary, organic semiconductors can be vacuum-metallized as amorphous layers. Two OLED structures are depicted in Fig. 30.
By means of such a permutation of layers, a bright emission of green light with a 10–12 cd/A quantum yield and roughly 4 lm/W at 2,000 cd/m² energy efficiency was achieved and utilized in products of the Pioneer Corporation.

T. A. Ali, A. P. Ghosh, and W. E. Howard of IBM and eMagin Corporation have modified this structure to integrate OLEDs on a silicon chip with the intention of using it for micro-displays in headsets. They start with a high work function metal anode and end with a transparent cathode and an ITO layer. Transparency of the metal cathode is achieved by its negligible thickness of only 10nm. They also modified the active light-emitting layer. By using diphenylene-vinylene (DPV) as a blue-green emitter and doping with red colorant, they were able to generate white light (Ali et al. 1999).

The worldwide technological development of OLEDs is very dynamic; in Germany, a group at the Institute of Applied Photophysics at TU Dresden has succeeded in lowering the operating voltage for OLEDs to 3 V and improving the performance efficiency by p-doping of the hole transport
layer (HTP) (Blochwitz 2001). Prototypes of OLED displays up to 40” have already been shown by companies such as Samsung (Samsung 2005) and LG Philipps (Pressetext 2004). Driving this development are the anticipated production savings over other displays.

**Variant 5: CNT FED**

The basic components of a field-emitter display are the rear plate with the cathode layer, a vacuum gap, and the subsequent front plate with an ITO layer on the interior side that serves as the anode.

The cathode layer on the rear plate (emitter layer) is one of the essential components of FE displays. The type, characteristics, and nature of the emitters are decisive for image quality, energy consumption during use, and service life.

There are several known emitter materials. Farthest along is the research and development of microtips made of molybdenum and tungsten and emitter layers made of carbon nanotubes.

Because of their unusual properties, the feasibility of using carbon nanotubes as field emitters was investigated shortly after their invention.

General requirements for field emitters include the following:

- Stability at high current density
- High conductivity
- Low energy loss
- High chemical stability

These requirements are well met by nanotubes. With their very high length-to-diameter ratio, high current density at low voltage, and high thermal and chemical stability, nanotubes were predestined to be well-suited materials as field emitters. Moreover, field emitter layers can be more easily produced using nanotubes than microtips and can be manufactured at a vacuum of 10-8 torr as compared to 10-10 torr for tungsten and molybdenum (Baughman et al. 2002). This permits more cost-effective manufacture of CNT FEDs than of microtips (Information Society Technologies 2003).

The most intricate component of a CNT FED is the cathode layer. It includes a glass substrate upon which a layer of conductor paths is imprinted. Above this layer the “cold cathode” is situated, an emitter layer consisting of nanotubes. Above that there is another electrode layer, the conductive paths of which lie crosswise to the first one. In this way the second orientation of the pixels is defined, which are situated at each of the junctions of the first and second layers. Electrons from the emitter layer can pass through the gaps etched into the second layer, through the vacuum, to the anode layer.
Between the cathode and anode layers is a vacuum and the distance (as a rule, less than 1 mm) is defined by so-called spacers. Opposite each pixel of the cathode layer is a phosphor area of similar size above a transparent conductor material, which functions as anode. The anode layer is situated on a glass substrate.

The rear electrode contact is made by means of a metal layer on the glass substrate (Burden 2001).

Field-emitter flat screens function much like cathode-ray tubes with many simultaneously emitting cold-field electron sources per pixel and achieve the same performance as the conventional CRT with respect to brightness, color reproduction, viewing angle, and rendering speed.

Source: Amaratunga (2003)
During operation, a voltage of 1–7 kV is applied at the anode, depending on the size of the vacuum gap and requirements of the display. Thus a difference in potential (voltage difference) is generated between anode and cathode, thus effecting the emission of electrons from the (nanotube) emitter layer. Acceleration of the electrons in the vacuum gap is thus crucial. Current flow, electron energy, as well as the type and quality of the phosphor determine the color and brightness of the pixels.

A significant advantage of field-emitter displays is that the application of an electric field produces a “cold” electron emission from the tip, with the result that it consumes much less energy than does the traditional cathode-ray tube, which must be considerably heated before it emits electrons.

**4.4.2.2 Scope of investigation and availability of data**

The scope (system boundaries) of the comparative assessments should cover the entire life cycle of the respective display technologies. The individual life cycle stages include:

- Raw material procurement, pre-production
- Display manufacture
- Use phase
- Disposal/recycling

For the CRT and LCD assessments we were able to rely on a very extensive American life cycle assessment study. The study, commissioned by the EPA Design for the Environment program, was carried out by Socolof, Overly, Kincaid and Geibig of the University of Tennessee, Center for Clean Products and Clean Technologies, and published in December 2001 (Socolof et al. 2001). It is notable for the cooperation of all major American and Asian manufacturers of CRTs and LCDs. The study took as its functional unit for investigation the life cycle of a computer monitor.

No quantitative life cycle assessment data is available for the other variants that were examined. For these technologies, qualitative descriptions of the manufacturing processes were carried out in order to arrive at a basis for making assumptions for the comparative assessments.

With respect to the particularly relevant use phase, quantified data could be provided for all technologies.

Data for the disposal/recycling phase are likewise only available for the first two variants.

Following the example of the existing life cycle assessment, the life cycle of a 15” LCD monitor and 17” CRT monitor were selected as the functional unit for the comparative life cycle assessment profile. Particularly for the use phase, the existing data was recalculated for this display size.
For all other variants, the same service life as current CRT and LCD devices is assumed. This specifically makes the assumption that for the OLED the current problem with long-term stability of the organic luminescent material will be solved.

4.4.2.3 Description of the life cycle stages

Numerous raw materials are used in the manufacture of displays. In the following, the essential production steps and raw materials utilized for each of the display technologies considered are described and summarized. Detailed illustrations can be found in the chapter on life cycle stages.

Production of a CRT monitor includes manufacture of the two main components, the panel glass and the glass bell; the glass contains a fair amount of lead. The individual luminescent phosphors are then applied to the panel glass and sealed with a protective coating. A pre-assembled shadow mask or aperture grille is then attached. The two glass components are fitted together to form the glass flask or picture tube into whose neck the cathode is then fused. Subsequently, the air is pumped out and the tube is sealed. After manufacture of the tube, other components such as the deflection unit are added in the final assembly (see Fig. 34).

The following section describes the usual steps in the manufacture of an LCD display. One should be aware that various methods can be used, particularly in applying the liquid crystal layer. First, the rear glass plate with TFT layer and the front glass plate and color filters are produced. After that, the ITO layer is sputtered or printed, followed by application of the hard layer and tempering. Then the polyimide (PI) layers are printed and the cured PI layer is rubbed to enable subsequent orientation of the LC molecules. After that spacers are sprayed on, followed by seal deposition and curing and application of external contacts for later wiring. During the subsequent cell assembly, the two glass plates are aligned and assembled to complete a panel. After curing in the hot press oven, the liquid crystal fluid filling is added to the panels and polarizer filters are applied (Crystec Technology Trading GmbH 2003)(see Fig. 35).

The manufacture of a plasma display begins with the fabrication of two glass plates, usually 3 mm thick, which are subsequently cleaned. Metal electrodes are applied in rows to the front plate. The next step is the preparation of the black matrix. The entire front plate is covered with a transparent dielectric ceramic layer, which cures at a temperature of almost 600°C. The front plate is then covered with a thin layer of magnesium oxide (MgO). On the rear plate, electrodes are also applied (in columns/matrix) and likewise coated with a dielectric ceramic layer. After curing of the ceramic layer, a magnesium oxide layer is applied. Subsequently, the so-
called barrier ribs are formed on the parallel electrode surfaces and the phosphors are deposited into the resulting channels. The rear plate is then fired, before the two plates are finally assembled into one panel and fused together. The air is then evacuated from the inner space and replaced by a gas mixture (mostly helium and xenon) at a pressure of about 500 torr (Deschamps 2000)(see Fig. 36).

The manufacture of OLEDs begins with the application of the transparent ITO layer to a glass substrate. In the following steps, all additional organic and metallic layers are then applied by means of thermal evaporation. The organic materials require a temperature of 300–500°C for evaporation, but silver requires a temperature of 1200°C. The layers are applied in a precisely followed series of complex process steps within a vacuum. Subsequently, the front plate is mounted and the entire assembly is sealed air-tight with a form of epoxy resin.

Presently, only one production plant capable of series production of the first OLEDs is in operation, at SK Display Corporation, a joint venture of Kodak and Sanyo (Webelsiep 2003). A prototype of an in-line OLED production system, funded by the Federal Ministry of Education and Research (BMBF), exists at the Fraunhofer IPMS in Dresden (IPMS 2003). The plant consists of eleven process modules, in which 300 x 400 mm samples are coated. The substrates move vertically through the deposition chambers. Up to twelve line sources are available for deposition of the organic layer systems. Additionally, two PVD and inorganic evaporation sources are integrated into each of the electrode deposition systems (see Fig. 37).

The following two illustrations make clear the reduction in manufacturing complexity of the OLED as compared to the LCD (described above).
Fig. 32. Comparison of LCD and OLED (1)

Fig. 33. Comparison of LCD and OLED (2)

From the diagrams it can be seen that the OLED can be manufactured much more efficiently than the LCD because, e.g., no backlight is in-
An assessment of sustainability effects in the context of specific applications

This makes it possible to reduce the depth of the screen from 5.5 mm in the LCD to 1.8 mm in the OLED.

An assessment of the materials required for a typical OLED:

- Glass (0.7 mm)
- 100 nm ITO
- 100 nm organic material
- 100 nm Mg:Ag (for the contacts)
- Glass (0.7 mm)

for a 17” display with a viewable area of 918 cm², this results in an organic materials consumption of ca. 370 mg per display (including waste). The annual production of 1 million 17” displays would require roughly 0.4 t of organic materials.

| Material          | Contained in the display | Total consumption incl. manufacture |
|-------------------|--------------------------|------------------------------------|
| ITO               | 12 µg/cm²                | 11 mg for 17”                      |
| Organic materials | 16–20 µg/cm²             | 15–18 mg for 17”                   |
| Mg, Ag            | 100 µg/cm²               | 92 mg for 17”                      |

Table 28. Estimate of typical OLED materials consumption

After production of the rear glass plate of the CNT FED, metal catalysts are applied to the pixel areas of the glass substrate by means of various procedures, including sputtering, lithography, microcontact printing, and ink jet printing. The carefully controlled growth of the CNT on the catalysts takes place in a precisely moderated CVD process at low temperatures (temperatures less than 500°C and lasting only for a few minutes) (NEDO). On the front plate, which also consists of glass, an ITO layer is applied as an anode to the interior face and is then treated with a phosphor layer. Finally, the two plates are combined to form a panel and bonded together (see Fig. 38).
Fig. 34. Product life cycle of a CRT monitor (Source: Socolof et al. (2001))
Assessment of sustainability effects in the context of specific applications

Fig. 35. Product life cycle of an LCD monitor (Source: Socolof et al., 2001)
Fig. 36. Product life cycle of a plasma display (Source: authors)
Fig. 37. Product life cycle of an OLED display (Source: authors)
Fig. 38. Product life cycle of a CNT FED (Source: authors)
The advantages of the new nanotechnology-based display technologies and their associated environmental impact may be summarized as follows.

Table 29. Advantages of the new nanotechnology-based display technologies

| Display technology | Environmental impact                           |
|--------------------|-----------------------------------------------|
| OLED               |                                               |
| Simple assembly, reduced number of production steps | Reduced facility expenditures                  |
| Minimal screen thickness (1.8 mm instead of 5.5 mm TFT LCD), minimal material consumption | Improved material efficiency                     |
| Low vaporizing temperature of the organic molecules (300–500°C) as compared to metals (Ag 1200°C) | Reduction of energy consumption during production |
| Organic phosphors  | Problem of long-term stability (shorter service life)? |
| Reduction of the specific energy consumption in the use phase | Increased energy efficiency                     |
| CNT FED            |                                               |
| Reduction of the specific energy consumption in the use phase | Increased energy efficiency                     |
| Minimal screen thickness (3.5 mm), less material use | Improved material efficiency                     |
| Very high resolution |                                             |
| Use of carbon nanotubes | Production process complicated by selected partial growth of nanotubes |

Detailed life cycle assessment data for the production and prior processes are only available for the CRT and LCD. For the other display technologies examined, the necessary processes could only be qualitatively described, as no material or energy data was available. A differentiated comparative assessment is not possible on the basis of these data.

