EUROPEAN PARLIAMENT

Scientific Technology Options Assessment

S T O A

The role of Nanotechnology in Chemical Substitution

STUDY

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Authors:

ETAG
European Technology Assessment Group
Institute for Technology Assessment and Systems Analysis (ITAS), Karlsruhe
Danish Board of Technology (DBT), Copenhagen
Flemish Institute for Science and Technology Assessment (viWTA), Brussels
Parliamentary Office of Science and Technology (POST), London
Rathenau Institute, The Hague

Dr. Ulrich Fiedeler, ITAS
E-mail: ulrich.fiedeler@itas.fzk.de

Administrator:

Mr. Miklos Györffi
Policy Department A: Economic and Scientific Policy
DG Internal Policies
European Parliament
Rue Wiertz 60 - ATR 00K076
B-1047 Brussels
Tel: +32 (0)2 283 25 05
Fax: +32 (0)2 284 49 84
E-mail: miklos.gyoerffi@europarl.europa.eu

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1 EXECUTIVE SUMMARY

OBJECTIVE

This project is one of ten projects the Scientific Technology Option Assessment (STOA) panel has initiated this year. The project is called: 'The role of Nanotechnology in Chemical Substitution'.

The aim of the project is to give an overview of already used and conceivable applications of Nanotechnology (NT) in order to replace hazardous chemicals.

The overall idea behind this project is to identify new applications of NT which could help to reduce the risks related to hazardous substances and chemical processes. One prominent example is the substitution of anti-fouling coatings used in the ship industry by nanotechnological based coatings, which are already under investigation (AMBIO-project, http://www.ambio.bham.ac.uk/).

BACKGROUND

The project is focused on the identification of concepts or ideas for substitution in the field of NT. **The assessment of the hazardous potential of the nanotechnological substitute itself *IS NOT OBJECTIVE OF THIS STUDY, NOR IS THE EVALUATION OF THE FEASIBILITY AND EFFICIENCY OF THE* concepts for substitution.** Related to the objective of this study three questions have to be addressed at the beginning of the project:

1. ***Which substances are considered as 'hazardous chemicals'?***

   Since this project is focused on determining the potential of NT, the issue of how a substance can be identified as hazardous is discussed only briefly. Nevertheless, to estimate the potential of substitution it must be clear what is to be substituted. Here, a pragmatic solution is chosen. **Only substances which are already known as toxic and dangerous to humans and the environment are considered.** This is presented in section 4.3.

2. ***What is meant by the term Nanotechnology and how can it be distinguished from biology and chemistry respectively?***

   There is no clear definition of NT nor is it possible to assign precisely an application to NT or to chemistry or to biology (see section 3). The term NT implies a great variety of different techniques, analytic tools and materials including their production. Nevertheless, to identify relevant applications of NT serving the aim of this project presupposes a certain concept of NT. The first approach used for this study is that everything is considered as NT what is claimed by proponents to be NT. In detail this means that all publications, which are published in journals carrying 'Nano' in their title (e.g. 'Journal of Nanoparticles Research'), and all projects carrying 'Nano' in their title are considered to belong to NT. Publications and projects dealing with typical NT objects such as fullerenes or nanotubes are also attributed to NT even if 'Nano' is not the headline. This is a pragmatic solution to start with. The question of whether a certain technical concept of substitution can be attributed to NT could not be explicitly discussed within the scope of this project.

For all presented examples the assignment to NT was accepted by the experts during the validation workshop. Furthermore, the relation of the presented examples of substitution to NT and the connection to other disciplines is described in one or two sentences for each case or field of substitution presented in section 7.

In this respect it is important to mention that the term NT has also a political dimension. In the all over competition on funding of research the assignment of benefits and useful applications to a certain discipline is crucial (see section 3.1 and 3.4).

3. ***What is the meaning of 'chemical substitution' in relation to NT?***

The original meaning of chemical substitution is quite clear and narrow: one chemical substance is replaced by another, for whatever reason (availability, costs, technical requirements).

Due to the fact that NT is neither a group of substances nor a group of products but an enabling technology the way NT can provide solutions is more fundamental than just replacing the function of the substitute. It is assumed that NT provides new effects which are not based on chemical properties of the related material but on the physical properties caused by its size and shape. It can be used to develop completely different processes or different products which serve the same purpose but in a completely different way.

Therefore in this report substitution is not restricted to the replacement of a hazardous substance by a less or non-hazardous substance. In this project this broader meaning of substitution is applied as it is in the chemical context. The interviews and the comments of the experts during the validation workshop have shown that it is a delicate but necessary challenge to broaden the meaning of the term 'substitution' without loosing its focus.

METHOD

Since most NTs are at an early stage of development and due to the fact that NT is an enabling technology there are only a few publications and only very few research projects directly addressing the substitution of hazardous substances by NT. Therefore, the **challenge of this project was to estimate a potential that has not yet been explored**.

The research for the findings is based on **two approaches**:

A **literature research** and **interviews with experts**.

The relevant literature was identified by the following criteria:

- Reports from governmental departments, research institutes, industrial associations, and other stakeholder groups which addresses NT and environmental issues.
- Journals, carrying 'Nano' in their titles.
- Certain journals in the field of applied chemistry.
- Journals addressing chemistry and environmental issues (e.g. Green Chemistry)
- broad keyword based searches in several data bases

This keyword based search was performed in

- journals of the American Chemical Society (ACS)
- journals covered by Science Direct

The considered journals are listed in appendix 10.5.

The experts for the interviews were chosen due to publications on NT related to environmental issues or even related to a case of substitution. They are all experts in the field of NT but with different backgrounds. The experts include representatives from industry, science, research management, and NGOs. Experts who were contacted are listed in appendix 10.6.

To **validate the findings** of the project nine **experts from different fields of NT** or chemistry with nanotechnological background **were invited to a workshop at the European Parliament**. Prior to the workshop a summary of the preliminary results of the project was sent to the experts. The workshop focused on the discussion among the experts but was open to Members of the European Parliament in order to give them the opportunity to give their views in the evaluation of the preliminary findings and related policy options. In addition the workshop was open to other persons active in the field of nanotechnology. The list of invited experts can be found in appendix 10.1.1. The results of the workshop are summarised in appendix 10.1.2 to 10.1.4.

FINDINGS

The findings can be subdivided into seven categories.

COATINGS

Most examples are to be found in the field of surface treatments like coatings, paints, and texturing surface.
Example: Self cleaning surfaces

Reduction of adhesion is relevant for many applications. For example is the reduction of adhesion one approach to substitute antifouling agents like TBT. In addition the use of cleaning agents could be reduced or even made superfluous. If these coatings are used to cover cladding it is assumed that the use of paint will reduce considerably.

FLAME RETARDANTS

There are several approaches to replace bromine flame retardants with products using NT. Bromine is used as a reaction inhibitant by absorbing oxygen. A similar effect could be realised by nanoparticles. If TiO_2, SiO_2, MgO, or ZnO nanoparticles are added to substances oxygen is accumulated and builds up an oxide layer.

FLEXIBILISER

Flexibiliser leads to elastic bindings between the polymer chains. It is known from tires that the addition of nanoparticles can enhance the flexibility of the rubber mixture. A similar effect is conceivable with plastics.

SUBSTITUTION OR REDUCTION OF SOLVENTS

Organic solvents or volatile organic compounds (VOC) in general are one group of chemicals which are often toxic, bio-accumulative and, due to their volatility, difficult to control. Solvents can not be directly substituted by NT. But in the literature it is often mentioned that NT may change processes in a way that in some cases solvents can be reduced or will even become dispensable in future.

CATALYSTS

Research on catalysts is an old and vast research field. In this field, the distinction between 'pure' chemistry and nanotechnology is especially difficult. Research in this field was already in the dimension of nanometers, therefore it is not clear to which extent further developments may be attributed to NT. The development of new catalysts is seldom directly aimed at substituting hazardous substances. Instead, in the development of new catalysts several objectives are pursued at the same time. Therefore, substitution of hazardous substances in this field is often very indirect. The effect of catalysts on human health and the environment, if they are released, could be detrimental. Their benefits and risks have to be balanced in detail.

A very well investigated example of a case of substitution is styrol synthesis where it was possible to reduce the by-production of heavy metals due to NT catalysts.

OTHER EXAMPLES: DRUG TARGETING

Within NT there exist several attempts to improve the efficiency of pharmaceuticals by bringing them directly to the cells where they are needed. Of course, the main goal is to reduce the side effects of the therapy, hence making the therapy more tolerable and effective. But especially chemotherapeutics are detrimental for the environment and the release of antibiotics causes severe problems due to resistance of bacteria.

REMEDIATION

A lot of the literature concerning nanotechnology and environmental issues deals with the potential of NT for cleaning up polluted air, water, and soil. Most of the research activities concerning the development and use of catalysts in respect to hazardous substances are not in order to avoid them but to decompose them after they have been released into the environment. These examples are not within the scope of the project. Nevertheless, it should be mentioned that most articles on environmental benefits attributed to NT are of this nature.

CONCLUSIONS

- The investigations of this project show that the **focus of this study is unique**.
- Nevertheless, considering the findings it can be concluded that at present times **NT can not contribute in an exceptional manner to a large increase of substitution of hazardous substances**. Instead it revealed that the contribution of NT with respect to the reduction of hazardous substances is manifold but incremental.

  However, most of the interviewed or invited **experts assign NT a considerable potential for substitution for the future.**
- For a **comprehensive assessment** of this potential, each **identified example has to be assessed case by case and in more detail** as it was performed in this project.

  This assessment has to start with following questions:

  1. Of what importance is the example under consideration?
  2. Are there other chemicals which could substitute the substance in question?
  3. Of what quality (feasibility, efficiency) is the suggested NT?

– To evaluate the benefit of the new nanomaterial in relation to the conventional one a **life cycle assessment (LCA) has to be performed**. This kind of detailed assessment is only useful if there are some signs related to a special case of possible substitution suggesting that is worth evaluating this special case in detail. One of those cases is biocide coatings on the basis of silver nanoparticles.

– The last conclusion deals with the **methodological challenges of the exploitation of unknown fields of application of NT for substitution**.

  How is it possible to find a connection in a systematic way between a hazardous substance and a particular NT which could facilitate the substitution of this substance?

  A first step in this direction is the **systematisation the functions NT** can provide. These functionalities could be **compared with the functionalities hazardous chemical** substances provide. Thus the question of which hazardous substances could be substituted by which NT is reduced to the question of which functionality of the hazardous substance could be provided by which NT.

2 PRELIMINARY NOTES ON THE SUBJECT

Not using substances which threaten human health and the environment is obviously the most effective way to avoid their harming humans and the environment.

To what extent can nanotechnology replace hazardous substances?

This is the main question the project seeks to answer. It is focused on the identification of concepts or ideas for substitution based on Nanotechnology (NT).

The aim of the project

is to determine the potential of NT for the substitution of hazardous substances in chemistry. The overall idea behind this project is to identify new applications of NT which could help to reduce the risks related to hazardous substances and chemical processes.

Structure of the Report

This report is divided into three parts. The first part encompasses chapters 3 to 5 where the analysis on the background of the subject is presented. There, relevant aspects regarding hazardous substances, substitution, and nanotechnology (NT) are outlined. In the second part all examples of possible substitution which have been determined are presented. These are presented in chapters 6 to 7.7. The conclusions are drawn in chapter 8. The scope, participants and the results of the validation workshop are presented appendix 10.1. Summaries of all interviews which were performed within the project are listed in appendix 10.3. In addition in the appendix all considered reports and journals as well as all persons who were asked for information for the project are listed (appendix 10.4 to 10.6).

The first part is structured as follows: Due to the fact that the term NT implies a great variety of different techniques, analytic tools and materials a brief overview is provided in section 3 against the background of the subject of this project. The next question is: how is it possible to associate hazardous substances with possible applications of NT in terms of their substitution potential. For three reasons this is the most challenging issue of the project. First, as mentioned above, NT encompasses a huge variety of techniques, processes, and materials. A very broad field has to be taken into account. Second, NT is an emerging technology. That means applications mostly exist only as ideas and concepts and have not even been proven in the laboratory. Based on this stage of development, it is very difficult to estimate the potential of applications not yet existing. And third, NT is an enabling technology. That means, a single NT can be used for several applications and products. Section 3.4 will describe how the project deals with these challenges.

Due to the fact that NT is not a substance, ‘substitution’ in this project does not only mean one-to-one substitution. For example, the problems arising from organic solvents can hardly be solved by substituting a solvent based on NT.[1] Instead, completely different solutions and alternatives for realising the functionality of the original product have to be considered. This is the only way to determine the whole potential of NT in terms of substitution. A detailed discussion of the meaning of substitution with regard to NT will be presented in section 4.

[1] With NT you may produce new materials but not new solvents. Fluids can be enriched with nanoparticles to give them new physical properties but thus can not create new solvent. Despite this fundamental constraint, in section 7.4 some attempts aiming at replacing organic solvents with the help of NT are presented.

The examples of substitution which are presented here are simply used to clarify the scope of the project and to discuss the meaning of chemical substitution within this report and will be discussed in more detail in chapter 7.

The orientation of the project towards substitution raises further questions. First, what is to be substituted or what is meant by the term ‘hazardous substance’. Since this project is focused on determining the potential of NT, the issue of how a substance can be identified as hazardous will be discussed only briefly. Nevertheless, to estimate the potential of substitution it must be clear what is to be substituted. Here, a pragmatic solution is chosen. Only substances which are already known as toxic and dangerous to humans and the environment are considered. This will be presented in section 4.3. The methodological approach is presented in chapter 5.

3 WHAT IS NANOTECHNOLOGY?

The term NT encompasses a wide range of tools, techniques and potential applications (see e.g. Paschen 2004, Nanoforum 2004, STOA 2002) . Most of them are concepts and ideas rather than real technologies. Most of the activities under the name of NT could be better described as nanoscience. Moreover, **many of these activities have already been performed before the term NT arose**[2.] The overstated discussion about NT can not be explained by its scientific and technical dimension alone. The dynamic of the public debates on NT, the expectations as well as potential disappointments associated with it play an important role in NT (Wood 2003, Berube 2004).

3.1 Political background of NT

The term NT was used for the first time by Norio Taniguchi in 1974. Thirty years later, **there is still no universal definition of NT** and not even a common view within the research community of what should be encompassed by NT (Schmidt 2003). This is important for the understanding of NT and the discussion about it. From the early beginning, **NT was accompanied by big promises and huge expectations**. This is closely linked to the dynamics of the scientific/political system. Several aspects of the research system, its struggle for funding, its relation to the media and to the public, and of course its relation to the political system are crucial for the understanding of NT. The real breakthrough of NT came with the National NT Initiative, a huge research funding programme launched by the Clinton Administration in 2000[3]. The documents of this initiative were full of promises, expectations, and fantastic visions and therefore gained great attention. Accordingly, research in the field of NT received large financial support (Roco 2003). Due to the fact that the term NT allows great freedom of interpretation, it has entered most of the research policy agendas of the developed nations.

The political background is discussed in more detail in: Glimell 2004, Nordmann 2004, and Schummer 2004.

3.2 Technical definition of NT

Unlike most established disciplines and technologies **NT is characterised primarily in terms of size**[4].

> 'Nanotechnology is made up of areas of technology where dimensions and tolerances in the range of 0.1 nm to 100 nm play a critical role.' (Glossary of the Nanoforum).

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[2] Just to mention a few: parts of material science, especially surface science or surface physics, microelectronics, parts of microbiology, parts of bionics, tissue engineering.

[3] 465 million dollar have been allocated for research in the field of nanotechnology in the fiscal year 2001 (NNI 2000). http://www.nano.gov/html/res/IntlFundingRoco.htm (20.4.2006)

[4] An exception seems to be microtechnology and microelectronics. But the scope of microtechnology, for instance, is relatively clearly defined, because it has its origin in techniques developed for microelectronics and didn't enter for example into biology.

This means that **the definition does not constrain the subject of NT.** For example, all **fields of biology** where structures in the range of nm are investigated and manipulated could be assigned to NT. For example, biological membranes, complex molecules like enzymes, or even cell compartments. Some researchers claim the cell is an archetype of a nano-machine (Jones 2004). From that point of view, the whole field of genetic engineering could be attributed to NT[5].

Chemistry is dealing with atoms and molecules, therefore it seems to be the paradigm of the vision of NT: To build up new structures atom by atom[6]. Usually, the very atoms and single molecules, with dimensions in the range of 0.001 nm, are not attributed to NT.

A third field closely related to NT is **material science**. In its early stages, material science was concentrated on bulk material and on more or less crude surface treatments. Due to new developments of analytic tools and process technology, it is now possible to construct planar surfaces with the accuracy of atomic layers. Other examples are coatings with a thickness of a few atoms, which are composed of different elements, or ceramics and other compound materials with crystallites in the nm range. A further subject of nanoscience is the design of structured material build up by building blocks of biological origin.

A field high expectations are placed on is **nanoelectronics** or molecular electronics. The aim of this research field is to build up electronic devices on the basis of complex molecules like DNA or building blocks like fullerenes[7] or carbon nanotubes **for the next generation microelectronics** when conventional (lithographic) structuring technology reaches its limits.

Apart from the ability to manipulate matter in the nm range most of the definitions of NT comprise a **further aspect**: The nm-size structure must **enable new functionalities**. A typical example is the effect of giant magnetic resistance. This effect describes the extreme increase in electronic resistance of a stack of layers with a thickness of several atoms when a magnetic field is applied. This effect is used in the read head of hard discs.

But in practice the new functionality is often unclear or not even mentioned. For example the miniaturisation of conducting paths down to several tenth of nm is called nanotechnology even though no new effect is caused by this small size[8].

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[5] Here are two further important definitions of NT presented:
National Nanotechnology Initiative (NNI) (www.nano.gov, 4. February 2005)

> ‘1. Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100nm range.
> 2. Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.
> 3. Ability to control or manipulate on the atomic scale.’