However, based on descriptions of the technology, the following assumptions could be made regarding energy consumption, pre-production, and production for the three variants, in order to at least be able to make an estimate of energy consumption:

- **PDP**: The same energy consumption as in the LCD is assumed.
- **OLED**: On the basis of the simpler assembly, lower energy consumption can be assumed (variant A: 10% energy reduction, variant B: 30% energy reduction).
- **CNT FED**: On the basis of the simpler assembly, lower energy consumption can be estimated for pre-production (Assumption: As with the
OLED variant A, 10% energy reduction). Also the energy expenditure for manufacturing – even if one assumes application of the most demanding production technology – is likely to be less than for the LCD; however, in order to allow for a safety margin for nanotube production, the same expenditure as for the LCD is assumed.

**Use phase**

As important as image quality and usability are from a technical point of view, because of their long use phase, electrical energy consumption is the decisive parameter for an environmental assessment of display technology.

To be able to compare our display technologies, we need one (common) energy consumption value for one (common) display size. In the case of the CRT and LCD displays, this was the 15” monitor size. The energy consumption data available in the literature is for various display sizes, which makes comparisons difficult at best. Cambridge University’s Department of Engineering assumes an energy consumption of 50–70 W for a 38” CNT FED with an image quality comparable to a CRT or plasma display (Amaratunga 2003). Samsung estimates 150 W energy consumption for a 42” CNT FED (Samsung 2003). Futaba produces an 8” full-color display with a 1000 cd/m² brightness, which consumes only 7 W. According to Mounier (2002), a 10” FED display will only consume 2 W. A new 20” OLED display by IDTech (IBM) with 1280 x 768 pixels uses 25 W at a brightness of 300–500 cd/m². In comparison, the energy consumption of a 19” LCD display is 40 W (VDI-Nachrichten 2003).

Energy performance data used in the case study are listed in the following table and were taken from a display technologies road map, details of which can be found in the appendix (see Table 51). Data for the year 2005 were converted to the respective display size in the case study as necessary.

**Table 30. Energy consumption of display technologies**

| Year | Technology | 2000 | 2005 | 2010 |
|------|------------|------|------|------|
| Size | LCD        | 140 W| 120 W| 100 W|
|      | PDP        | 300 W| 200 W| 100 W|
|      | CNT FED    | 70 W | 70 W | 40 W |
|      | OLED       | no data | 60 W | 30 W |
|      | CRT        | 200 W| 230 W (HVT) | 200 (HVT) |

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81 Source: New Energy and Industrial Technology Development Organization (2000)
**Disposal / Recycling**

Hard data for this life cycle stage for the CRT and LCD displays are found in the life cycle assessment by Socolof et al. (2001). No quantitative data is available for the other display technologies. One can see from the assessment data for the CRT and LCD that this phase plays a minor role in the overall assessment and is not quantitatively addressed in the rest of the process.

4.4.3 Life cycle inventory analysis

In the life cycle inventory analysis, the material and energy relationships between the display technology being studied and the environment are recorded, i.e., the input flows from the environment and the output flows that are returned to the environment are noted. The goal of the life cycle inventory analysis is to establish a data inventory based on functional equivalents for the selected variants.

Complete quantitative life cycle inventory data are available for the CRT and LCD. On this basis and using assumptions described below, an assessment of the energy consumption of all display technologies for the pre-production, production, and use phases was made.

A simple comparison of the total mass of the major components of a 17” CRT and a 15” LCD monitor makes obvious the considerable difference in mass between traditional tube technology and flat screen technology – and that includes the other displays.

| Component         | CRT    | Share in % | LCD    | Share in % |
|-------------------|--------|------------|--------|------------|
| Glass (lead glass in CRT) | 9.76   | 46.1       | 0.59   | 10.3       |
| Steel             | 5.16   | 24.4       | 2.53   | 44.1       |
| Plastics          | 3.04   | 14.4       | 1.78   | 31.0       |
| Misc.             | 3.20   | 15.1       | 0.83   | 14.6       |
| Total             | 21.16  | 100.0      | 5.73   | 100.0      |

A look at the bottom line for material and energy consumption over the entire service life underscores the advantages of flat screen technology. As an example, the total energy consumption of a CRT display is 7.3 times higher than the total energy consumption of the respective LCD display.

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82 Source: Socolof et al. (2001)
due to the increased amount of energy needed for glass production. Detailed data regarding material, chemical substances, and energy totals from the life cycle assessment utilized can be found in the appendix (Table 52ff).

The environmental advantages of the LCD versus the CRT become clear, particularly in the comparative list of environmental categories. With the exception of two environmental impact categories, the LCD shows better results than the CRT.

**Table 32.** Quantitative comparison of environmental categories of the CRT and LCD\(^{83}\)

| Impact category                           | Units per monitor | CRT       | LCD       |
|-------------------------------------------|-------------------|-----------|-----------|
| Renewable resource use                    | Kg                | 1.31E+04  | 2.80E+03  |
| Nonrenewable resource use                 | Kg                | 6.68E+02  | 3.64E+02  |
| Energy use                                | m³                | 2.08E+04  | 2.84E+03  |
| Solid waste landfill use                  | m³                | 1.67E-01  | 5.43E-02  |
| Hazardous waste landfill use              | m³                | 1.68E-02  | 3.61E-03  |
| Radioactive waste landfill use            | m³                | 1.81E-04  | 9.22E-05  |
| Global warming                            | kg-CO2 equivalents| 6.95E+02  | 5.93E+02  |
| Ozone depletion                           | kg-CFC-11 equivalents| 2.05E-05 | 1.37E-05  |
| Photochemical smog                        | kg-ethene equivalents| 1.71E-01 | 1.41E-01  |
| Acidification                             | kg-SO2 equivalents| 5.25E+00  | 2.96E+00  |
| Air particulates                          | Kg                | 3.01E-01  | 1.15E-01  |
| Water eutrophication                      | kg-phosphate equivalents| 4.82E-02 | 4.96E-02  |
| Water quality, BOD                        | Kg                | 1.95E-01  | 2.83E-02  |
| Water quality, TSS                        | Kg                | 8.74E-01  | 6.15E-02  |
| Radioactivity                             | Bq                | 3.85E+07  | 1.22E+07  |
| Chronic health effects, occupational      | tox-kg            | 9.34E+02  | 6.96E+02  |
| Chronic health effects, public            | tox-kg            | 1.98E+03  | 9.02E+02  |
| Aesthetics (odor)                         | m³                | 7.58E+06  | 5.04E+06  |
| Aquatic toxicity                          | tox-kg            | 2.25E-01  | 5.19E+00  |
| Terrestrial toxicity                      | tox-kg            | 1.97E+03  | 8.94E+02  |

\(^{83}\) Source: Socolof et al. (2001)
What further potential savings or improvements can these other display technologies offer – particularly as compared to those based on nanotechnology? This is a question for further discussion.

Inasmuch as quantitative analyses with respect to substance inputs are not available, eco-efficiency potentials in the area of energy consumption can only be estimated. To do so, existing CRT and LCD data, as well as assumptions derived from them, for the product life cycle stages of pre-production, manufacturing, and use were used to arrive at energy consumption values.

Table 33. Energy consumption of the display technologies in the individual life cycle stages per monitor

| Technology   | Preproduction [MJ] | Production [MJ] | Use [MJ] |
|--------------|--------------------|-----------------|---------|
| CRT          | 366                | 18300           | 2290    |
| LCD          | 633                | 1440            | 853     |
| PDP          | 633                | 1440            | 1422    |
| OLED 10%     | 570                | 1296            | 427     |
| OLED 30%     | 443                | 1008            | 427     |
| CNT FED      | 570                | 1440            | 498     |

Fig. 39. Energy consumption of the display technologies in the individual life cycle stages per monitor

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84 Source: Socolof et al. (2001), authors’ own calculations
The energy consumption chart makes clear that the OLED variants, due to lower energy consumption in the use and production phases, fare particularly well when compared to current LCD displays.

Energy efficiency increases and thus an improved eco-efficiency of ca. 20% for the OLED 10% variant and 35% for the OLED 30% variant over the entire product life cycle are possible in this field. Of course, this is dependent on R&D success in achieving the envisaged material and energy efficiencies, as well as solving the problem of long-term stability of luminescent substances.

Under these assumptions, the CNT FED display would also score significantly better as compared to the LCD due to its greater efficiency in the use phase. The eco-efficiency potentials are very much dependant on the CNT FED production process being made as efficient as LCD production.

With respect to difficult-to-assess substances, the study by Socolof et al. (2001) looks at lead, mercury, and liquid crystals. A considerable amount of lead is present in the glass used in the CRT, as well as in the frit, although the lead in the glass is firmly bound in the glass matrix. Mercury is required in small quantities for the LCD backlight (3.99 mg). The mercury is vaporized by application of a voltage and generates ultraviolet light. During the process of manufacturing the backlight there is the risk of mercury emissions due to lamp breakage, mercury leakage, and waste. The risk can be minimized by process optimization and protective measures, but cannot be fully eliminated. Moreover, mercury emissions are also a component in the production of electric energy, as was already discussed in the case study on lighting applications. For the LCD display, an electrical energy production contribution of 3.22 mg mercury was assigned; for the CRT, due to its higher power consumption, 7.75 mg. Similar mercury emissions will occur with the other display technologies.

Due to the lack of sufficient information, no final assessment on the toxicity of the liquid crystals could be made. Toxicological tests done by liquid-crystal manufacturers showed, e.g., that in 95.6% (562 out of 588) of the liquid crystals tested, a potential toxic hazard did not exist. In 99.9% (614 out of 615) of the liquid crystals tested, it could be shown that no carcinogenic risk exists. The German Federal Environment Agency also came to the conclusion that liquid-crystal substances from the company Merck represent a very low risk and that no special requirements are necessary for the disposal of LCDs (Merck KGaA 2000). Instead of liquid crystals, other organic materials are used in OLEDs. Potential risks from extremely dangerous substances in OLEDs are unlikely. The safety data sheets provided

85 Source: authors (Database: authors, Socolof et al. 2001)
to us by the Fraunhofer IPMS regarding some of the substances used in OLEDs do not indicate any potential hazards.

The carbon nanotubes used as field emitters in CNT FEDs are grown on the substrate in a carefully controlled CVD process; the result is tightly sealed in the product. Therefore the potential for the release of carbon nanotubes appears to be very low.

4.4.4 Life cycle impact assessment

To complete the impact assessment, it is necessary to have access to emissions data which can be allocated to specific environmental impacts. Since these are estimates and furthermore a direct relationship between energy consumption and the relevant emissions exists, this would also be seen in the categories greenhouse effect, acidification, and eutrophication and not provide any new knowledge. We therefore make no presentation with respect to this.

4.4.5 Case-study Summary

The objective of this case study was an investigation of the eco-efficiency potential of new nanotechnological products currently being developed for the display industry. For this purpose, OLED and CNT FED displays were compared with conventional CRT, LCD, and plasma displays.

Due to differing stages of development of the technologies under investigation, the resulting eco-efficiency potential assessments come with a certain degree of uncertainty. In the overall product life cycle, the manufacturing phase is responsible for an ever increasing share of the environmental impacts. The successful implementation in mass production of the material and energy efficiency increases offered by OLEDs will make it possible to realize significant eco-efficiency potentials. At the very least, a 20% savings in energy as compared to LCDs over the entire product life cycle should be possible.

Likewise, development of the eco-efficiency potential of the CNT FED will become possible once the manufacturing process, particularly in the highly complex production of nanotubes for field emitters, becomes as efficient as current processes. Risk potentials from these new technologies are unlikely.
4.5 Case study 4: Nano-applications in the lighting industry

4.5.1 Contents, goals, and methods

Light in its many applications is a large consumer of energy. In Germany, about ten percent of the electrical energy consumed is used for lighting (ZVEI 2003). In this case study we investigate the ecological potential of new nanotechnology-based solutions for lighting. The German agenda “Optical Technologies for the 21st Century” identifies light-emitting diodes as an efficient and environmentally favorable light source and is promoting them in the course of its “Optical Technologies” development program under the title “Nanolux – white light-emitting diodes for lighting.” Specifically, this case study investigates white LEDs (light-emitting diodes) and compares them with conventional light sources (the incandescent and the compact fluorescent lamp). Evaluation of the ecological relevance is carried out by means of a comparative life cycle assessment. Quantum dots and their potential for improvements in efficiency in the lighting industry are also qualitatively addressed.

4.5.2 Scope of the investigation

4.5.2.1 Introduction

Light can be defined as electromagnetic waves with frequencies in the visible range and thus perceivable as having a particular brightness and color. Waves of other frequencies have names that primarily characterize their use, but no color. Many of our present-day light sources are thermal radiators. This includes the Sun, candles, incandescent, and tungsten-halogen lamps. The luminous color of the object is dependent upon its temperature; i.e. such light sources generate light as a secondary product of heating up.

The other group of light sources generates light by electric radiation, luminescence, or crystal radiation. This includes discharge-type lamps (including compact fluorescents) and the even more advanced light-emitting diodes, which are rapidly and continually being developed in order to make them competitive on the mass market.
The following diagram provides a survey of the most important lamp types today. Other discharge-type lamps include the low-pressure sodium-vapor lamp, ultraviolet, sodium-xenon, xenon, reflector lamps, various automotive lamps, etc.