European Commission: „Towards a European strategy for nanotechnology“ (COM(2004) 338 final)

> ‘The term ‘nanotechnology’ will be used here as a collective term, encompassing the various branches of nanosciences and nanotechnologies.
> Conceptually, nanotechnology refers to science and technology at the nano-scale of atoms and molecules, and to the scientific principles and new properties that can be understood and mastered when operating in this domain. Such properties can then be observed and exploited at the micro- or macro-scale, for example, for the development of materials and devices with novel functions and performance. ‘

[6] NSTC-Report "Nanotechnology: Shaping the World Atom by Atom", http://www.wtec.org/loyola/nano/IWGN.Public.Brochure/IWGN.Nanotechnology.Brochure.pdf (28.3.06)

[7] See glossary

[8] ‘Nanoelectronics is the engine of innovation for almost all branches. In Germany, even today there are 70.000 employees in the chip manufacturing and supply industry depending on nanoelectronics. The market for electronic devices in Germany accounts for up to 20 billion Euro.’(English U.F.)
Wolf-Dieter Dudenhausen at the 25th Nov. 2003, Source: Press release 219/03 of the BMBF

A detailed discussion of the problem of defining NT is presented in Schmidt et al. (Schmidt 2003).

3.3 Main characteristics of NT

Beside the vague definition, NT is phenomenologically characterised by four central aspects, which have to be considered in assessing the potential of NT for substitution of hazardous chemicals. These are listed below:

1. **The main characteristic of NT is its diversity**
   Due to the broad definition of NT, a lot of quite different techniques and activities are summarized under this term.

2. **NT is predominantly an enabling technology**

   This means that NT is only part of a larger system, giving the product the crucial functionality. So generally there are many very different products for very different purposes using the same NT. To estimate the substitution potential of NT for every context of use, each application has to be assessed separately.

3. **Most application concepts for NT are in an early stage of development**

   A third characteristic aspect of NT which is also linked to the diversity of NT, is the diversity of development stages of NTs. For some simple applications like an improved rubber mixture for tyres, nanoparticles have been used for several years. Yet many product concepts, like most of the drug delivery systems, are still far from being implemented, others like the nano-assembler are pure science fiction.

   To summarize, most of the concepts attributed to NT are pure science, application ideas are rare, at times they even do not even exist.

4. **The debate on NT is a crucial property of NT itself.**

   A fourth characteristic of NT is the existence of a debate on NT even though there are only a few products on the market and the impact on the public is marginal. The outcome of this debate can significantly influence the development of the technologies concerned. This could be observed in other debates on new technologies, like the debate on nuclear energy, stem cell research or genetic engineering.

3.4 What is NT in this project?

As a first approach, everything is considered as NT which is claimed by proponents to be NT. In detail this means that all publications, which are published in journals carrying 'Nano' in their title (e.g. *Journal of Nanoparticles Research*), and all projects carrying 'Nano' in their title are considered to belong to NT. Publications and projects dealing with typical NT objects such as fullerenes or nanotubes are also attributed to NT even if 'Nano' is not the headline. This is a pragmatic solution to start with. **The question of whether a certain technical concept of substitution can be attributed to NT is not explicitly discussed.** For all presented examples the assignment to NT was accepted by the experts during the validation workshop.

At this point it should be mentioned that the political issues discussed in section 3.1 lead to complications regarding the identification of research activities related to NT.

Bionics is an example of a discipline that deals with objects or structures in the nm range and even provides functionalities common materials do not provide. The discipline of bionics was developed before NT became established. A well-known example of bionics, the lotus effect[9], is now a prime example of NT. Of course there is a kind of competition funding between scientists working in the field of bionics and biotechnology and those working in the field of nanoscience. Therefore, they have an **ambivalent attitude** towards NT. Apparently **they accept being assigned to the field of NT, while participating in a research project. But when publishing their results, they tend to deny their relation to NT**. In this project this is particularly important because biocide coatings are the most eminent example of the substitution of hazardous substances by NT. On the other hand, research on this issue originates from biology and particularly from bionics.

This ambivalent attitude aggravates the problems of assessing the potential of NT, as mentioned in section 3. The classification of their research as NT by the researchers themselves is not necessarily a good criterion to judge if it is NT or not. For that reason, the relation of the respective work to NT and the connection to other disciplines is described in one or two sentences for all cases or fields of substitution that is presented in section 7.

[9] Leaves of the lotus flower have the ability of self cleaning due to their micro structured surface.

4 SUBSTITUTION

4.1 Background

From its early beginning chemistry has been confronted with the problem of handling toxic substances. During a long learning process, with errors leading partly to catastrophic consequences, reasonable precautionary measures have been developed[10.] One of the consequences is that chemistry is one of the most regulated fields[11]. Nevertheless, there are still a large number of chemicals that, apart of their beneficial effects, produce negative side effects. The most effective way to avoid these side effects is to substitute the hazardous substances by less dangerous ones, offering the same or even more benefits. This is why the substitution principle plays a crucial role in the new EU chemicals policy (REACH system).

Although it seems to be simple, the approach raises several questions:

– **Which substances are dangerous and should be substituted?**
  If a substance has already been used for a while and experience has been gained on its impacts on human health or on the environment it usually becomes obvious whether this substance is hazardous or harmless. But in some cases it is very difficult to make a differentiation. For example due to its properties asbestos became a very promising material for the construction industry. It took a long time to realize its risks to human health even though there was already clear medical evidence of the detrimental effect of asbestos on the health of workers in the 1920s (Ahrens 2006).

– **What are appropriate substitutes?**

  Usually, the substance identified as hazardous has a very specific functionality in a product or in a synthesis process. The substitution of this substance by another will modify the product or the process. However, it is not always obvious if this modification is acceptable in terms of the quality of the product or the process.

– **How can it be known whether the substitute is less hazardous than the original substance?**
  The fear is always present, that one evil is being replaced by another by using a substitute that possibly entails new risks. The most prominent example, which shows the whole complexity of this problem, is the substitution of ammoniac used in cooling systems by chlorofluorcarbon (CFC) in the 1930s. The substitute was chosen because it is not inflammable, and non-toxic. Only in the 1970s was it realized that CFC destroys the ozone layer in the atmosphere.

– **What are the costs of the substitution?**

  In the chemical industry, the substitution of hazardous substances is related with new investments and higher production costs. Enterprises specialized on products containing hazardous substances are therefore confronted with enormous challenges in the future.

  Due to the fact that the chemical industry is highly interrelated (process chains are long, by-products are used as feedstock for other products etc.) the prices of several substances could be reduced to a minimum and **substitution is a considerable challenge**.

[10] The catastrophic release of toxic agents by chemical production plants in Seveso and Bhopal and publications on the problems related to the unconstrained use of DDT (Rachel Carlson: Silent Spring) are crucial factors substantially contributing to the change of perception of the chemical industry.
[11] Important regulations from the EU are the Council Regulation (EEC) 793/93 or the Existing Substances Regulation (ESR).

4.2 What does substitution mean in respect to NT?

The original meaning of chemical substitution is quite clear and narrow: one chemical substance is replaced by another, for whatever reason (availability, costs, technical requirements). The ideal case with hazardous substances is that the substitute has the same functions as the original substance but without its hazardous potential. In practice, the substitute usually changes the properties of the whole product or of the process or even of the whole production chain and is much more expensive.

The meaning of substitution in the context of hazardous substances **has become broader**.

> 'In this context the scope ranges from simple substitution (e.g. exchanging substances) to risk management as a whole (i.e. prevention of hazardous substances, reduction or prevention of exposure, etc.).'(Ahrens 2006).

Another definition is provided by Joachim Lohse et al. 2003:

> 'Substitution means the replacement or reduction of hazardous substances in products and processes by less hazardous or non-hazardous substances, or by achieving an equivalent functionality via technological or organisational measures.'

This definition implies **not only the replacement of a hazardous substance** by a less hazardous one **but also the use of another technology or the reorganisation of the process** in order to reduce or avoid the hazardous substance. Due to the fact that NT is neither a group of substances nor a group of products but an enabling technology, in most cases **the latter meaning of substitution is used in this project.**

The way NT can provide solutions is more fundamental than just replacing the function of the substitute. It can be used to develop completely different processes or different products which serve the same purpose but in a completely different way. Or it enables changing the properties of a material and achieves the intended functionality of the product as a whole by using a new and different approach. From the view of the customer this is entirely irrelevant. However, it means that with NT it is generally not possible to only substitute a toxic substance[12]. Often a lot of further conditions must be fulfilled to reduce or avoid the toxic substance concerned.

In the following some examples are listed to illustrate the broad variety of the possible forms of substitution in the field of NT:

Example: antibiotics[13]

Instead of antibiotics, it is possible to introduce silver particles in a coating in order to reduce the growth of bacteria on the surface of e.g. an acoustic hearing apparatus. This seems to be one of the few examples of a substance-by-substance substitution.

Concerning the relation to NT in this case it might be argued that the antibiotic effect only arises from the ions which are released from the silver and has nothing to do with the size of the particles. The particles serve as silver ion source which will be dissolved from the coating. Therefore it can be questioned if it is really a 'nano-effect'[14].

[12] The first example below is an exception.
[13] In this project antibiotic are not considered as a hazardous substance which has do be substituted, even though it is demanded to reduce the load on the environment as much as possible for the reason of medical resistance. Here, it serves as an example for a one-to-one substitution.
[14] On the other hand there exist investigations about the size effect of silver nanoparticles, see Morones 2005.

Example: Biofouling

To avoid the growth of organisms of different types on surfaces in a marine or freshwater environment usually coatings incorporating biocides (chemicals that kill organisms) are used. Instead of these biocide containing coatings there exist several approaches of nano-structuring the surfaces which prevents biofilm formation and bacterial adhesion as well as the attachment of larger organisms. [15]

Example: brominated flame retardant

Halogen containing flame retardants primarily works by chemical interference with the oxidation taking place in the gas phase during combustion. Highly energetic OH and H radicals formed during combustion are saturated by bromine, hence stopping a further exothermic combustion process. As a by-product during the combustion process highly toxic dioxin and furan is produced. It has currently not been proven that the described functionality can be achieved with NT. But NT provides concepts for the development of flame retardants. For example varnish for wooden furniture can be enriched with nanoparticles on the basis of silica. When heated up, they form a ceramic-like coating that prevents the exchange of oxygen and in addition serves as thermo isolation. But these concepts can not be applied to thermoplastics, where additive flame retardants like brominated flame retardants are used.

This example shows that the functionality of the chemical compound to be substituted is usually not provided by NT. Therefore, this project will focus on the general functionality of the hazardous chemical (flame retarding) rather than on the chemical functionality (saturation of OH-radicals) of the compound in the material concerned.

Example: lead-containing batteries

Usually, the separation layer in a Li-ion battery consists of an organic compound which is not very temperature stable. This lack of stability can be overcome by a coating based on nanoparticles. Due to this coating, Li-ion batteries will become suitable for use in automobiles (*elements* 14, 2006a). This would allow the replacement of the lead-containing batteries used at present. This is an example of a substitution (here of lead) enabled by nanotechnology. But the example also shows that such a replacement is often very indirect. Here, a whole system, the lead battery, is replaced by another system, the Li-ion battery, which provides the same functionality but with quite a different construction.

Example: solvents

Solvents are often problematic. Usually they are volatile and often toxic and bio-accumulative like tri-chlorine ethylene. Solvents can not be directly substituted by NT. But in literature it is often mentioned that NT might change processes in that way, that in some cases solvents can be reduced or will even become dispensable in future (Royal Society 2003, p.2). One way to realize this is to design new catalysts with the help of NT. For some applications these catalysts enable a reaction to take place in water as solvent, thus avoiding the problems of volatile organic solvents. This example is typical in so far as it is characterized by a high degree of uncertainty associated with an estimated high potential for NT. Especially in the field of development of catalysts, this can often be observed.

[15] See for example the EU project AMBIO http://www.ambio.bham.ac.uk/ (21.4.2006).

Example: insecticides

There are two approaches by which NT could contribute to a reduction in use of pesticides. One should be presented here as an example of a very indirect kind of 'substitution'[16].

It is expected that NT will enhance the performance of information and communication technology in a way to increase the precision of monitoring and dosing will increase. It is assumed that due to this development less plant protecting agents will be used in agriculture (Royal Society 2003, p.3).

This example shows that the relation between the reduction of a hazardous substance and NT can be very weak. Nevertheless, these kinds of relations are often mentioned in publications on the environmental benefits of NT.

So far, it does not seem useful to restrict the project to a certain kind of substitution. Nevertheless, the guiding principle is to focus on substitutions which are as direct as possible. The problem of the broad meaning of the originally quite clear term 'chemical substitution' was also subject of the discussion of the validation workshop (see appendix 10.1).

4.3 How to identify a hazardous substance?

The question of how to determine the toxicity of a new substance has accompanied

chemistry from its beginning. But this question achieved a new quality in the 1960's when it was realized that chlorine hydrocarbon-containing pesticides accumulate in animals and in the human body (Scheringer 1999). The complexity of the side effects of chemical substances became apparent. Here starts the discussion about the question of how to determine the impact of substances when they have left the production site and enter the environment. A related question is what a responsible handling of hazardous substances will look like?

The problem of identification of hazardous substances is not subject of this project. Here, it should only be mentioned that it is neither a straight forward activity nor it is impossible. However, to estimate the potential of NT for substitution, it is necessary to know what should be substituted. Therefore, a decision has to be made.

There are a huge number of substances that are already known to be toxic. But it is not useful to search for substitutes for all of them.

Properties of substances which help to assess their hazardous potential

To assess the hazardous potential of a substance a difference should be mad between the properties of the substance and the context the substance is used in. For an insecticide it is essential to be toxic; the same applies to a drug. But the side effects should be as low as possible. Therefore, in most cases it is useful for insecticides to be bio-degradable. An example for the complexity of assessing the hazardous potential of a substance is the above mentioned CFC-case. With regard to the original purpose and context of use this chemical was not hazardous. Only the ozone layer of the atmosphere is affected by its detrimental impact.

The most striking criterion for substitution is the toxicity of a substance. Beside this property a further condition has to be taken into account: the release of the substance, which is related to the context of use. The list of properties presented below can be used as guideline for the selection of the most important substances. This list is derived from experience with substances that have entered the environment. Whether this list is comprehensive enough, and whether these criteria are useful is still subject of an ongoing political and scientific debate.

[16] The other example could be finded in section 7.6.

For most of them there exists a consensus and they are also used in legal regulations.

These properties are:

- **Toxicity**, e.g. carcinogenic, mutagenic, or toxic for reproduction (CMR), endocrine disrupting chemicals, (EDCs) (e.g. phtalate)
- **Persistence**, e.g. persistent organic pollutants (POPs)
- **Mobility,** e.g. heavy metals, chlorine hydrocarbons, volatile organic compounds (VOCs)
- potential for **bioaccumulation**

The last three items on this list do not describe a specific toxicity but the potential and the character of exposition related to the substance, like the bio-degradability of insecticides mentioned above. Substances meeting these three criteria must be handled with care, because they may become a severe risk if it later turns out that these substances are toxic under certain conditions.

4.4 List of hazardous substances

In the following, some of the most prominent hazardous substances[17] are listed. **This list serves as a first approach.** It is neither complete nor is it ordered. Nevertheless, this list includes all substances of which nanotechnological concepts for substitution have been identified within this project:

Heavy metals

Most heavy metals are toxic, persistent, and highly mobile.

Dirty dozen

There is a world-wide agreement on the hazardous potential of twelve substances – the so called dirty dozen:

aldrin, chlordane, DDT (**dichlorodiphenyl trichloroethane), dieldrin, dioxin, furan, endrin, heptachlor, hexachlorobenzene, mirex, PCBs (polychlorinated biphenyls), toxaphene**

Most of these are insecticides. But due to the general acceptance of their hazardous potential the release of these substances into the environment has been stopped in Europe. However, some of them are still produced and exported to less developed countries with less strict environmental regulations, hence the production of these substances has been reduced but not terminated.

There is also a broad agreement on the hazardous potential of the substances listed below which so far are not subject to strong legal regulations:

Brominated flame retardants

The most used brominated flame retardants are polybrominated diphenyl ethers (PBDEs), tetrabromobispehol A (mostly used as reactive flame retardant) and hexabromocyclododecane (HBCD).

Chlorparaffine, tributylzinn (TBT), **artificial musk compounds**, **cyanide**, **polycyclic aromatic hydrocarbon** (PAH), **bisphenol A**, **phtalate**

[17] See for example: http://toxnet.nlm.nih.gov/, http://hazmap.nlm.nih.gov/index.html.

Another group of hazardous substances are **volatile organic solvents (generally called VOC for Volatile Organic Compounds).** They are highly mobile and often toxic. Typical examples are: perchlorethylene, tetrachlorethene (Per), trichloroethylene (Tri), 1,1,1-trichlorethane, methyl chloroform, dichloromethane (DCM), methylene chloride, trichlorobenzene, toluene.

A more general group of hazardous substances is summarized under the term **toxic organic pollutants**. Beside the VOC mentioned above, compounds such as trichlorophenol (TCP), 2,4-dichlorophenol (2,4-DCP), and sodium benzoate belong to this group.

Prioritisation of hazardous substances

For further analysis this list has to be ordered. A prioritisation has to be developed. The following criteria could help in the prioritisation process:

- toxicity, especially in combination with persistence, mobility, bioaccumulation potential
- amount of material used
- variety and amount of products containing these substances
- distribution of the products (e.g. are the products only used for special applications or are they products of everyday life)
- release of the substance by the products
- contact with humans (exposition)
- degree of existing regulations and agreements on the respective substance

Ranking all substances would go beyond the scope of this project. Nevertheless, the above listed criteria could be used as a guideline for selecting the hazardous substances on which the development of substitution by NT should focus.

Nature of the applications in which hazardous substances are used

Another approach to address the question what kind of hazardous substances should be substituted is to categorize the systems in which the substances are used. This approach is complementary to the prioritisation of the substances by their properties. It allows the identification of possible fields of substitution from the application side.

The systems are categorised by their containment in terms of the release of substances:

- **closed system**
- **semi-open system**
- **open system**

Closed system means that the substance used in a process or as agent is contained or fixed in a product so that it cannot escape into the environment. An example are the latest dry-cleaning systems used for textiles. Despite the use of volatile substances like (tetrachloroethene) the construction of the dry-cleaner systems prevents the solvent from being released.

Semi-open system means a system where the substance is fixed in a product like antifouling coating but where it will escape to the environment during use. This is typical for most varnishes. According to their functionality in protecting the coated object, these coatings are usually exposed to weathering (rain, wind, sun, variation in temperatures), and to physical stress like strain resulting from different expansion coefficients or abrasion by dust particles carried with the wind. Or the substances are simply released by out gassing or elution. This is the case for flexibilisers like phtalates.