![Fig. 40. Overview of the most important types of lamps](image)

### 4.5.2.2 Subject of the investigation

The case study looked at the use of light sources for illumination. For this purpose, three different types were compared: The two traditional light sources, the incandescent lamp and the energy-saving lamp, and the white LED based on nanoscale layers.

#### Variant 1: the incandescent lamp

The incandescent lamp, with a luminous efficiency of ca. 15 lm/W (WKO 2003), is the most widely used electric light source. It can be arbitrarily switched on and off and is used in all fields of interior and exterior lighting. The average service life is roughly 1,000–1,500 hours. The incandescent filament, a double-coiled wire between two lead-in electrodes inside a glass bulb, begins to glow when an electrical current is applied. A gas mixture inside the glass bulb prevents rapid vaporization of the filament. Tungsten, with its high melting point of roughly 3,400°C, is used for the

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86 Source: Following Grezcmiel (2001)
filament, as it provides a longer service life than would other metals (Wuelfert 2000).

When the current passes through the bulb, the filament is rapidly heated up to a temperature of about 2,600°C. This causes bright light to be radiated. The electrical energy is converted into light very inefficiently – 90–95% of the energy is converted into undesired heat. The incandescent lamp has a very poor energy efficiency. Only a small percentage of the energy is converted into visible light. The energy efficiency can be enhanced by increasing the filament temperature; this requires filling the glass bulb with a halogen mixture to maintain the service life of the lamp. This further development is called the tungsten-halogen lamp. In halogen-filled lamps, the tungsten wire may achieve a temperature of roughly 3,000°C.

**Variant 2: the energy-saving lamp (compact fluorescent)**

Saving energy and resources is a guiding principle of our time. Using discharge-type lamps allows us to apply energy much more efficiently for lighting than in the case of conventional incandescent lamps. They include the common fluorescent tube lamp, often found in the home and workplace. In particular, energy-saving lamps (compact fluorescents) – a miniature, enhanced form of the fluorescent lamp – make four to five times better use of electrical energy than do incandescent lamps. They are more expensive than normal incandescents, but convert up to 25% of the energy applied to light and have a luminous efficiency of about 60 lm/W (WKO 2003). Moreover, compact fluorescent lamps have a service life of 8,000 to 14,000 hours (KEVAG 2003).

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**Fig. 41. Structure of a fluorescent lamp**

87 Source: Popular Mechanics (2002)
A gas mixture, e.g. mercury, is a major component in discharge-type lamps. When, as a consequence of an applied voltage, a current begins to flow, electrons move from one electrode to the other. The electrons collide with the mercury atoms in the gas mixture inside the tube. These collisions cause energy in the form of ultraviolet light to be released. The ultraviolet light is absorbed by the phosphor coating (e.g. metallic salts) on the inner surface of the glass tube. The phosphors are thus stimulated and emit visible light. A discharge-type lamp requires a ballast, which provides the necessary high-voltage for ignition and also the normal operating voltage.

**Variant 3: the (white) light-emitting diode**

Recently the use of white light-emitting diodes (LEDs) has come into discussion as an alternative to conventional light sources such as incandescentes and fluorescent tubes; this is because it is generally assumed that LEDs can more efficiently produce light. Light generation by means of light-emitting diodes is based on semiconductor lighting technology. This makes it possible, for the first time, to generate a cold light without a significant heat component. The technical problem is that although the internal quantum efficiency of an LED is very high, only a small portion of the light can be decoupled from the component. Internally, up to 90% of the energy can be transformed into visible light, but only about 20–30% (this number is increasing) is externally available (CJ-Light GmbH 2003).

Light-emitting diodes have a very long service life. The service life of the LED is characterized by the number of broken components during a given period and by the decrease of light flux as compared to the original value (50%). A complete failure of all components during service life is practically impossible when operating norms are observed. Service life, efficiency, and light color of the LED depend very much on temperature, with the consequence that the thermal balance must be carefully observed when using LEDs. Additionally, the light-emitting diode can be destroyed by application of a too-high voltage. Additional electronic components in the form of a ballast are necessary for LED systems and modules.

The maximum service life of 100,000 hours can be achieved in red, yellow, and orange LEDs under normal ambient temperatures and at 50% of the maximal allowed current recommended by the manufacturer. The service life of white light-emitting diodes is greatest at an ambient temperature 30 K below the specified value and at 50% of the original current rating (FGL 2003). White LEDs have an average service life of about 15,000 hours.

At the core of light-emitting diodes are semiconductor crystals that generate light when a current is sent through them. Inside the crystals is an n-conducting region having a surplus of electrons (negative charge) and a p-
4.5 Case study 4: Nano-applications in the lighting industry

conducting region with a deficit of electrons (positive charge). Between those is a transition area (called the p-n junction or depletion zone). By applying a voltage, the electrons in the n-region gain enough energy to overcome the depletion zone. As soon as these electrons arrive at the p-region, they unite with the positive charges. Energy is released, which is discharged in the form of electromagnetic radiation. The semiconductor material determines the color of the light emitted. The colors red, green, yellow, and blue can generated. The materials are produced on the basis of aluminium indium-gallium phosphide or aluminum gallium arsenide (AlInGaP or AlGaAs) for red and yellow LEDs, and (indium) gallium nitride (InGaN or GaN) for green and blue diodes (FGL 2003).

Fig. 42. Structure of an LED

There are two ways to produce white LEDs: By the additive mixture of colors or by luminescence conversion. In the first case, a white LED is produced by combining chips emitting light of different colors into one LED. The various emitters (e.g. red, blue, and green) are placed together so tightly in the device that from a sufficient distance they cannot be distinguished by the human eye and appear as one color; thus producing the impression of white light. This method is also suitable for producing many other colors of light. LEDs producing colored light in this manner (including white) are also called multi-LEDs. The white light produced by multi-LEDs, however, is not as convincing as that produced by means of luminescence conversion. The rendition of the color quality using the multi-LED is poorer; the differing brightness and operating conditions of the various LED chips make this a complicated and therefore expensive solution. Generation of white light by luminescence conversion is achieved us-

88 Source: FGL (2003)
ing a combination of a blue or ultraviolet LED and a luminescence dye. When current is flowing, part of the short-wave light is absorbed by the dye, exciting it to emit light. Yellow-orange (long-wave, low energy) light is emitted. The superimposition of various spectral colors is perceived as white light.

Only with the development of white light LEDs, did the devices first become interesting for illumination purposes. The first white light LED was developed by the Japanese firm Nichia in 1995 and was based on the blue LED, also developed by them; it has been commercially manufactured since 1997. At the same time as Nichia, the Fraunhofer Institute for Applied Solid-State Physics (IAF) developed a white light LED as well as – in close cooperation with Osram OS – a manufacturing process. The know-how was transferred there and production began in summer 1998. Agilent (Lumileds) likewise began mass production of white LEDs in summer 1998. General Electric (GELcore) and Toyoda Gosei have been in production since 1999. White LEDs are now offered by almost all major manufacturers. Today LEDs are increasingly used for the most varied lighting purposes. Table 34 lists possible applications of LEDs according to their properties.

Table 34. Properties and applications of light-emitting diodes\(^{89}\)

| Properties                              | Application                                      |
|-----------------------------------------|--------------------------------------------------|
| UV- and IR-free illumination            | Museum and showcase lighting                     |
|                                         | illumination of fine art                         |
|                                         | refrigerated display cases                       |
|                                         | medical lighting                                 |
|                                         | illumination of light-sensitive materials        |
| Low-voltage                             | damp and subaqueous locations                    |
|                                         | portable applications                            |
| Small-size                              | furniture lighting                               |
|                                         | directional lighting                             |
|                                         | displays                                         |
|                                         | surface-mount applications                       |
| Low-temperature                         | area lighting, cabinet lighting                  |
|                                         | furniture lighting                               |
|                                         | refrigerated display                             |
| Energy saving and long service          | transit shelter lighting                         |
| lifestationary or mobile                | emergency and exit lighting                      |
|                                         | garden lighting                                  |
| Durability                              | mobile applications                              |

\(^{89}\) Source: Haller (2003)
4.5.2.3 **Scope of investigation and availability of data**

The scope (system boundaries) of the comparative assessments includes the entire life cycle of the light sources. The individual life cycle stages include:

- Raw material procurement, pre-production
- Manufacture of light sources
- Use phase
- Disposal/recycling

Data from the most recently available research study was used for the assessment of incandescent and energy-saving lamps. The study, authorized by the Federal Energy Office of Switzerland, was completed by Mani and published in August 1994. Mani worked closely with the manufacturer OSRAM to collect the required data. Specifically, the data on raw materials procurement and light source manufacturing were taken from this study. For the third variant, white LEDs, quantitative data was only available for the production of the 0.35 g semiconductor chip, the core of the LED. The data on LED chip production that included pre-production and raw materials procurement data were taken from the GABI database and are for 1999. No detailed assessment data were available for the other components of the white LED (the housing, series resistor, fluorescent material, etc.). This must be seen in perspective, however, as the greatest share of the environmental impact results from the use phase.

In the submitted comparative assessment of incandescent and energy-savings lamps (Mani 1994), a 75-watt incandescent lamp manufactured by OSRAM (variant 1) was compared to a 15-watt energy-saving Dulux EL lamp with integrated electronic ballast also by OSRAM (variant 2a). As the performance parameters of energy-saving lamps have regularly been improved (particularly with regard to service life), the case study also considers the current energy-saving lamp Dulux EL Longlife (variant 2b), however the production data is based on the former Dulux EL. These conventional lamps are compared to two white LEDs, the “white LED of today” (variant 3a) and the “white LED of tomorrow” (version 3b), each having a power rating of 1 watt. These two variants make possible an assessment of currently available LEDs (assumed luminous efficiency: 18 lm/W) as well as the potential of future efficiency enhancements (assumption: 65 lm/W).
A defined quantity of light was established for the assessment profile. The average quantity of light emitted by the Dulux EL energy-saving lamp from Mani, 6,579 million lumen-hours (lmh), was established as the reference value and functional unit for the profile. The result is arrived at by multiplying the service life of the Dulux EL by the mean luminous flux. The resulting technical data for the five variants used in the case study can be found in Table 35.

Table 35. Technical data utilized for the case-study variants

|               | Var. 1 | Var. 2a | Var. 2b | Var. 3a | Var. 3b |
|---------------|--------|---------|---------|---------|---------|
| incandescent  |        |         |         |         |         |
| lamp          | 75     | 15      | 15      | 1       | 1       |
| Dulux EL 15   | 1,000  | 8,000   | 13,000  | 15,000  | 15,000  |
| Dulux EL      | 960    | 900     | 900     | 18      | 65      |
| Longlife      |        |         |         |         |         |
| Luminous flux | 897.5  | 822.4   | 900     | 18      | 65      |
| (lm)specified |        |         |         |         |         |
| Luminous flux (lm) average | 12 | 55 | 60 | 18 | 65 |
| Luminous efficiency (lm/w) | 0.898 | 6.579 | 11.7 | 0.27 | 0.98 |
| Quantity of light per life cycle (Mlmh) | 6.579 | 6.579 | 6.579 | 6.579 | 6.579 |
| Reference quantity (Mlmh) | 7.33 | 1.00 | 0.56 | 24.36 | 6.71 |
| Quantity of lamps used for reference quantity | | | | | |
| Weight of light source including packaging (g) | 42.8 | 177.1 | 177.1 | 0.35* | 0.35* |

* Here only the LED chip is being referenced, not the complete LED light source.

4.5.2.4 Description of the life cycle stages

Raw material procurement and production

A great number of raw materials are used in the production of light sources. In the following, the essential production steps for three of the light sources are shown, with special reference to the production of LEDs. The manufacture of incandescent lamps consists of four major production steps: Production of the glass envelope, production of the tungsten filament and its support structure, production of several small components, and final assembly of all components.

90 Source: Mani (1994), Gabi 4 database (2001) and own calculations
The production of compact fluorescent lamps also consists of four major steps: Production of the glass envelope, production of the luminescent material, production of the electrode structure and various small components, and final assembly of the components.

The production of light-emitting diodes generally follows a different procedure than that described above and is depicted in the following chart. The wafer-processing and subsequent steps will be explained below.
Fig. 45. Stages of production for the LED

The core of a light-emitting diode is the LED chip (consisting of elements from the third and fifth groups of the periodic table), which is produced in the wafer-processing stage. After the mono-crystalline base material is cut into individual wafer-like discs, various semiconductor layers are applied to the wafers using the epitaxial process. This refers to the controlled epitaxial growth of a substance on a mono-crystalline base, the substrate. A key technology in this process, Metal-Organic Chemical Vapor Deposition (MOCVD) has proven to be the best method for the manufacture of optoelectronic and electronic semiconductor layers in modern light sources such as LEDs and lasers, high-output solar cells, and high-frequency electronics and power electronics. Aixtron AG, who builds MOCVD plants worldwide, is the market leader in this field.

In Metal-Organic Chemical Vapor Deposition, nanolayers are grown from gaseous, metallo-organic substances on wafer slices. Pre-reactions of the elements to be deposited are avoided by either conveying them into the reactor in a hydrated form or by means of associated organic molecules (metal-organics). These substances are also called “precursors.” The source substances are transported by means of a carrier gas (hydrogen, nitrogen) across a substrate surface in the reactor heated to 350° to 1200°, depending on the material system. In this procedure, the precursor molecules dissociate thermally (pyrolysis) on the substrate surface (Dadgar 2003).

The core of an MOCVD plant is the Planetary Reactor. Geometrically arranged wafers revolve like the planets on a likewise rotating carrier disk.
In this way the wafers are evenly exposed to the process gases. Growth of the layers on the wafer is determined by the quantity and composition of the process gases, temperature, pressure, and time. Up to 50 different layers are needed to produce functional chips; these layers are applied to the wafer during a 5–6 hour production “run.” At this point the MOCVD process is complete and the coated wafers leave the reactor. The crystalline deposit of the materials can be very precisely controlled, thus allowing the controlled deposition of the various materials one above the other to create the desired layer properties. A modern blue LED, for example, consists of a great number of different materials such as gallium nitride, used as the base material; indium gallium nitride, for the luminescent layer; and aluminum gallium nitride to enhance efficiency. Silicon and magnesium are used for the n- and p-regions (Krost & Dadgar 2002). In the MOCVD process, by manipulating gas valve switching times and the gas flow, ultra-thin layers and abrupt boundary layers can furthermore be produced. The process parameters are easily scaled up to large reactors for mass production. The process can be universally implemented, as there exists a metallo-organic precursor for each chemical element (Grahn 2003).

![Fig. 46. Schematic representation of the chip structure of an AlInGaP LED](image)

After the wafers leave the reactor, they are characterized (contacts of the pn-transitions). Thereafter electrical contact points consisting of a gold alloy are applied by means of a lithographic photoresist process and an additional layer of metal is applied to the backside of the wafer. To avoid energy losses in the gold alloy, it undergoes an annealing process that lowers its resistance to a fraction of the original value. In the next steps the wafer is attached to an adhesive film, enclosed in a tension ring, and cut with a diamond saw into individual segments or dies 0.35mm by 0.35mm in size. The functionality of the dies is then checked (Aixtron AG 1999). In the case of blue- or ultraviolet-emitting diodes used in the manufacture of white LEDs, the diode chip in the reflector is covered with a drop of luminescent dye. Thereafter the various components of the light-emitting diode are assembled.
LEDs come in a great number of structural configurations. Diverse metal/glass – or more commonly, epoxy or plastic – housings are used. The latter can easily be produced in suitable numbers for mass production. 

T-type LED: This form is the original structural shape of the light-emitting diode. It consists of the LED chip, the contacts, gold or aluminum connecting wire, and the plastic housing. After fixing the chip to the reflector on the metal lead, the contact to the second lead is established using a thin gold wire. Finally this is all molded into a stable unit with epoxy resin or other plastic material. The optical characteristics of the LED are determined by the reflector geometry, the shape of the plastic housing, and the position of the chip inside the housing (Vossloh Schwabe Deutschland GmbH 2003).

SMD LED: There are also the LED soldered to the back of the printed circuit board and the SMD (Surface Mounted Device), an extremely miniaturized form of the LED. Unlike the standard LED, the SMD LED has no metallic reflector. There are many different SMD structural shapes and sizes, varying according to application.

COB LED: Tightly packed, effective heat-dissipating solutions can be achieved using chip-on-board (COB) technology. The raw chips are directly installed on the circuit board. The chip connections and the board are connected with gold wire. The chip is covered and protected with a drop of epoxy resin. This technology allows more light to be radiated from a smaller surface.

LED modules are standardized or customized LEDs that consist of several LED-bearing circuit boards. These are readily used by manufacturers of display and signal light technology. The boards to which the diodes are attached can have many possible shapes. By varying the dimensions, mounted components, and wiring, the housing shapes can be varied with relative freedom (Haller 2003). Furthermore, the first LED modules which could someday replace conventional lamps already exist: The socket-mount LED module. It combines LED, necessary electronics, and the standard base (e.g. E27) to form a complete lamp that may be used in an existing luminaire housing.

Use phase

Incandescent and energy-saving lamps are used everywhere: in business and industry as well as in the home; however the incandescent lamp is used much more commonly in the private household. More common in the business place is the energy-efficient fluorescent tube. Because of economic reasons already discussed, white LEDs are still used mostly in spe-
cial applications. In order to nonetheless assess and compare potential environmental impacts for the entire field, white LEDs are compared in this case study to conventional light sources.

The use phase is of major consequence in the life cycle assessment profile, as light sources are a significant consumer of electrical energy in this phase. The energy consumption is based upon the production of a specific reference light quantity (RLQ), which serves as an equivalence value. Specific energy consumptions of the variants are derived from multiplying power input, service life, and number of lamps required.

### Table 36. Energy consumption of each case-study variant

| RLQ = 6,579 Mlmh | Variant 1 | Variant 2a | Variant 2b | Variant 3a | Variant 3b |
|------------------|-----------|------------|------------|------------|------------|
|                  | incandescent lamp | Dulux EL 15 | Dulux EL Longlife | white LED of today | white LED of tomorrow |
| Power input (W)  | 75        | 15         | 15         | 1          | 1          |
| Service life (h) | 1000      | 8000       | 13000      | 15000      | 15000      |
| Lamps required for RLQ (quantity) | 7,33 | 1,00 | 0,56 | 24,36 | 6,71 |
| Energy consumption for RLQ (kWh) | 550 | 120 | 109 | 365 | 101 |

Emission factors for the current electrical power mix in Germany as taken from the GEMIS 4.1 database and listed in the appendix (Table 56) form the basis for the calculations of environmental impacts in the use phase (GEMIS 4.1 2003).

**Disposal**

There are no legal regulations governing the disposal of incandescent lamps, as the environmental impact of almost all substances they contain is negligible due to their nature and the amounts involved. Therefore almost all incandescent lamps are disposed of in the household waste. The disposal of compact fluorescents, however, is regulated. In 1996, the German Waste Avoidance, Recycling and Disposal Act came into effect. It places discharge-type lamps (in the case of disposal and recycling) into the category of waste requiring special attention. The lamps must be collected separately and classified as hazardous waste or be recycled.

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91 Source: Mani (1994), Gabi 4 database (2001) and authors’ own calculations
The regulations governing the disposal of electrical and electronic devices changed in 2002. Following modifications to the European Waste Catalogue, in January 2002, almost all electronic devices and electrical devices are now classified as waste requiring special handling. They may not be disposed of in household or ordinary waste. The fluorescent tube and the light-emitting diode are also listed in this catalogue. They are classified as materials for special handling and supervision – the energy-saving lamp because of its mercury content and the LED because of possible quantities of arsenic, gallium, phosphor, or compounds containing them (Senatsverwaltung für Stadtentwicklung Berlin 2003). Newer developments include the EU regulations on to-be-disposed-of electrical and electronic devices, in effect since February 2003. The directive 2005/96/EG regulates the disposal of electronic and electrical devices, whereas directive 2005/95/EG limits the use of certain hazardous substances in these devices. The European directives stipulate that the listed products (including fluorescent tubes and LEDs) must be returned to and accepted by the manufacturers and properly disposed of. Additionally, directive 2002/95/EG contains several exceptions with regard to the avoidance of certain hazardous substances in products. For example, it is explicitly mentioned that no more than 5 mg mercury will be allowed in compact fluorescent lamps in the future. The directives are to be incorporated into national law by August 2004; draft regulations for the disposal of electrical and electronic devices, based upon the Waste Avoidance, Recycling and Disposal Act, already exist.

Detailed data for this life cycle stage are included in the environmental assessment by Mani (1994) for the incandescent lamp and the energy-saving lamp. No quantitative data is available for LEDs. As it is clear from the assessment data for the incandescent lamp and the energy-saving lamp that this stage only plays a minor role in the overall investigation, the question of disposal will not considered quantitatively, but only discussed with respect to problematic substances (mercury).

4.5.3 Life cycle inventory analysis

In the life cycle inventory analysis, the material and energy relationships between the lighting system being studied and the environment are recorded, i.e. the input flows from the environment and the output flows that are returned to the environment are noted. The goal is to establish a data inventory based upon functional equivalents for the selected variants. Since quantitative data for disposal are not available, calculations can only
be made for manufacturing, inclusive of raw materials procurement, and the use phase.

The total absolute material and primary energy amounts needed for the manufacture of the quantity of lamps required to generate the set reference light quantity (RLQ) of 6.579 million lumen hours are listed in the table below. The total material flows for the five lighting variants can be found in Table 57 in the appendix.

Table 37. Material and energy requirements for the production of the lamps for the RLQ\(^{92}\)

| RLQ = 6.579 Mlmh | Variant 1 incandescent lamp | Variant 2a Dulux EL 15 | Variant 2b Dulux EL Longlife | Variant 3a White LED of today | Variant 3b White LED of tomorrow |
|------------------|-----------------------------|-------------------------|-------------------------------|------------------------------|---------------------------------|
| Material require- | 669.4 g                     | 453.3 g                 | 253.8 g                       | 2671.5 g                     | 735.9 g                         |
| ments, total      |                             |                         |                               |                              |                                 |
| Product quantity, | 313.7 g                     | 177.1 g                 | 99.2 g                        | 8.5 g*                       | 2.3 g*                          |
| Primary energy requirement | 14.7 MJ                     | 32.6 MJ                 | 18.3 MJ                       | 5.9 MJ                       | 1.6 MJ                          |

* Here only the LED chip is being referenced, not the complete LED light source.

In looking at the material quantities for the first three variants, consideration must be given to the packaging. The ratio of materials required to product quantity is 2.1–2.6:1. The large material quantities for LED chip production in proportion to product quantity reflect the fact that semiconductor technologies require considerable volumes of raw materials such as ore and stone and auxiliary materials in order to produce a small, highly complex quantity of product. The ratio is 314:1. Moreover, an assessment of a complete LED lighting system must also consider materials for the housing, ballast resistor, packaging, etc.

The situation is different for the primary energy requirement. The primary energy requirement for LED chip production is lower than that for conventional light sources. The difference must again be put into perspective, as the missing system components in the LED lighting system must be included. Production of the circuit board for the ballast for the Dulux EL15 energy-saving lamp alone consumes 17.3 MJ of the indicated 32.6 MJ/BLM. It can therefore be assumed that the primary energy requirement of an LED lighting system is comparable to that of conventional lighting sources.

\(^{92}\) Source: Mani (1994), Gabi 4 database (2001) and own calculations
If energy consumption in the use phase is compared to that of the production phase, it becomes obvious that, depending on the variant, 97–99% of the energy is consumed during the use phase, with the result that the deviation caused by the incomplete consideration of the LED lighting system can be viewed as minimal. The central measure for the environmental assessment of light sources being used for illumination is energy consumption during the use phase and the associated emissions. Energy consumption for raw materials procurement und manufacture of the light sources is minimal. Moreover it becomes very clear that the current white LED is at a disadvantage by a factor of 3 as compared to the energy-saving lamp. Only, if the future scenario for the white LED comes to pass, i.e. a luminous efficiency above roughly 65 lm/W is achieved, will energy consumption become comparable to energy-saving lamps.

This fact is also generally confirmed by the calculated emissions, which accumulate as relative quantities. Here again, emissions resulting from power consumption during the use phase dominate. These emission quantities are shown in brief in the table below and in detail in Table 58 in the appendix.

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93 Source: Mani (1994), Gabi 4 database (2001) and author’s own calculations
The total emission quantities expressed in the bar chart also make clear that the white LED of today is better than the conventional incandescent, but at a disadvantage by a factor of three when compared to the energy-saving lamp. Only if the future scenario for the white LED is realized, will the emissions become comparable to those of energy-saving lamps.

With respect to critical substances used in the light sources, mercury (found in the energy-saving lamp) and arsenic (used in the manufacturing process for the white LED), in particular, must be considered. Technological improvements in recent years have made it possible to significantly reduce the proportion of mercury contained in fluorescent tubes. The energy-saving lamp Dulux EL by OSRAM contained as much as 10 mg of mercury in 1994; currently the compact fluorescent by OSRAM contains roughly 4 mg of mercury; this represents its emission potential, in the case of release caused by improper disposal. If lamps break at the waste disposal site, mercury can escape directly into the environment. Mercury and numerous mercury compounds are volatile and highly poisonous, which is one of the main reasons for disposing of these lamps as hazardous waste or recycling them. Furthermore, mercury emissions in the production phase and the use phase must be considered in the overall assessment, as emissions also take place, for example, during power generation.