Another example of a semi-open system is the use of lubricants. They enter the environment through evaporation (e.g. if the system is heated up) or through leakages, especially when exposed to weathering. The use of asbestos is a typical case of a semi-open system, too. It is fixed in the construction material but will be released whenever different components rub against each other or during other forms of physical stress.

Open system means that the substance or the product containing the substance is intentionally released into the environment. This is the case for all kinds of plant protection agents, e.g. for insecticides. It is inherent to the mode of functioning that substances in open systems spread.

Combustion and exhausting systems are special cases of open systems. Usually, the hazardous substances are produced during the combustion process. Substitution in this case means to substitute the fuel to avoid the production of hazardous emissions. However, it is often easier to change the combustion conditions to prevent the formation of these substances. An example of the contribution of NT is the enrichment of diesel fuel with ceroxide particles. These particles serve as catalysts in the combustion chamber of the engine, thus reducing the formation of soot.

In addition to the list of properties mentioned above, this categorisation helps to select those hazardous substances that have the highest hazardous potential. Attempts at substitution should be focused on these substances.

5 METHODOLOGY

Since most NTs are at an early stage of development and due to the fact that NT is an enabling technology there are only a few publications and only very few research projects directly addressing the substitution of hazardous substances by NT. Therefore, the challenge of this project was to estimate a potential that has not yet been explored.

5.1 Approach

The research for the **findings is based on two approaches:**

A **literature research** and **interviews with experts**.

Literature

The relevant literature was identified by following criteria:

- Reports from governmental departments, research institutes, industrial associations, and other stakeholder groups which addresses NT and environmental issues. The considered reports are listed in appendix 10.3.
- Journals, carrying ‘Nano’ in their titles.
- Certain journals in the field of applied chemistry.
- Journals addressing chemistry and environmental issues (e.g. Green Chemistry).
- broad keyword based searches in several data bases

The considered journals are listed in appendix 10.5.

Experts

The experts for the interviews are chosen due to publications on NT related to environmental issues or even related to a case of substitution. They are all experts in the field of NT but with a different background. The experts include representatives from industry, science, research management, and NGOs. To identify relevant actors and different perspectives publications of pressure groups like VCI (the German chemicals industry association), and big industries, like Degussa, cefic (European chemical industry council), but also incorporated societies like Greenpeace and WWF are considered.

Experts who have been contacted are listed in appendix 10.6.

5.2 Research strategy

The specific journals are reviewed differently. **Recent issues of journals specialised on NT are examined manually title by title.** The same applies to journals on chemistry which focus on environmental issues. **Other issues of these journals and the other journals** are examined with the help of **keyword-based research**. Concerning the subject of the journal, either the keyword ‘nano*’ (all words starting with ‘nano’) is used (for journals with an environmental background) or the combination of the keywords ‘nano*’ together with keywords like ‘substitution’ ‘hazardous’, and ‘replacement’ are used. Subsequently, the results are examined manually title by title.

This keyword based search was performed in

– journals of the American Chemical Society (ACS)

– journals covered by Science Direct

5.3 Validation

To **validate the findings** of the project nine **experts from different fields of NT** or chemistry with a nanotechnological background **were invited to a workshop at the European Parliament**. The group of experts comprised representatives from industry, science, research management and NGOs. Prior to the workshop a summary of the preliminary results of the project (Deliverable No. 2: Input for the Validation Workshop) was sent to the experts. Some of the experts were invited to present a short assessment of the summary. The summary of the results and the opinions of the experts were the basis of the discussion. The workshop focused on the discussion among the experts but was open to Members of the European Parliament in order to give them the opportunity to give their views on the evaluation of the preliminary findings and related policy options. In addition the workshop was open to other persons active in the field of nanotechnology.

The list of invited experts may be found in appendix 10.1.1.

The results of the workshop are summarised in appendix 10.1.2 to 10.1.4.

6 CATEGORISATION OF THE FINDINGS

The projects, research activities, and concepts in the field of nanotechnology (NT) which are related to the substitution of hazardous substances or to their reduction have been subdivided into several categories:

Coatings

Most examples are to be found in the field of surface treatments like coatings, paints, and texturing surface. These approaches are summarised under the term coatings.

Flame retardants

Bromine containing flame retardants are broadly used but bear risks to human health and to the environment. Nanotechnological concepts reducing or avoiding them are summarised in this section.

Flexibilisers

Due to the fact that consumers have physical contact with many products made of plastics, flexibilisers are an important possible harmful substance which is targeted for substitution.

Substitution or reduction of solvents

Solvents, especially organic solvents, are often toxic and mostly volatile. On the other hand, they play an important role in chemical processes. Especially gluten, paints, resins, and other coatings often contain toxic organic solvents. The concepts of NT which aim to reduce solvents are summarised in this section.

Catalysts

The development of catalysts is a broad and important field in chemistry. It is expected that NT will contribute considerably to the development of new catalysts. Developments leading to the reduction of hazardous substances are summarised in this category.

Other examples

In this section all examples are summarised which do not belong to one of the groups mentioned above.

Filtering/Remediation

With respect to environmental issues, the vast majority of literature on NT deals with possible applications in the field of filtering and remediation. Even though this subject does not fall strictly within the scope of the project, some NT applications are listed due to the fact that they are related to the overall objective of this project, reducing environmental load and threats to human health.

The information on the products which are listed as example for a certain nanotechnological approach is taken from the producer website. At this point it has to be mentioned, that the functionality promised by the producer and the nanotechnological origin has not been verified. It refers to that what the producer state themselves.

Within this project it is not aimed to cover all products which fit with a certain nanotechnological approach. The presented products are to illustrate the nanotechnological approach.

7 FINDINGS

7.1 Coatings

7.1.1 Self cleaning surfaces

Relation to the project:

The use of cleaning agents could be reduced or even made superfluous.

Reduction of adhesion is relevant for many applications. For example is the reduction of adhesion one approach to substitute antifouling agents like TBT. Biofouling reduces efficiency and function in many marine technologies, shipping is only one. Biofouling also causes problems in many areas of process techniques (e.g. in water cooling or supply systems, air-conditioners, filter systems, and even the perishability of beer[18]). Therefore, to understand and overcome biofouling is the aim of a huge body of research.

Apart from biofouling the reduction of adhesion is also relevant for many other technical applications. But for the majority of these applications the reduction of adhesion does not lead to reduction or replacement of hazardous substances but to reduction of energy losses and disfunctionality by obstruction.

Function and relation to NT:[19]

The most prominent examples are trials to reproduce the lotus effect technically.

Barthlott et al. have realised that the complex structure of the surfaces of lotus leaves in combination with the water repellent material (wax) is the reason why the leaves are always clean even though they are growing in muddy water. The structure consists of a microscale mound-like structure which is covered by a nanoscale hair-like structure (Chen 2006). In nature the water repellent property is realised by wax which is a soft material. Due to this softness, the structures suffer from weathering and other physical stress. Therefore, the leaves of the plant are always reproducing the structure.

There are several approaches which are not based on the lotus effect. Often anti-adhesive coatings are realised by flour-based chemicals (see for example Weinelt 2005). It is not clear if these approaches can be accounted as NT.

Application area:

All surfaces which have to be cleaned (Weinelt 2005). But due to the mentioned stability problem for surfaces like floors, windows of cars and other surfaces which have to withstand physical stress, this technology is currently not an option. Especially interesting are surfaces which are exposed to rain, like the walls of high buildings. The rain washes the dirt away without any further aid.

Toilets in the field of transportation: In addition to reducing chemical agents, water consumption can be reduced which is an important factor especially for means of transportation like planes.

[18] The brewery Carlson is performing research on coatings for PET-bottles to reduce biofouling which increases the durability of the beer, especially without cooling. (Interview Bachmann/Luther).

[19] There are several approaches to realise non adhesive coatings which do not base on NT (Krollmann 2005, dps – Degussa ProSurface (http://www.creavis.com/site_creavis/en/default.cfm?content=
internalstartups/dps (17.7. 2006)). But the distinction between NT and chemistry in this field is not really possible.

A promising application is the substitution of antifouling paints. Due to the huge importance of this problem there exist several activities in the field. At the moment, the AMBIO project is the only one to address the problem by nanotechnology.[20] Another project where NT plays a minor role was performed by WWF (Watermann 2001).

Anti adhesive and biocide coatings are also interesting for the food industry. But in this field they do not serve as a substitute but reduce cleaning costs and increase product quality (Interview Liedberg).

Examples:

There are several enterprises advertising their product as long lasting anti adhesive and easy to clean coatings (see for example Degussa [TEGOTOP® 105][21] and Weinelt 2005, Nanofilm [Clarity Defender™][22], Nanogate®, Applied Physics and Advanced Technology [Anti-Grafitti Paiting][23], Protectosil®[24], x-clean®[25] (NANO-X GmbH), [mpc coverax[26]]).

Assessment:

Anti-adhesive coatings:

There are a **lot of activities and** there exist **several products** in the field of NT based on anti-adhesive coatings. Main issues which still have to be improved are costs, durability, and adhesion of the coating.

The **relation to substitution** of hazardous substances **is indirect**, but if these coatings could be applied widely, considerable reduction in cleaning agents could be achieved. Additional benefit could be expected: reduction of energy and water (for cleaning) consumption. In relation to process technology cost could be reduced by enhancement of the operating life of reactors and heat exchangers.