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94 Source: authors (database: authors, Mani 1994, Gabi 4 database 2001)
Table 39. (Potential) mercury emissions of the case-study variants

| Variant | Hg emissions in raw materials procurement / manufacturing (mg) | Hg emissions in use phase (mg) | Hg quantity contained in product and potential release risk (mg) | Total (mg) |
|---------|---------------------------------------------------------------|-------------------------------|---------------------------------------------------------------|------------|
| RLQ = 6.579 Mlmh | Variant 1 incandescent lamp 0.004 | 6.65 | 10.00 | 6.65 |
| | Variant 2a Dulux EL 15 0.26 | 1.45 | 2.24 | 11.71 |
| | Variant 2b Dulux EL Longlife 0.15 | 1.32 | 4.41 | 3.70 |
| | Variant 3a white LED of today 0.03 | 4.44 | 1.22 | 4.44 |
| | Variant 3b white LED of tomorrow 0.01 | 1.23 | | |

The (potential) mercury emissions mostly arise during the use phase. Only in energy-saving lamps are considerable emission quantities added by the mercury contained in the product itself. Here it is clear that current energy-saving lamps with respect to total quantity still are better than current white LEDs. Only in the white LED of tomorrow scenario would a significant avoidance of mercury emissions be possible.

No quantitative data for arsenic and its compounds was available for evaluation. The most common materials for the production of LED chips are aluminum indium gallium phosphide and aluminum gallium arsenide (AlInGaP and AlGaAs) for red and yellow LEDs, and indium gallium nitride (InGaN and GaN) for green and blue diodes (FGL 2003 and others). Since the production of white LEDs requires either blue, green, and red diodes or else blue-emitting diodes, these substances might also be present in white LEDs. Gallium arsenide, like gallium nitride and gallium phosphide, belongs to the semiconductor groups III/V. With respect to handling and disposal, arsenic and its compounds are of the greatest significance. The toxicity of arsenic and its compounds varies greatly, but the substances used in the semiconductor industry tend to represent a certain hazard potential. The carcinogenicity, mutagenicity, and reproductive toxicity of many arsenic compounds is indisputable (BLU 2002).

As a semiconductor material, gallium arsenide is not poisonous. But in the presence of oxygen and water, an ultra-thin, very toxic layer may form

95 Source: Mani (1994), Gabi 4 database (2001) and authors’ own calculations
on the surface of the material, which could cause environmental damage at a conventional landfill disposal site. Furthermore, an extremely poisonous gas is produced in the manufacture of gallium arsenide: arsine (arsenic hydrogen), chemical formula AsH3, which is used to guarantee the purity of the semiconductor material. Even minimal concentrations of a few arsine molecules per million gas particles in the air can cause severe health damage or be even lethal. The arsenic-hydrogen bond is highly toxic. It blocks nerve receptors and can impede the transport of oxygen in the body.

Therefore, light-emitting diodes also require special disposal treatment and supervision due to the possibility that they may contain arsenic, gallium, and phosphor compounds. According to the European directives, listed products must be accepted in return by the manufacturers and properly disposed of. A recycling procedure for LEDs does not yet exist (Grezcmiel 2001). Researchers at the University of Marburg found an alternative to arsine years ago. The alternative substance is less volatile and has a much lower vapor pressure. It is considerably less harmful for the environment than arsine. The substance is of interest for semiconductor industry, because the much lower hazard risk reduces the costs of a semiconductor production facility. Waste quantities are also much lower (Thimm 1999).

4.5.4 Life cycle impact assessment

To complete the impact assessment, it is necessary to have access to emissions data which can be allocated to specific environmental impacts. Since the data shows a direct relationship between energy consumption and the relevant emissions, this would also be seen in the categories greenhouse effect, acidification, and eutrophication and not reveal any new knowledge; we therefore refrain from making this presentation.

4.5.5 Light sources based on quantum dot technology

4.5.5.1 Definition and background physics

Quantum physics describes particles having wave functions. This particularly applies to electrons, as the smallest stable particles with a rest mass. Should the wave function of the electron be increased until it reaches the geometric material realm, quantum mechanical effects can be anticipated, leading to interesting new properties.
This holds true for nanoparticles below about 20 nm in size (typically 1–5 nm). They are at the borderline between individual molecule and dimensional crystal. The movement of the electrons is constrained by the minuteness of the nanoparticles. Since the electrical and optical properties of solid bodies are determined by their electrons, a discretization of energetic states and a broadened band gap between valence band (completely filled with electrons) and conduction band (not completely filled so electrons are mobile) can be observed with decreasing material size (Haase & Kömpe 2003). The resulting new properties can only be explained with the help of quantum physics. Such nanoparticles are therefore called quantum dots and are more or less zero-dimensional.

The electrons feel "squished" by the restricted particle boundaries and thus the distance (band gap) between original state and excited state increases with the decreasing size of the particles. If an electron shifts from the excited state into the original state, light is emitted; its wavelength and energy level are dependent on the band gap. It is therefore possible to generate wavelengths ranging from UV through the visible spectrum on up to the infrared (350–2300 nm) using quantum dots of the same composition (Evident Technologies 2003). The optical properties are determined by the size of the quantum dots. This is what makes the quantum dot so interesting for lighting technology. Earlier it was only possible to generate light of different wavelengths by combining different substances. Quantum dots even permit using substances for light generation that were previously unsuitable (Bertram & Weller 2002). Additionally, more than 50% of the atoms lie at the surface due to the small size of the quantum dots, thus permitting a precise tuning of light-emitting properties and suggesting that the emission of several colors from a single dot may be possible (SNL 2003). Quantum dot crystals used in combination with other crystals or phosphors can emit any desired color.

Quantum dots can be produced technically by means of epitaxial growth, for example in vacuum precipitation processes or by chemical methods from colloidal solutions (Rubahn 2002).

4.5.5.2 Applications of quantum dots

By irradiating a solid body with light of a suitable wavelength, electrons can be advanced from the valence band to the conduction band. The energy input must be at least as great as the band gap. After a short time, the electron falls back to the valence band, with the surplus energy often being emitted in the form of light. The energy or the color of this emitted fluorescent light corresponds to the band gap energy. Several methods are being applied for using quantum dots to produce light.
Direct-charge injection: In direct-charge injection, electrons in the quantum dots are brought into the excited state by the transport of electrons or electron voids and the resulting collision processes. Research on this method is taking place at the Massachusetts Institute of Technology (MIT, Cambridge) and elsewhere; in 2003 they succeeded in making a major step forward in development. The problem in direct-charge injection is to stimulate as many of the electrons flowing through the carrier material as possible to electron excitation in the quantum dots and thus light production. MIT researchers were able to augment the efficiency of direct-charge injection by a factor of 25 by placing CdSe dots (cadmium selenide) between two organic layers (Riebeek 2003). With this technology an efficiency increase of up to 100% (all injected charges generate light) may be possible, more than with any other light source. This would raise the energy efficiency of light sources to a new dimension. The colors being emitted are two to three times as pure as those of ordinary OLEDs (Riebeek 2003). After further development, this technology, an extension of OLED display technology, will revolutionize flat-screen technology. The durability and stability of quantum dots are positive factors in this respect.

Stimulation by UV light: Researchers at the Department of Energy’s (DOE) Sandia National Laboratories, Albuquerque, have chosen a different approach. They developed the first white light-emitting device using quantum dots (SNL 2003). In contrast to direct-charge injection, stimulation is effected by UV light (380–420nm wavelength) rather than a current. The quantum dots are covered and encapsulated with suitable organic molecules such that they emit light in the visible spectrum when stimulated by ultraviolet light. The required UV light is produced by traditional LED technology. Therefore the efficiency cannot be higher than that of blue-light LEDs. However, it is higher than in traditional white-light LEDs, as their phosphor materials show poor absorption for the blue wavelength and thus low efficiency. Optical backscatter losses of traditional phosphor materials reduce the efficiency by 50%. This can be overcome with the new technology. In 2004, researchers tried to increase the concentration of quantum dots in the capsules to enhance light efficiency and to understand the behavior of quantum dots in higher concentrations.

So far, researchers at MIT and Sandia have mainly used quantum dots of the semiconductor materials cadmium sulfide and cadmium selenide, which contain the poisonous heavy metal cadmium and are therefore not appropriate for mass production. Harmless alternatives, however, are being investigated, including nanocrystalline silicon and germanium with a surface of light-emitting manganese ions. The Nanoelectronics Research Centre (NRC), at the University of Glasgow, has already produced Si-SiGe quantum-dot-based LEDs, which according to the researchers, would be
ideal as light sources in optical circuits, because they can be directly integrated into the Si chips (Tang et al. 2003).

In addition to the direct generation of light, quantum dots are also used as markers in fluorescence microscopy of biological and medical preparations. They are tied to biomolecules (e.g. DNA fragments) and stimulated to emit light of various colors when irradiated with UV or blue light. Compared to current dyes, quantum dots are more stable and tend less to fade. This allows more detailed investigation of a preparation and the differentiation of details becomes easier. By using quantum dots, different parts of the preparation can be colored differently, thus allowing the recognition and determination of various parts of the tissue simultaneously (Bertram & Weller 2002). Use of quantum dots promises faster, more flexible, and less expensive tests and immediate biological analyses and patient diagnoses. However they must be prepared with sufficient precision if they are to be used in medicine and research.

Components containing quantum dots also promise improvements in the development of lasers, detectors, optoelectronic switches, and memory elements (e.g. optical high-density memories). Nano-electronics also has great hopes for the application of quantum dots. Due to their high quantization energy, nanoparticles are capable of storing discrete amounts of electrons (charge carriers) (Bertram & Weller 2002). Attempts to use quantum dots as memory devices are already being made by several firms. According to Bertram and Weller (2002), a combination of quantum dots as memory cells with a molecular switch leading to a braid of nanowires would be the first step on the way to the nanocomputer. Generally it can be stated that research work around the world on quantum dots technology has recently greatly intensified.

4.5.5.3 Summary and prospects for the implementation of quantum dots

Quantum dots are nanoscale particles at the boundary between molecule and solid body. Their composition and tiny size are responsible for their extraordinary optical properties, which may be adjusted to meet specific requirements by changing the size and chemical composition (of the surface). Under stimulation they can be induced to emit light. In contrast to other light sources, they generate an extremely pure and bright light and can at the same time emit an entire spectrum of colors by stimulation of a single wavelength.

It is anticipated that quantum dot technology will have a firm place in display technology in the long term, especially in combination with OLEDs, however their development is not yet as far along as that of the
4.6 Case study 5: The risk potential of nano-scale structures

OLED. The use of quantum dots will further enhance the efficiency of light sources, generate more brilliant colors, and reduce the number of necessary manufacturing steps in display manufacture. These are economic and environmentally relevant advantages in favor of quantum dots and the use of their optical properties in lighting technology. However, an industrial application is not to be expected in the near future.

4.5.6 Case-study Summary

The objective of this case study was an investigation of the eco-efficiency potential of new nanotechnological products in the lighting industry. For this purpose, white LEDs were compared to conventional light sources including the incandescent lamp and the energy-saving lamp (compact fluorescent), and the future potential of quantum dots was considered.

The case study demonstrates very clearly that energy consumption during the use phase is by far the most significant factor in the environmental assessment of light sources for lighting purposes. The current white LED compares more favorably to the classic incandescent lamp, but is at a disadvantage by a factor of three when compared to the energy-saving lamp. Only at luminous efficiency values above approx. 65 lm/W, values which were assumed for a future white LED, will they be able to compete with the energy-saving lamp with respect to environmental impact. This was confirmed by Arpad Bergh, president of the US Optoelectronics Industry Development Association (Interview by Siemens NewsDesk 2003). He makes the assumption that the luminous efficiency of the white LED must be increased to 85–100 lm/W before it will become interesting for everyday illumination purposes.

It can be assumed that the use of quantum dots in the future will make possible increases in the energy efficiency of light sources. Quantum dot technology is expected to have a firm place in display technology over the long term, particularly in combination with OLEDs. Actual application of quantum dots in commercial products, however, is still some years away.

4.6 Case study 5: The risk potential of nano-scale structures

The following section presents and discusses the potential risks of nanotechnological applications. The discussion specifically focuses on nanoparticles, as nanoparticles are already being produced and applied on a large scale and thus form the basis for numerous other applications; fur-
thermore, relatively broad discussions on the risk potential of nanoparticles are already taking place. The chapter consists of four parts.

The first part looks at those risks that already can be expected on the basis of the properties of intentionally manufactured nano-scale products, agents, and materials; furthermore, a literature survey on the problematic effects of selected substances and structures for humans and the environment is presented. The second part, taking as its example the nanoscalar titanium oxide found in suntan lotions, discusses the problem of equating substances of micro- and nano-size. The third part analyses the life cycle of nanoparticles. Finally, we compile the results of the study and illuminate possible consequences of these findings. In the course of the case study, a written survey was conducted and experts in the field of nanoparticle toxicology from Great Britain, Germany, and the United States were polled. The results are noted in the relevant sections of this chapter. A detailed presentation of the survey results can be found in the appendix.

4.6.1 Potential risks of nanotechnology

Development of the potential of nanotechnology is only at its starting point, with relatively simple applications and products already entering or at the threshold of the market, many of which involve the application of nanoparticles. One example is nanoscalar carbon black, added to automobile tires to improve abrasion resistance, which has already been in use for a very long time. In many cases, the examples discussed can also be viewed as a continuation of lines of decades-long development. Many of these examples still compete with older traditional solutions. In such cases, nano-scale innovations are thus only replacing or enhancing already existing conventional solutions. The novelty of these examples is for the most part only to be found in the nanoscalar size of the particles.

Nonetheless, the question arises as to the extent to which the drive into the area of nanotechnology entails new types of effects. Do nanoscalar materials have new (or do they enhance already known) properties that could be detrimental to the environment and/or human health? Such new and/or enhanced effects are normally to be expected. After all, it is such altered or enhanced properties that make nanomaterials interesting for production purposes.

However, questions concerning new (or enhanced) properties or effects and possible negative side effects and consequences have so far rarely been systematically investigated or formulated. The neglect of side effects is partly the result of institutional delay. Established procedures for regulating hazardous substances have not yet been adapted to address these
new issues. The non-governmental organization ETC Group (ETC Group 2002), for example, notes that the addition of considerable quantities of titanium dioxide nanoparticles to high-sun-protection-factor suntan lotions required no new investigations in the USA. Conventional titanium dioxide had already been tested and approved; new applications of titanium dioxide nanoparticles were considered to be equivalent to pre-nanotechnology applications with respect to environmental and health impacts (see ETC Group 2002). Whether this equivalency is justified, cannot be settled here, but in light of the altered properties found at the nano-level, it should at least be addressed.

This is of particular importance, knowing as little as we do, so far, about the environmental and health aspects of nanoparticles. Those investigations that have been conducted on the effects of ultra-fine particles resulting from combustion processes are alarming.

However it should be noted that the common properties of nano-scale systems are predominantly due to the scale of the materials and products. This means, on the one hand, that in nanotechnology’s role as a cross-sectional technology, problems may occur that are primarily “contingent on the technology.” On the other hand, other problems may arise from a specific combination of circumstances within the context of specific applications. The technologies as well as the application contexts may greatly diverge and likewise the potential risks to environment and health that need to be addressed. For example, nanotechnological procedures and products and their impact in the field of biotechnology will differ fundamentally from those in areas such as electronics and thin-film technology. Moreover, different impacts on the various environmental compartments can also be expected.

### 4.6.1.1 Technology-specific characteristics of nanoparticles as possible hazard sources

An initial preliminary technical characterization of nanoparticles and nano-structured surfaces reveals the following lowest common denominators. It can be stated, that:

- We are dealing with structures in the nano-dimensional realm
- Properties of the molecules are altered in this dimension (thus leading to desired effects and behavior)
- In particular, the ratio of surface to volume changes

Additionally, one must specifically mention that substances such as fullerenes and nanotubes do not generally exist in the natural environment. The impact of such new materials on environment and health is difficult to foresee.
In addition to the properties of nanoscalar materials already mentioned, the following aspects are of particular importance:

- Mobility in environmental compartments and inside the organism
- Reactivity and reactive specificity
- Bioaccumulation
- Persistency
- Non-occurrence in nature
- Pulmonary intrusion
- Water solubility, liposolubility
- Carrier and piggyback effects
- Agglomeration, dispersion
- Other properties

As science learns more about conditions of implementation and application contexts, other aspects must also be considered, for example:

- Nature of application and quantities
- Contained / non-contained (open/closed) applications
- Aspects of the life cycle such as raw material expenditures, recyclability...

In an attempt to characterize nanomaterials in a standardized manner, we can make the following statements: Nanotechnological systems and products, particularly nanoparticles, for the most part currently represent the further development of known processes and products.

The key difference is that it is increasingly possible to shape things at the atomic and molecular level. This means several scientific and technical disciplines can contribute to the production of nano-scale building blocks and components.

Industrially produced nanomaterials cannot be viewed as a uniform substance or materials group, thus making the assessment of potential risks and hazards even more difficult. There is, in fact, an enormous range of structures and materials in the nanoscalar dimension. Their distinguishing characteristics:

- A large number of chemical elements and compounds are utilized
- They exist at the nano-scale level in various sizes and have various surface structures
- As yet, no particularly worrisome group of substances to be singled out for investigation has been identified.

Consequently there can be no simple answer to the question, as to whether nanoparticles are safe and what impact they will have on human life and the environment. The differences in size, shape, surface, chemical composition, and biopersistence require that each nanomaterial be individually investigated with respect to possible environmental and health
hazards. Very similar compounds may have very different effects. It is also known from toxicity research that certain substances may be comparatively harmless as long as they are applied to the skin or taken orally, but can be extremely toxic when inhaled (Colvin 2003a, Hoet 2004). The question, as to whether and to what extent general statements on hazards caused by specific substance groups or structures can already be made, will be dealt with later in this paper.

**Nanoparticles**

Nanoparticles can be classified as belonging to the transitional area between the realm of individual atoms and molecules and that of larger ensembles.

Many of the particularly interesting new properties of nanoparticles are due to the altered ratio of surface to volume. Because of their incredibly small size, nanoparticles have an enormous surface relative to their volume. They are, therefore, very reactive, reacting comparatively quickly and aggressively, in part even spontaneously with their environment. The reason for their reactivity is found in the surface of the nanoparticle. Due to the altered surface volume ratio, the surface of the nanoparticle has many more free electrons, which, due to their position on the surface, are capable of reacting with their environment. Thus nano-scale materials and substances are more reactive than structures having a smaller relative surface area. For this reason, existing, known substances that now can be produced in nano-sizes can suddenly have properties and effects very different from those of their larger counterparts.

Some experimental results have already given rise to the question as to whether nanoparticles because of their tiny size and pulmonary intrusiveness and low biodegradability alone may provoke certain toxic effects almost independently of their specific composition. Other findings have contradicted this thesis. Asked whether the effects of nanoparticles are rather the result of their size, or their chemical composition, or the nature of the surface, the experts surveyed in the course of this project responded:

- Negative effects are due to size, as well as chemical composition, and surface structure. A weighting of the three aspects is currently not possible.
- Likewise, dosage, coating, shape, distribution in the tissue, distribution of charge or electrical potential between molecules, and degree of agglomeration may also have an influence.
- Effects are also determined by the condition of the human body: condition of the immune system, intake path (skin, respiratory, direct injection, etc.), and general state of health.
• One survey participant held the opinion that there might be differences between the effects of individual free nanoparticles and those bound in, for example, a composite material. Nanoparticles are also capable of adsorbing molecular contaminants. Adsorption can assist foreign matter in gaining access to parts of the body and the cell, from which it otherwise would be blocked. Transport of such biological contamination could be a greater risk for biological systems than nanoparticles as such, scientists say (New Scientist 2003).

**Behavior of nanoparticles released into the environment**

The problem of assessing nanoparticle effects is further complicated by the fact that a possible negative impact also depends on the agglomeration behavior of nanoparticles. It is known from the behavior of ultra-fine particles in combustion processes that they already begin to attach to each other shortly after combustion to form larger groups of particles (agglomerates). Oberdörster points out that agglomerated particles are neither more nor less problematic than other particle forms, but that individual nanoparticles can cause severe problems. It is likewise known that nano-scale titanium dioxide agglomerates more easily in aqueous than in lipophilic solutions. So far, it has not been possible to make generalized assumptions about the behavior of nanoparticles in differing media. This statement is also confirmed by our expert survey. General statements of the kind “All fullerenes agglomerate” cannot be made. The statements given on common behaviors are far less general and were all qualified:

• Nanoparticles can definitely form aggregates in gaseous and liquid media.
• Aggregates spread less evenly than individual nanoparticles.
• Airborne particles agglomerate homogeneously within ten seconds if the concentration is relatively high (10⁷–10⁸ particles/cm³). Lower concentrations need a considerably longer period of time.
• Agglomeration behavior depends on the surface coating, chemical reactivity, and electrical potential.
• If through the accretion of further atoms and molecules larger agglomerates are formed, the total surface area and thus the reactivity of the agglomerate may again change.
• The larger the surface, the greater the possibility that substances will aggregate. Agglomeration is also determined by the surface reactivity.
• Aggregated particles may de-aggregate again in the human body.
• Toxicity of particles may deteriorate during their life span.
Ultra-fine particles and nanoparticles

The presently limited knowledge of expected and possible effects and concerns about the negative effects of nanoparticles is based partly on analogies to the knowledge on ultra-fine particles. Ultra-fine particles (PM0.1) are the same size as nanoparticles; however, they are not industrially manufactured, but are the result of combustion processes. Ultra-fine particles have an average diameter of less than 0.1 micrometer (µm).

Epidemiological investigations of larger particles (diameter less than 10 micrometers) suggest with comparatively strong evidence that chronic exposure to particles in the air has a harmful effect on the cardiovascular system (Dockery et al. 1993, Kunzli et al. 2000). It is presently under discussion whether ultra-fine particles automatically cause greater damage than do larger particles because of their greater surface. Only a few studies on ultra-fine particles exist, but there are indications that such particles are more dangerous than larger ones (Howard 2004b).

Indications for negative effects of ultra-fine particles were also found by in-vitro investigations. Diabeté (2002) writes: “By means of in-vitro tests it was shown that ultra-fine synthetic particles have a stronger cytotoxic effect than larger particles of the same chemical composition. Flue dust from a waste incineration plant containing nano-scale particles increased the release of pro-inflammatory cytokines in lipopolysaccharid-stimulated macrophages and inhibited the formation of NO radicals. In co-cultures of macrophages and pulmonary epithelial cells it was shown that they release more cytokines than the total of the respective individual cell cultures.” These indications may suggest that nanoparticles, which are in part even smaller, in similar concentrations could a priori likewise be harmful to the cardiovascular system. Since ultra-fine particles are combustion byproducts, equating the effects of the two types of particles can only be done to a limited extent. Nanoparticles may cause additional and/or other problems (Colvin 2003a, Kreyling et al. 2004).

The above statements were confirmed by the results of the survey. According to the experts, substantial empirical data on the toxic impact of ultra-fine particles in the context of air pollution caused by articles of natural and combustion origin exist. The effects of ultra-fine particles on the pulmonary system, the cardiovascular system, and human blood are well documented. Claims about possibly harmful effects of inhaled particles from combustion processes, however, do not allow any direct conclusions about industrially manufactured nanoparticles. An example for a possible similarity between both classes of particles is the capability of ultra-fine particles to bypass the body’s defense mechanisms, penetrate cells, navigate through the body, and cause inflammatory reactions. Findings derived from particle toxicology thus point to concerns which should not be disre-
garded. On the other hand it is necessary to develop new methods of inves-
tigation and assessment that are suitable for industrially produced nanopar-
ticles.

4.6.1.2 Impact on health and environment

The following summarizes conclusions that suggest some possible effects. Results from relevant studies and the more or less substantiated conjec-
tures of researchers in this field are also presented. These statements are meant to be representative only – they could be supplemented by more examples – even so, no general conclusions about nanotechnology can be drawn from them. What does become clear, however, is that this is a field with a high degree of uncertainty and a large number of unknowns, whose systematic assessment has not yet begun.

Effects on the human body

Nanoparticles are very mobile: in animal subjects they have entered the liver, the brain, and even the fetus. Howard (University of Liverpool, England) reports a possible migration of nanoparticles into the fetus. His analysis was not yet available at the time of publication, but he was confident that evidence to support his initial conclusions would soon be available (Howard 2004a). Howard assumes that there is a natural transport path for nanoparticles, which they use to enter the body and move within it. He assumes that nanoparticles pass through the caveoles (openings) of the cell membrane. The openings have a width between 40 and 200 nm and seem to play a role in transport of macromolecules and proteins. Caveoles are big enough to transport nanoparticles (Howard 2004b). There is nothing known about possible effects in the body. One should add that the particles investigated by Howard were specifically prepared to pene-
trate such membranes.

Oberdörster (University of Rochester, New York) traced the distribution of carbon particles of 35 nm diameter after applying them to the nasal mucous membrane of rats. One day later the nanoparticles were found in the brain. The ends of the olfactory nerves had absorbed the particles and transported them into the bulbus olfactorius. Concentrations increased until the experiment was stopped seven days later. It is unclear what effects the particles have on the brain (Oberdörster 2004). Oberdörster reports in the context of the survey, that the same effect appears with other substances (30 nm virus, 50 nm colloidal gold, 30 nm Mn oxide) and also if applied to primates. Mn oxide caused reactions in rats that suggested inflammation at a concentration of 450 µg/m³ and twelve days’ exposure. In a somewhat older study, Öberdörster et al. reported carbon, between 20 and 29 nm in
size, being found in the livers of rats after six hours of inhalation (Oberdörster et al. 2002). The particles entered the blood circulation via the lungs. Oberdörster et al. emphasize that translocation into the blood and the organs may vary with other nanoparticles.