The stability of technically structured surfaces to generate the lotus effect is the main problem which is hindering this application of NT to a broader use.

For transparent application areas, adhesion is still a problem.

Biofouling:

If anti-adhesive coatings could be used as substitution for antifouling paints a huge potential could be assumed. But all NT-based coatings used in the WWF project do not show promising results. A main challenge is that application conditions differ greatly from laboratory conditions[27] (Interview Watermann).

[20] As mentioned in section 3.4 the discrimination between NT and biology or chemistry is in this field especially difficult.
[21] Source: http://productkaleidoscope.degussa.com/productkaleidoscope/en/produktkaleidoskop/performance_materials/care_specialties/tegotop_105.html (4.7. 2006).
[22] http://www.nanofilmtechnology.com/about_nanofilm/about-nanofilm.htm (4.7. 2006).
[23] http://www.fata.unam.mx/producto.jsp?l=2 (4.7. 2006).
[24] http://www.protectosil.de/protectosil/en/info/downloads.html (5.7. 2006).
[25] http://www.nano-x.de/html/x-cleanr.html (17.7. 2006).
[26] http://www.mpc-coverax.de/ (17.7. 2006).
[27] A main problem is the fast covering by peptides.

7.1.2 Biocide coatings

Relation to the project:

As mentioned above in the section on antifouling coatings, toxic substances like TBT are used at present. On the basis of NT there are other approaches to realise biocide effects and therefore to replace or avoid TBT. But the **majority of these coatings are designed for medical or hygienic applications**. The idea is to reduce the consumption of disinfectants or in case of devices like catheters, for example, to reduce the consumption of antibiotics.

Mainly, two approaches could be identified:

1. ***Silver particle-based coatings***

   Function and relation to NT:

   One approach is to include biocide particles, e.g. silver particles, within coatings. Here it is not clear if the silver particles serve only as source for silver ions which act as a biocide agent or if the particles themselves have a biocide impact. It seems that such coatings are more efficient if the particles are smaller than 10 nm (Morones 2005).

   Application area:

   This kind of biocide coatings are already used for catheters and hearing devices[28] (INM, Paschen 2004, p. 91). Other applications in the medical area like coatings for surgery tools are under discussion. There are even many consumer products like textiles advertising hygienic benefits from the use of silver nanoparticles and washing machines which are coated with silver nanoparticles. These products are already on the market. But these applications are not within the scope of the project, because no hazardous substance is reduced.

   Examples:

   x-add®[29] (NANO-X GmbH), Bioni Perform[30] (Bioni CS GmbH /FhG-ICT)

   Assessment:

   It is assumed that **silver particle-based coatings are predominantly used for medical applications** or in the food industry. If these coatings are also useful for bigger surfaces like walls in clinics or for the reduction of biofouling in marine technologies cannot currently be predicted. Therefore, the reduction of larger amounts of antibiotics is questioned. Nevertheless, if these coatings can prove their efficiency, they could be very useful.

   There are also some **consumer products like textiles** advertising hygienic benefits from the use of silver nanoparticles and **washing machines** which are coated with silver nanoparticles. **These products are already on the market.**

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[28] INM-Leibniz Institut für Neue Materialien gGmbH, http://www.inm-technology.de/kompetenzen/un-ternehmen/applikationen/mikrobizide_schichten/?PHPSESSID=e244d52ee9f6ad7fef745c253996c3ab.

[29] http://www.nano-x.de/html/x-addr.html (17.7. 2006).

[30] http://www.ict.fraunhofer.de/deutsch/presse/nanoschimmel200509.html (17.7. 2006).

2. *Photocatalytic Particles*

Function and relation to NT:

Another approach to realise a biocide coating is the incorporation of ZnO or TiO2 nanoparticles. By irradiation with UV-light they can produce hydroxyl radicals from water attached to the film (Fernandez-Garcia 2004, p. 4084, Paschen 2004, pp. 94). These radicals have a biocide effect. In addition, these radicals can be used for cracking organic compounds (Bergeron 2005). Similar approaches are performed with fullerenes (Pickering 2005, Hoffknecht 2006, p.39).

Application area:

These coatings could be used for biocide coatings in clinical applications, for example in disinfectant tiles, but also for swimming pools to reduce the use of chlorine for disinfection. A side effect is that organic dirt is decomposed and can be wiped away. The decomposition of organic compounds could be also of interest to clean facades of houses, hence reducing the use of cleaning agents.

Another application area which is widely discussed with respect to the photocatalytic effect of TiO2 nanoparticles is their use for remediation (see chapter 7.7.). Considerable research is performed whether photolysis of TiO2-nanoparticles could be used for decomposition of persistent organic compounds. Other applications are the decomposition of smoke and of odours. Both kinds of application have not been considered because they are out of the scope of the project.

Examples:

Caparol (CapaSan)[31], JUSTaddWATER®[32], x-view®[33] (NANO-X GmbH).

Assessment:

For **sun-exposed outdoor applications** like walls of facades these coatings seems to be **promising for considerable reduction of cleaning agents and paints**.

For indoor applications, it is questionable if these kinds of application could really lead to a reduction in the use of hazardous chemicals. Due to the fact that TiO2 only produces radicals in the UV-range of light which is filtered out by common window glass, the remaining fraction or the production by artificial lightening of UV-light **seems not to be sufficient for indoor applications**.

7.1.3 Coatings for various purposes

Paints, sealings, corrosion protection

Function and relation to NT:

There are various approaches to enhance the efficiency and to alter the functionality of coatings with the help of NT. The introduction of special nanoparticles (e.g. SiO2-, or ZnO-based particles) in paints can enhance the durability of the coating. Therefore, the amount of paint required can be reduced, leading to a reduction in the use of hazardous substances, e.g. volatile organic compounds (VOC) like organic solvent (Bergeron 2005, p.15).

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[31] http://www.caparol.de/caparol/content?id=4920 (19.7. 2006).
[32] Hessen Agentur 2005, p. 31.
[33] http://www.nano-x.de/html/x-viewr.html (17. 7. 2006).

Due to continuous development in coatings it is probable that successive coatings like wood preservatives, which are often linked with the use of hazardous substances, can be replaced. For the same reason, it is conceivable that pigments which are at present based on heavy metals like Cd will be replaced by nanoparticles (Interview von Gleich/Steinfeldt). But at the moment, no project aiming at the latter concept could be found.

The reduction of organic solvent can be achieved by dry coating. Precondition is the electric conductivity of the object to be covered. There are some NT approaches to cover insulators like plastics with conductive coatings, e.g. consisting of carbon particles, and make them accessible for powder coating techniques (Interview Pridöhl, Interview Bachmann/Luther).

Corrosion protection

There are some corrosion protective coatings based on NT (Shchukin 2006).

Examples

Ormocere[34] (FhG-ISC) (delivers many more properties than merely corrosion protection)

Several coatings from Nano Tech Coatings (NTC) GmbH and the INM-Leibniz Institut für Neue Materialien gGmbH

x-tec®[35] (NANO-X GmbH)

Chromating

Metals, especially aluminium, have to be chromate to guarantee the adhesion of varnish. During this process, toxic chrome compounds are produced.[36] With the sol-gel procedure, coatings based on nanoparticles can replace chromating. A life cycle analysis on this case of substitution already exists (Steinfeldt 2004, p. 57).

Examples:

Clearcoat U-Sil 100 und 110[37] (Nano Tech Coatings [NTC] GmbH)

Tribological coatings

NT provides coatings with extremely great hardness or with a self-lubricating effect. These kinds of coatings can reduce the use of lubricants, which have often toxic ingredients. At present, coatings of great hardness and with good tribological characteristics are often realised by chromium compounds (Zentralverband Oberflächentechnik 2003). Chromium VI is highly toxic. In some cases, they could be replaced by nanotechnological hard coatings on the basis of Diamond-like carbon (DLC), carbides or nitrides are already used (Picas 2003, Luther 2004). Because the coatings fulfil several functionalities at the same time, the possibility of replacement cannot be assessed in general but has to be estimated on a case by case basis. Especially for cutting tools these coatings are already state of the art. But they do not replace toxic coatings or materials.

[34] http://www.isc.fraunhofer.de/alteseiten/ormocere/index_o0.html (17.7. 2006).
[35] http://www.nano-x.de/html/x-tecr.html (17.7. 2006).
[36] The directive 2000/53/EC on end-of-life vehicles (ELV) orders the elimination of the use of chrome in automobile manufacturing by 2007.
[37] http://www.ntcgmbh.com/html/produktinfo_content.html (17.7. 2006).

Example

Nanomer®-Gleitlack (INM-Leibniz Institut für Neue Materialien gGmbH)

nanoGlide® (Nanogate)

Assessment

In general, it should be stated that **NT in the field of paints and sealings** as well as in other fields of incremental chemical developments like **tribological coatings** is not focused on the improvement of only one aspect. The improvements are **usually oriented towards several aspects at the same time**, like behaviour in drying, viscosity, adhesion, durability, etc.

In relation to substitution the examples in this field show that its **potential for replacing hazardous substances is indirect**. The mentioned **expectations have to be verified by a detailed analysis**. On the basis of the present data it seems not possible to estimate the existing potential. Instead, the **replacement of hazardous substances seems to a minor side effect** of activities aiming at other purposes.