Nanoparticles may enter through the human lungs because they are too small to be filtered or to be destroyed by the protective mechanisms of the respiratory system (pulmonary mucus and macrophages). The pulmonary mucus that lines the lungs like a carpet is unable to filter fine and ultra-fine particles from the air or to transport them upwards. In the alveoli that lie beneath, where the gaseous interchange between lungs and blood occurs, macrophages absorb undesirable substances. Macrophages do not recognize structures/substances smaller than 70 nm as matter extraneous to the body.

The problem of nanoparticle translocation may become aggravated; as Donaldson (Napier University, Edinburgh) commented in the survey, if – as planned – nanoparticles are added to the human blood for medical treatment in the future. However, medical applications would be subjected to much stricter regulations and testing than the particles in industrial production that are being considered here.

There is likewise the suspicion that nanotubes could be harmful for the human organism. Lam introduced 0.1 and 0.5 mg carbon nanotubes into mice via the windpipe. After seven days all test animals had developed granulomae and in some cases inflammations, which after 90 days had worsened (Lam 2003). Warheit obtained comparable results in similar investigations with rats, but the granulomae did not continue to worsen after 30 days (Warheit et al. 2004). The two studies differ not only in their laboratory animals, but also in the nanotubes used. Warheit used “laser-evaporated nanotubes,” Lam used “HiPco and carbon-arc nanotubes.” The differing degrees of intensity of the inflammations could be caused by the differing nanotubes, suggesting a varying impact of similar substances. Furthermore, Warheit reports that in his test 15% of the rats died from a mechanical blockage of the upper respiratory tract due to agglomerated nanotubes. This suggests the necessity of integrating the behavior of released particles into the assessment of possible negative effects.

In the project survey, Kreyling (GSF - Forschungszentrum für Umwelt und Gesundheit) suggested that nanotubes might also be carcinogenic. It is known from the toxicology of mineral fiber that incorporation (especially inhalation) of biopersistent fibers of 20 µm length and above greatly increases the risk of cancer. Because of their length of more than 50 µm and their extraordinary stability, it cannot be ruled out that nanotubes, first of all, are biopersistent (they cannot be dissolved or broken down in concentrated acids), and secondly, increase the risk of cancer after inhalation.
So far, the impact of nano-scale titanium dioxide when inhaled is also unclear. This is, first of all, a concern for the labor force producing nano-scale titanium dioxide. Colvin points out that titanium dioxide may cause inflammation in the lungs (Colvin 2003a). Rehn et al. administered a coated and an uncoated form of ultra-fine titanium dioxide (diameter < 100 nm) in single doses to rats in work-place relevant dosages (0.15, 0.3, 0.6, and 1.2 mg). They could not, however, prove inflammation and assume that both forms of titanium dioxide are inactive in the lungs (Rehn et al. 2003). On the basis of another test arrangement, Bermudez et al. found contradictory evidence. In an inhalation experiment, rats, mice and hamsters were exposed to airborne ultra-fine titanium dioxide particles (e.g. 10mg/m³) for 13 weeks. In rats and mice they found indications for inflammation of the pulmonary tissue, which disappeared with decreasing exposure. In both species, the self-purification mechanism of the lungs appeared to be overloaded by such concentrations, which was visible in the delayed clearance of the particles. Rats showed more severe symptoms of inflammation than mice and hamsters showed none, which was interpreted to be a sign of their higher capacity for pulmonary particle clearance (Bermudez et al. 2004).

Oberdörster reported in the survey that nano-scale titanium dioxide causes pulmonary cancer in rats. High doses were applied in the test and it is not clear whether human beings are exposed to such high doses. Pulmonary cancer in rats was the result of two years’ enforced inhalation of nano-scale titanium dioxide in high concentrations (10 mg/m³ and 250 mg/m³). Whether these results can be transferred to humans is therefore questionable.

In summary, one can state that there is the suspicion of a problematic impact of nanoparticles. Simultaneously, the experts responding to our survey confirmed that investigations were carried out under laboratory conditions administering substances of mostly very high dosages to laboratory animals. Exposure of humans to equally high concentrations is hardly imaginable except in case of severe industrial or transport accidents. A current overview of this analysis and the unanswered questions is provided by Oberdörster et al. (2005) and IOM (2005).

**Impact on the environment**

In addition to the above-mentioned experiments, which attempt to investigate the effects of nanomaterials on humans by means of animal testing, there are a few investigations on the environmental toxicity of nanoparticles. Generally it must be noted that the behavior of nano-scale materials and substances in the environment needs to be studied (Tomson et al. 2003).
Research on the behavior of nanomaterials in different environmental compartments and conditions is only just beginning. Researchers at Rice University are investigating the effects of nanomaterials in the soil (biopersistency, dissolution, biodegradation, aggregation, adsorption into environmental matrix) and aquatic environments (dissolution and suspension in aqueous media, sedimentation) as well as the effects of bio-accumulation (earth worms and aquatic animals) (Tomson et al. 2003).

Preliminary results of these investigations show:
- Aggregation of nanoparticles may differ in various aqueous media.
- Adsorption of foreign matter on the surface of nanoparticles is very high.
- Adsorption/desorption of organic compounds in nanoparticles could be long-term.
- Nanomaterials in natural aquatic environments could considerably change the behavior and mobility of pollutants.

Brumfiel (2003) reports that researchers at Rice University have investigated the behavior of buckyballs. They dissolved buckyballs in water, which was poured onto the ground. The buckyballs behaved with very different consequences in the ground. When buckyballs agglomerated and formed particles of micrometer size, they were absorbed by the soil like any other organic substance. When they spread without agglomeration, it was observed that water formed a kind of protective shell around the buckyballs. In this way the buckyballs may be able to pass through the soil without being absorbed and thus represent a hazard to ground water. Moreover, there are indications that nanomaterials could enter the food chain. Brumfield reports that nanoparticles might be ingested by earthworms (Brumfield 2003).

There are concerns in research on the possible consequences of nano-scale structures for the environment with respect to the ability of nanoparticles and microparticles to take up heavy metal, radionuclides, and other hazardous substances as foreign matter. It is notable that nanoparticles would react with heavy metals and be able to transport them.

Wiesner (Rice University) undertakes research on the behavior of nanomaterials in water and has made the following statements: “Nanomaterials can move with great speeds through aquifers and soil ... nanomaterials provide a large and active surface for sorbing smaller contaminants, such as cadmium and organics. Thus, like naturally occurring colloids they could provide an avenue for rapid and long-range transport of waste in underground water” (see Colvin 2002).

One international research project concluded that nanoparticles can form in the intermixing of mining effluents and running fresh water. The
nanoparticles pick up highly concentrated toxic heavy metals found in mining operations run-off. Here, too, the scientists assume that the particles might transport the poisonous metals further down the river due to chemical bonding (see Vista Verde 2002).

At the same time that scientists succeeded in making nano-scale water-soluble in order to be able to administer a medication more or less directly to the desired location, they made it possible for these particles to move freely in the groundwater.

Eva Oberdörster (Southern Methodist University, Dallas) reported on a survey in the context of her latest investigation into the impact of fullerenes on large-mouth bass and water fleas. Although the fullerenes were toxic for water fleas, the fish did not die and showed no indication of disease. However there were indications for cerebral damage and possible inflammation; furthermore, the fullerenes produced strong reactions in the fish, although the dosage applied in the investigation (1 ppm) would rarely appear in practice unless the result of an accident, the researcher reported. High concentrations of nanoparticles with unknown consequences could occur when used in suntan lotions or cosmetic products that are washed away from human bodies in water. At the same time, the behavior of nanoparticles must be taken into consideration. Presumably, individual nanoparticles would show different characteristics than agglomerated ones when inhaled or released in aqueous form.

Additionally, Oberdörster reported that not all artificially produced nanomaterials had the same effect. Her investigations revealed, for example, that fullerenes are toxic for E. coli bacteria. Coated single-walled nanotubes however are not toxic for E. coli.

Similar to the situation in the health field, it must be stated that although systematization of the field has progressed, little detailed knowledge is available with regard to actual effects in the environment. The IOM (2005:40) states that “the assessment of the environmental impact of nanomaterials, as for any other materials, will have to focus on residence time in the environment, toxicity (acute and long-term), bioaccumulation potential and persistency in living systems. Little is known about [any] of these.”

Both Oberdörster et al. (2005) and US-EPA (2005) systematize the contexts and underscore that nothing is so far known about the potential impact of nanoparticles in the environment.

In a summary of research results compiled by the US Nanotechnology Initiative Funding, Dunpy Guzman et al. (2006) conclude with regard to exposure, environmental fate, and transport that: “it is unknown if engineered nanoparticles, especially those coated to reduce aggregation, will behave similarly (compared to incidental nanoparticle aerosols), the expo-
sure assessment studies … have focused on worker exposure, but exposure of the ecosystem and the public to nanoparticles, from either manufacturing or the use and disposal of nanoparticle-based products, needs to be quantified … Transport studies to date have been limited to aerosol transport in the atmosphere and transport studies in porous media. However, each ecosystem component must be considered: soil, sediment, oceans, surface waters, groundwater, and the atmosphere.”

Regarding toxicity, a number of studies are listed that suggest negative effects. “Many believe that surface coatings have the potential to greatly alter the toxicity, solubility, reactivity, bioavailability, and the catalytic properties of underlying nanoparticles, thus minimizing their health and environmental impacts. Unfortunately, these coatings may not persist indefinitely after release of the underlying nanoparticle into the environment” (p.1405). Studies of CdSe quantum dots with a surface coating do indicate that the coating prevents the cytotoxicity of the quantum dots; however, the stability of the coatings is unclear. Finally the authors also point to the potential global impact, particularly the atmospheric impact, referring to studies which show that nanoparticles are key components in many biogeochemical processes.

Summarizing the current status of knowledge it must be stated that with respect to the possible effects of the nanoparticle even the most recent surveys tend to look like catalogues of questions and that little verified knowledge exists. This also holds true for problem studies such as those undertaken by E. Oberdörster (IOM points out that the effects found by E. Oberdörster are not necessarily consequences of nanoparticles) as well as for “all-clear” messages, which likewise are frequently based on single studies.

4.6.2 Nanoscalar titanium dioxide in suntan lotions

The use of nano-scale titanium dioxide in suntan lotions addressed in the following case study. Titanium dioxide is increasingly used as an effective protective substance against ultraviolet radiation in several cosmetic products. Nano-scale titanium dioxide was chosen for this case study essentially for two reasons. First, because it involves a non-contained application on a large scale. Secondly, because it is the application of the substance which highlights the problem of assessing the effects of new nanomaterials.

The inclusion of nano-scale titanium dioxide in suntan lotions is scientifically disputed. Titanium dioxide in its micro-size has a long tradition as
a component in suntan lotions. Only more recently have manufacturers been producing and adding nano-scale titanium dioxide to suntan lotions.

As we know now, a nano-scale substance can have completely different characteristics (chemical, optical, etc.) than its micro-scale counterpart. Nano-scale titanium dioxide is transparent, while micro-scale titanium dioxide is white and therefore is used as a pigment, for example, in wall paint. Nevertheless nano-scale titanium dioxide was classified as equal to micro-scale titanium dioxide regarding effects by the respective regulatory authorities in the USA (Food and Drug Administration 1999) and the EU (SCCNFP 2003).

The classification and regulation of nano-scale titanium dioxide and its impact on the human organism can serve as an example for the discussion processes concerned with nanoparticles and their hazards and risks. Nano-scale titanium dioxide was also chosen for this case study because it is at the center of the arguments brought forward by ETC Group against nanotechnology. The NGO is demanding a worldwide moratorium on nanotechnology research. Using the example of nano-scale titanium dioxide, the NGO underscores the repeatedly expressed considerations of scientists with respect to possible hazards and lack of knowledge about the environmental behavior of nanoparticles. At the same time, the NGO criticizes the regulatory equation of macro-scale and nano-scale titanium dioxide, which does not sufficiently consider their differing behavioral characteristics.

Titanium dioxide belongs to the group of physical light protective filters (also called inorganic or mineral filters). These are metal oxides, which filter the UV light predominantly by reflection and diffusion. Major representatives are TiO2 and ZnO. They are biologically and chemically stable and very rarely cause irritations and phototoxic or photo-allergic reactions. With their high capacity to absorb ultraviolet radiation, nano-scale titanium dioxide and zinc oxide are ideal for use in cosmetics.

4.6.2.1 Hazards of nano-scale titanium dioxide

The cosmetics industry defends its use of nano-scale titanium dioxide in suntan lotions with own investigations demonstrating the innocuousness of titanium dioxide. The safety of nano-scale titanium dioxide was also confirmed by the Scientific Committee on Cosmetic Products and Non-food Products Intended for Consumers (SCCNFP), an EU body, in October 2000. The committee decided that along with its conventional counterpart, nano-scale titanium dioxide could also be included in the list of approved UV filters: “The SCCNFP is of the opinion that titanium dioxide is safe for use in cosmetic products at a maximum concentration of 25% in order to
protect the skin from certain harmful effects of UV radiation. This opinion concerns crystalline titanium dioxide, whether or not subjected to various treatments (coating, doping, etc.), irrespective of particle size, provided only that such treatments do not compromise the safety of the product” (Europäische Kommission 2004). The SCCNFP decision was based however solely on industrial studies not accessible to the public.

In the application of suntan lotions containing nano-scale titanium dioxide, the question arises as to whether it can reach living cells, enter, and either damage them or migrate even further into the body. Moreover, it is not known whether titanium dioxide particles can transport other undesirable substances into the body. Colvin assumes that the risk from titanium dioxide risk is much lower than that of sun bathing itself (Colvin 2003a).

Scientific investigations on coated nano-scale titanium dioxide report that when applied to the skin, the majority of the titanium dioxide remains localized in the upper layers of the skin (stratum corneum). The concentration of titanium dioxide in the upper layers of the stratum corneum decreases drastically over the time, as the skin regenerates (exfoliation). In the deeper layers of the skin, however, the concentration of titanium dioxide particles decreases much more slowly over time (Rickmeyer 2002).

Pflückner reports that coated nano-scale titanium dioxide can be found in hair follicles, which are found in the deeper layers of the skin. However, there are no indications for their movement from the follicles into living cells (Pflücker et al. 2001). This confirms the results of earlier investigations (Lademann et al. 1999). Rickmeyer reports that only very low concentrations of coated titanium dioxide were found in the tissue surrounding the follicles. Contact with living cells “exists only in an evanescently minimum scope” (Rickmeyer 2002). Bennat/Müller-Groymann report that nano-scale titanium dioxide in fatty solutions can penetrate the skin better than in aqueous solutions and do not rule out the possibility of penetration of particles into deeper layers of the skin (Bennat/ Müller-Groymann 2000).

However, Tinkle et al. report that beryllium particles of one-half to one micrometer in size rubbed into the skin have reached the epidermis and in rarer cases the deeper dermis thus bringing them into contact with living cells (Tinkle et al. 2003). Admittedly this result does not say anything about the impact of titanium dioxide on the skin, but it makes clear that in addition to particle size substance class must also be considered in judging possible effects.

The safety of nano-scale titanium dioxide is also being called into question elsewhere. A report by the Royal Society of Engineering e.g. suggests that with the reduction of particle size the number of free radicals on the surface of titanium dioxide increases, possibly leading to skin damage
(Royal Academy of Engineering 2003). This view is backed by an investigation by Dunford et al. and Uchino et al., who report that when titanium dioxide is exposed to sunlight, in vitro as well as with human cells, the cell’s DNA is damaged by photocatalysis (Dunford et al. 1997, Uchino et al. 2002, Colvin 2003a). Rickmeyer assumes that these photocatalytic effects may be reduced drastically by coating, but cannot be entirely avoided (Rickmeyer 2002). Moreover it is known that nano-scale titanium dioxide causes cell death in the fetuses of Syrian hamsters (Rahman et al. 2002).

Butz (2006) reports on the results of the Nanoderm research project being promoted by the EU, which is specifically investigating the absorption of titanium dioxide by the skin. His conclusion is that, normally, penetration is restricted to the stratum corneum disjunctum, occasionally Ti is found in s.c. compactum, Ti is rarely detected in the stratum granulosum, Ti is detected in the stratum spinosum in most cases, and Ti spots in the dermis are identified as contaminations.

Moreover Butz states: “To our surprise, the particle shape had no influence, it appears that TiO2 particles are mechanically rubbed into the horny layer / hair follicles / furrows without diffusive transport and thus far there is very limited exposure to vital tissue, but there are open questions: particles in the 1–2 nm range might behave like small macromolecules and penetrate; transglandular pathway clearance from follicles (+ glands?)”

All in all, these research results suggest that nano-structured titanium dioxide as used in the cosmetics industry does not penetrate into the deeper layers when used on healthy skin and that possible negative effects on the cells do not represent a problem of the first priority. Regarding potential effects within the individual environmental compartments, however, little is known.

4.6.2.2 Expert survey

In the course of the expert survey, a number of new as yet unconsidered aspects emerged with respect to this case study. Asked about possible negative effects of nano-scale titanium dioxide, the experts gave the following answers: The majority was of the opinion that there are no indications for the penetration of nano-scale titanium dioxide through all layers of the skin. Only one expert was generally more skeptical about the problem, but without providing any new information. They all agreed on the following problem: No investigations have looked at application to wounds or persons with dermal allergies. And there are no investigations on application to inflamed and (sun) burnt skin. In both cases there is the possibility of nano-scale titanium dioxide coming into contact with blood and/or living cells. Studies on the persistence of particles in the body, par-
4.6 Case study 5: The risk potential of nano-scale structures

particularly in babies and children, are required. Therefore, precaution is still necessary. One expert noted: Nano-scale titanium dioxide can easily penetrate the skin when coated with electrophilic, oily molecules.

4.6.2.3 Summary

The case study on the use of nano-scale titanium dioxide in suntan lotions illustrates the problems associated with future applications of nanoparticles. A number of experts question the full safety of the application. At the same time, a number of important investigations on the effects of nano-scale titanium dioxide in the human body are lacking, although the main use, i.e. application to the healthy skin, appears to be unproblematic, according to our latest knowledge. However, the fact that this is a non-contained, environmentally open application could cause a number of problems. We do not know how the structures/substances behave in nature after being washed off or leaving the skin in the course of natural skin exfoliation. In light of already occurring problems with suntan lotion residues on lake and sea shores, these questions should not be neglected.

Another problem is that nano-scale titanium dioxide is already being produced in large quantities, yet no knowledge is available on potential hazards in the production plants. The question of the effect of coatings on nano-scale titanium dioxide also remains unanswered. Assuming they really prevent catalytic effects, it is not known how long the coatings remain stable and how they react in surroundings other than on the human skin.

The EU’s equal treatment of micro-scale and nano-scale titanium dioxide is at the very least problematic in its lack of consideration of possible consequential environmental effects. Furthermore, publication of the related industry studies should increase the trust in the EU decision. At the same time, it is necessary to pursue unanswered questions regarding the safety of particles. With this in mind, the initial avoidance of non-contained applications, a reasonable measure based on the precautionary principle, should only be discontinued when, as in the case of nano titanium dioxide, essential, fundamental knowledge is available.

4.6.3 Life cycle analysis of nanomaterials

As already remarked, possible harm by nanoparticles may occur especially in environmentally open applications. A look at the life cycle of nanomaterials reveals several points where such a release may take place:
1. Nanomaterials production processes vary greatly. Industrially manufactured nanomaterials are not generally produced by combustion processes (with the exception of CVD/DVD and flame-assisted deposition), but mainly in liquid or closed gas-phase reactors. Therefore, direct exposure to nanomaterials ought to be limited. Exposure in the work place and research laboratory and possible exposure of man and environment due to accidents are all problematic.

2. Products: Most nanoparticles are contained or immobilized in products. Examples include nanotubes in video monitors or particles in paint coatings. The probability of release is presumably low.

3. Disposal and recycling: Behavior during disposal and recycling has not yet been extensively investigated, but release of individual nanoparticles is presumed to be limited. However, one must recognize that only very preliminary knowledge exists concerning this problem.

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**Fig. 48. Potential release pathways of nanoparticles**

In the course of the survey, most experts pointed out possible risks that occur during the life cycle. Exposure at the work place, accidents during manufacture and transport, and environmental pollution via industrial wastes are mentioned as possible sources. In the case of possible contami-
nations due to accidents, it is entirely unclear, so far, what impact the individual nanomaterials have on affected ecosystems and humans. The problems will become worse if additional consumer goods are produced without thorough testing or even no testing at all in the future, as is the case in the cosmetics industry. Closely connected to the question of the effects of accidents, waste, and disposal is the issue of biopersistency. It is necessary for the effectiveness of some nano-applications, such as those that must release their effects in a specific part of the body. However, sufficient knowledge for an assessment of long-term effects is not yet available.

One expert remarked in this context that a great deal of future production of nanomaterials will take place under cleanroom conditions, which will reduce the exposure of production staff. Presently, it is absolutely unclear whether and to what extent workers in plants or researchers in laboratories are exposed to particles. Industrial accidents still represent a potential risk. Likewise, one expert pointed out that due to the currently still small volume of nanoparticles being produced, the sum risk of exposures in the work place is rather small.

In the field of medical applications, the experts assumed that existing test procedures would reveal potential risks, before mass production takes place. On the basis of the differing approval procedures in specific fields, the question arose as to whether the same would be guaranteed, for example, in the field of consumer goods.

In summary, one can conclude that:

- most manufacturing takes place in contained systems
- Particles are often securely integrated in products and thus risks are limited
- the problem of disposal and recycling is unsolved
- intended and unintended release is problematic

These statements probably must be amended for new and modified production systems.
4.6.4 Discussion

The behavior of nanoparticles differs from that of structures at the macro-level; this also holds true for identical substances. Some of the studies discussed above document a surprising behavior. As shown, there are numerous reasons for concern as well as clear indications of toxic effects of nanomaterials, particularly nanoparticles, on the environment and human health. Nanotubes and buckyballs could be of special significance in this respect.

The knowledge we have is all preliminary, in part even contradictory, and deals with only a fraction of all possible effects. At the same time, the transferability of the knowledge gained so far appears to be low. The survey of the experts revealed that current knowledge is much too incomplete to form the basis for a comprehensive risk assessment or to implement evidence-based risk management. For this reason measures based on the precautionary principle are required.

Asked whether general statements can be made about the toxicity of nanoparticles, the experts’ responses were mainly negative. It is too early to classify nanomaterials into groups and categories that could be characterized with respect to their negative effects. Classification is only possible when specific nanoparticle properties responsible for toxic effects are identified. The statement that smaller particles are, as a rule, more toxic than larger ones, as their surface-volume ratio is greater was repeatedly made. Admittedly, the chemical composition and physical structure must always be considered. One expert even limited this rule to those particles having low solubility. One expert proposed a classification according to:

- Biopersistency
- Biologically accessible surface area
- Aggregation behavior in various environments

This type of classification seems to encompass the greatest known potential hazards and thus, with the inclusion of mobility in environmental compartments and in the human body, could become a guideline for future research on risks.

In addition to the uncertainty about possible negative effects, it can also be stated that the occurrence of negative effects due to manufactured particles presently appears to be relatively rare. As a consequence, continued research on the behavior and potential effects of nanoparticles in case of a release is required. Since general statements are not currently possible, there is likewise an urgent demand for classification.
Several experts remarked in the course of the survey that the possibilities offered by nano-scale structures and systems are enormous. To suspend development efforts now already on the basis of a profound suspicion of possible toxicity, would be far out of proportion in relation to the expected gains from nanotechnology. Instead, attention should be given now to establishing scientifically based criteria for the evaluation of risk and risk management.

Since research on the risks of nanoparticles is still in its infancy, only very general advice for handling nanomaterials can be given:

- Differences in size, surface structure, and chemical composition require that the possible effects on human health and environment for each individual nanomaterial be investigated.
- There is a great need of classification.
- Non-contained applications of some nanoparticles and nanostructures should be avoided until potential environmental effects have been addressed. This holds true for the majority of nanoparticles at present.
- The behavior of nanomaterials released during disposal should also be investigated.
- Biodegradability and increased tendencies for agglomeration could be ways to minimize or to avoid environmental hazards (ecotoxicity).

In this context the development of a strategic research and development concept is important. It should provide the necessary means and also maintain a balance between technological development and understanding of effects. This would mean a better intercoupling of both research directions. One expert proposed a comprehensive concept for the investigation and assessment of possible hazards:

“In my opinion, the most urgent need for action with respect to regulation is in the development of a new, strategic concept for the toxicological evaluation not only of the sites and organs where absorption occurs, but also the secondary target organs. This concept should be based on modern, genomic, proteomic and toxiconomic investigations with high-throughput technology. This concept would not only allow comprehensive evaluation and specific regulation of a new product, but would provide the manufacturer, in connection with a suitably equipped toxicological laboratory, with a prompt risk assessment. Such a strategic concept should be developed in interaction between research, manufacturers, and the regulatory authorities. In this way Germany could extend its leading position in the field of sustainable development of new nanoproducts.”

Basically it seems important, on the one hand, to understand the basics of the effect of nanoparticles; on the other hand, more research must be carried out in those areas where production quantities are foreseeable. Ref-
erences from the experts as to contamination resulting from accidents in production and transport underscore the urgency. A further research focus can be found in answers given to the question as to whether certain nanoparticles or structures are intended for use in open applications; if so, their potential impact must be more closely investigated beforehand.