7.2 Flame retardants

Function and relation to NT:

There are several approaches to replace bromine flame retardants with products using NT. Bromine is used as a reaction inhibitant by absorbing oxygen. A similar effect could be realised by nanoparticles. If TiO_2, SiO_2, MgO, or ZnO nanoparticles are added to substances oxygen is accumulated and builds up an oxide layer (Interview Reller). These inorganic particles introduced in plastics reduce fume generation, dropping properties and wicking in the case of combustion (Luther 2006, Interview Pridöhl, Interview Reller). A similar concept especially for wooden elements is to add silica nanoparticles (silane) to the resin which forms a ceramic-like layer under heat exposure. This layer has a heat insulating effect and prevents oxygen exchange between air and wood, and in addition reduces fume generation (Interview Pridöhl).

For transparent applications nanotechnological aerogels are used as insulators for glass doors (elements 2006).

Examples

AEROSIL®, Degussa, (elements 2006), p. 23

Nanobinder (INM-Leibniz Institut für Neue Materialien gGmbH)

(http://www.inm-technology.de/kompetenzen/unternehmen/applikationen/nanobinder/)

Exolit 422 (Clarient Inc.)

layered silicates (could be used to change the gas permeability) (Südchemie)

(Luther 2004)

Assessment

The **size of the particles seems not to be essential** in most of the applications mentioned above. But due to the small size the particles do not alter material properties like flexibility and appearance. The use of silicates in plastics and for **coating of flake boards and compressed wood was already used for several years**, even before NT achieved its current attention (Interview Fichtner). **Some people argue that the substitution of bromine flame retardants has already been solved technically**. There exist a broad variety of chemical substitutes (Interview Döring).

Often not all properties of flame retardants containing bromine can be realised by bromine free flame retardants. On the other hand, similar to coatings the **addition of nanoparticles does not only aim at replacing the hazardous substances but at realising new properties** (Interview Keßenich).

7.3 Flexibiliser

In plastics, the bindings between the polymer chains are essential for the property of the material. If the bindings are rigid the plastic will become brittle. Flexibiliser leads to elastic bindings between the polymer chains. It is known from tires that the addition of nanoparticles can enhance the flexibility of the rubber mixture. **A similar effect is conceivable with plastics** (Interview Reller).

Although the substitution of flexibilisers is an important issue, in the field of NT **no research activity in this direction** could be found within the investigations for this project.

7.4 Substitution or reduction of solvents

Examples which are related to the reduction of solvents are characterised by a high degree of uncertainty but are associated with an estimated high potential for NT.

Relation to the project:

Organic solvents or volatile organic compounds (VOC) in general are one group of chemicals which are often toxic, bio-accumulative and, due to their volatility, difficult to control. There exist several attempts to substitute toxic organic solvents by non-toxic or by water-based solvents. **Solvents can not be directly substituted by NT**. But in the literature it is often mentioned that NT may change processes in a way that in some cases **use of solvents can be reduced** or will even become dispensable in future (Royal Society 2003, p. 2).

Function and relation to NT:

Often in reports there is the expectation that NT will lead to the reduction of use of organic solvents but there is **no indication how this can be realised** (Royal Society 2003, 2004, p. 11). There are paint producers who promote their nano-based products by mentioning the reduction of solvents in the paint (Nanoflon®[38] ([Shamrock Technologies Inc.] Sivento® [Degussa] Protectosil®).

Water-based solvents

In some cases, NT is used to replace the organic solvent by water. For example, microemulsion systems are being evaluated as aqueous-based ‘green’ solvents to replace chlorinated organic solvents in dry-cleaning applications and as solvent delivery systems for pharmaceutical applications (Acosta 2005).

[38] http://www.coatingsworld.com/corp_capabilities.php (5.7. 2006).

‘Because microemulsions contain domain sizes between 1 and 100 nm, they can be considered ‘small’ vessels or nanophases for conduction reactions’ (Acosta 2005, p. 1275).

Another way to realise the substitution of an organic solvent by water is to design new catalysts with the help of NT. For some applications, these catalysts could enable a reaction to take place in water as solvent, thus avoiding the problems of volatile organic solvents.

Powder coating

Another approach is to extend the application field of dry coating (powder coating). In this field, NT could be used to improve the quality of the coating. Because powder coating can only be applied for conductive materials NT could be used for covering the workpiece with a conductive coating before powder coating is applied.

Assessment:

Even though **paint producers claim to reduce solvents by use of NT** it seems to be **more likely that the use of NT is to improve other properties of the paint**. The **estimated high potential** for NT for the reduction of solvents **could not be verified** within the project.

7.5 Catalysts

Relation to the project:

For two reasons catalysts are exceptional examples of applications of NT in respect to the scope of this project. First their **relation to NT is not as clear** as it is for other applications and second their use **points less in a direction of substitution**. Apart from a few cases catalysts lead less directly but more indirectly to a reduction of hazardous substances.

Concerning the first issue, the relation of catalysts to NT, it is expected that due to NT the development of catalysts will become more effective and successful (see for example Haruta 2003). One reason is that NT delivers new analytic instruments, which could help to understand the fundamental processes concerned. Another reason is the increase in computing performance which makes it possible to simulate complex reactions.[39]

On the other hand, **research on catalysts is an old and huge research field**.[40] In this field, the **distinction between ‘pure’ chemistry and nanotechnology is especially difficult**. Heterogeneous catalysts[41] were from its beginning mostly in the dimensions of nm (Interview Pridöhl, Interview Reller, Interview Fichtner). Zeolites[42] are an example of a well-known material which has been used for long time in petrol chemistry but which is nowadays termed as nanomaterial (Knötzinger 2002).

Related to the second issue **for catalysis, the distinction between ecological benefits and substitution is often not useful**. Catalysis can help to save energy because it can reduce the process temperature, it can reduce the amount of by-products due to their selectivity, it can enable processes which are not possible without it.[43] These new processes could lead to the substitution of processes with greater detrimental effect on human health or the environment (Steinfeldt 2004).

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[39] Even though this increase in computing performance is not related to NT, this approach mentioned above is often attributed to NT.

[40] The catalyst market was worth about $30 billion in 1999 and is forecast to reach
$100 billion by 2015 (Buff 2003 cited in Bergeron 2005, p. 14).

[41] see glossary.

[42] see glossary.

[43] The most prominent example is the synthesis of ammoniac with Fe as catalyst (Haber-Bosch-Systhesis).

In summary, usually the use of catalysis will lead to a reduction of the environmental burden even though they do not substitute another substance as can be seen from the example of the fuel additive below.[44]

Function and relation to NT:

In heterogeneous catalysis, the electrochemical potential on the surface of the catalyst is different than in the solution of the reactor. Therefore, on the surface of a catalyst reactions between the reactants are more likely than anywhere in the solution. There are two aspects in the field of catalysts which have a relation to NT. The first one is simply that nanomaterial is often used or expected to be used as a carrier for catalysts. With the help of the carrier material the active surface is increased and by this means also the efficiency. High porosity of some nanomaterials leads to an extremely high surface to volume ratio. The second relation to NT is caused by the shape of the catalytic material itself. The electrochemical potential not only depends on the material but on the ratio of surface atoms to volume atoms (dispersion). Both aspects are the reason why the size of heterogeneous catalysts is usually in the nm range. For example the platinum particles in catalysis for automobiles are in the dimensions of 2 to 20 nm. To attach the catalytic nanoparticle, a carrier system is required (van Heerbeek 2002, Astruc 2001). In order to increase the efficiency of the whole system the surface-to-volume ratio of the carrier material should also be as high as possible, as mentioned above. Therefore, carbon nanotubes are often expected to be a good catalyst carrier system.

Selectiveness

A crucial aspect of catalysis is selectivity – the catalyst should only enhance the reaction between certain molecules, other reactions should be suppressed. One approach is to build structures (templates) which allow only certain molecules to come together due to the shape of the structure and the size of the reactant. These structures are also in the dimension of nm. An example is the group of zeolites mentioned above. This field is called template chemistry, the underlying principle could be compared with the functionality of enzymes.

Another approach to control the selectivity is pursued by alloys (created by means of functionalised nanoparticles) (Interview Bachmann/Luther).

To economise on expensive metals, work is being done on mixed oxides as an alternative (Interview Fichtner).

Examples:

The special type of catalysts activated by light is already mentioned in section 7.1.2.

Cerium oxide nanoparticles (Envirox® from Oxonica®[45]) are used as a fuel additive in order to make the combustion process more efficient and to reduce exhaust emissions

(Fernandez-Garcia 2004, p. 4088).

A very well investigated example is the styrol synthesis where due to NT catalysts the by-production of heavy metals was able to be reduced (Steinfeldt et al. 2004).

A new catalyst system consisting of Ir(0)n nanoclusters plus HCl. The resultant catalyst system hydrogenates acetone at 22 °C with high efficiency and high selectivity (Özka 2005).

[44] This is not necessarily the case, because it is conceivable that catalytic behaviour could also produce unwanted side-effects which could be larger than the benefits.
[45] http://www.oxonica.com/energy/envirox.htm (5.7. 2006).

A new catalyst is a solid solution of gallium and zinc nitrogen oxide 5,6, (Ga1-xZnx)(N1-xOx), modified with nanoparticles of a mixed oxide of rhodium and chromium. The mixture functions as a promising and efficient photocatalyst in promoting the evolution of hydrogen gas (Maeda 2006).

Direct splitting of water under visible light irradiation with an oxide semiconductor TiO_2-nanoparticles to generate H_2 as fuel (Zou 2001).

Using nanostructured zeolites makes the oxidation of toluene to benzaldehyde more environmentally benign for two reasons. First, the reaction is initiated by visible light, which reduces energy consumption. Second, using visible light accesses low-energy reaction pathways that help eliminate wasteful secondary photoreactions and increase the yield of the desired product. In this study, selectivity for benzaldehyde using the nanostructures was 87 %, compared to less than 35 % for the same reaction with conventional zeolite material (Masciangioli 2003).

Silver (Ag) or gold (Au) nanoparticles are used as catalysts to decompose off odours and act as filters for air purification.

This application is not an example of substitution related to the scope of the project but it can reduce the use of water and washing agents.

Assessment

As mentioned above, **only very few developments of catalysts are performed with the purpose of substituting hazardous substances**. Nevertheless, the **use of catalysts is usually accompanied by environmental benefits**. NT contributes to the understanding of fundamentals in catalysis research with analytic tools, interdisciplinary approaches and interdisciplinary exchange of knowledge. This contribution will lead to further developments in catalysis especially in order to increase selectivity.

On the other hand, **especially for catalysts it is necessary to assess the potential toxicity and environmental damage** they can cause if they are released to the environment. Due to the small size of the catalytic particles, they are often very mobile and might be distributed widely. For example at present it is not clear what effects platinum particles which are already released from car catalysts cause in the environment. In general, it is not clear which consequences the mining of rare elements and its distribution will have on the environment. Due to the fact that they are extremely rare, biological systems have not adapted to them by evolution (Interview Reller).

Usually, the benefit of catalysts exceeds their negative effects but this cannot be assumed generally and has to be evaluated for every special case.

In general, there seems to be no lack of attention concerning the contribution of NT and especially the development of nanoparticles for further development of catalysts.[46]

Here it should be mentioned that catalysts are often mentioned in connection with remediation (Bergeron 2005, p.14). For example there exist various approaches to combine catalysts and filter systems (Interview Pridöhl). Another huge field is the decomposition of toxic or persistent organic compounds (see section 7.7).

7.6 Other examples

In this section all examples are summarised which do not belong to one of the groups mentioned above.

[46] There are already several review papers on nanoparticles as catalysts (Fernandez-Garcia 2004, Kakkar 2002).

Soldering

Solder includes lead (Pb), tin (Zn), and indium (In). Especially lead is known to be toxic. An approach to substitute solder is to generate conductive plastics by carbon nanoparticles as conducting filler, hence to glue instead of soldering.

Assessment:

This approach is **interesting for the chip industry** for reasons **other than the substitution** of lead because the heat load to the sensitive microelectronic devices can be reduced.

Insecticides I

There exist some attempts to alter the application of insecticides by NT. The idea is to immobilise the chemical agents of plant protectants by NT and to delay their release (Interview Bachmann/Luther, Interview Pridöhl). It is perceived that this could be realised by nanocapsules releasing the insecticide continuously (Interview Reller).

Assessment:

With these concepts it is **hoped to reduce the amount of plant protectants** which have to be used because it is argued that the agents could be placed directly where they are needed. In addition, the agents are not evaporated or washed away by rain. These concepts are based on mini-emulsion technology but they are **still at the development stage and not yet on the market** (Interview Keßenich).

Insecticides II

Furthermore, it is expected that NT will enhance the performance of information and communication technology by increasing the precision of monitoring and dosage. It is assumed that due to this development lesser amounts of plant protecting agents will be used in agriculture (Royal Society 2003, p. 3).

Assessment:

Here, the **relation between the reduction of a hazardous substance and NT can be very weak**.

Drug targeting

Within NT there exist several attempts to improve the efficiency of pharmaceuticals by bringing them directly to the cells where they are needed. Therefore, the amount of pharmaceuticals can be reduced, which is especially important for chemotherapy or application of antibiotics.

Assessment:

Of course, the **main goal is to reduce the side effects of the therapy**.[47] But especially chemotherapeutics are detrimental for the environment and the release of antibiotics causes severe problems due to resistance of bacteria.

Lead-containing batteries

Usually, the separation layer in a Li-ion battery consists of an organic compound which is not very temperature stable. This lack of stability can be overcome by a coating based on nanoparticles. Due to this coating, Li-ion batteries will become suitable for use in automobiles. This would allow the replacement of the lead-containing batteries used at present.

[47] It could be argued that due to the concept of drug targeting the cost of the therapy will be reduced, because less expensive pharmaceuticals are needed. But in this calculation the additional cost for the drug targeting system must be considered.

Another approach is to replace a lead-containing battery by a fuel cell. NT contributes to the same extent to that replacement, as it is used to improve components of the fuel cell, e.g. considerable research is performed to realise the H2 storage, and NT is used to improve the membrane[48] in the fuel cell.

Assessment:

These is an **example of a substitution** (here of lead) **enabled by nanotechnology**. But the example also shows that such a replacement is **often very indirect**. Here, a whole system, the lead battery, is replaced by another system, the Li-ion battery/the fuel cell, which provides the same functionality but with quite a different construction.

Substitution of new products based on completely different techniques

In the literature, it is sometimes stated that due to NT common products could be realised by a completely different approach which is more environmentally friendly. For example using carbon nanotubes in computer displays may diminish the environmental impacts by eliminating toxic heavy metals and drastically reducing material and energy use requirements compared to cathode ray tubes (Masciangioli 2003).

Assessment:

These examples are not in the scope of the project, because the project focused on the substitution of chemicals instead of whole devices. In addition, it is **difficult to balance the potential benefit of the product with its potential negative effects because the products do not yet exist and very little is known about their production conditions and their context of use**.

7.7 Remediation

A lot of the literature concerning nanotechnology and environmental issues deals with the potential of NT for cleaning up polluted air, water, and soil. For example as mentioned above, considerable research is performed to investigate whether photolcatalysts of TiO2-nanoparticles could be used for decomposition of persistent organic compounds. In this project, these approaches are summarised under the term remediation. Most of the research activities concerning the development and use of catalysts in respect to hazardous substances are not in order to avoid them but to decompose them after they have been released to the environment (see for example: Nanoforum 2006, Xu 2005, Zhang 2003). **Because the project is focused on substitution or more generally on the avoidance of hazardous substances, these examples are not within the scope of the project**. Nevertheless, it should be mentioned that most articles on environmental benefits attributed to NT are of this nature.

Examples:

Due to the fact that in the field of NT which is related to environmental issues a lot of research activities are aimed at remediation, some representative examples are listed below.

Nanoparticles of Fe are an effective tool for the transformation and detoxification of a wide variety of contaminants, such as chlorinated organic solvents, organoclorinate pesticides, and PCB

(Bergeron 2005, p. 10, Wu 2005, Cao 2005).

[48] One challenge which is technically not sufficiently solved is the material of the membrane which separates H2 from O2. This membrane has to withstand heat and must be as thin as possible in order to enable an efficient ion transport, and it has to be durable for the whole lifetime of the fuel cell.

Considerable research is performed on whether photocatalysts of TiO2-nanoparticles could be used for decomposition of persistent organic compounds. Other applications are the decomposition of smoke and of odours (Rohe 2006, Masciangioli 2003).

Iron hydroxide granulates with nanostructured surfaces are used to adsorb arsenic in the field of drinking water conditioning (product: Bayoxid E33[49] [LANXESS]) (Hessen Agentur 2005). Another promising material for this purpose is Ceria (CeO2) molecules combined with CNT (Bergeron 2005, p. 9).

For further examples see Masciangioli 2003, Bergerson 2005 and the website of the U.S. Environmental Protection Agency (EPA):

http://es.epa.gov/ncer/nano/research/nano_remediation.html

http://es.epa.gov/ncer/nano/research/nano_green.html

http://es.epa.gov/ncer/nano/research/nano_treatment.html

7.8 NT as risk

Although **this project is explicitly not aimed at this question**, the appreciation of NT as a potential danger should be mentioned.

The majority of literature concerning nanotechnology and environmental issues is related to potential risks NT could produce. Especially the toxicity of nanoparticles is considered as a potential threat. Even though these issues are addressed early and several research activities in that field are already being performed (Founding of CEBN[50], NanoCare[51], Renn 2006, Workshop on risk governance of nanotechnology 2006[52]) a single hazard could cause a great deal of mistrust or at least a heated debate (cf. discussion about NanoMagic in USA). A general problem is the fact that it is not possible to anticipate all contexts of use and all possible ways of releasing nanoparticles. The example of CFC has shown that the reaction chains might be very complex.

Research on toxicity has to accompany the development of new nanoparticles. But in addition a systematic monitoring of uses and contexts of use of products containing nanoparticles has to be performed.51

Inherent in the process of substitution, balancing of positive versus negative effects has to be performed. If no data and no experience on the effects of the NT under consideration is available, the substitution process should be carefully performed and should be accompanied by systematic scientific research. This is especially true for nanoparticle-based catalysts, which are not attached to a carrier system or could be released by the use as it happens with platinum particles used in catalysts for automobiles.

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[49] http://reports.westernreal.de/reports/lxs_ar_2005_de/downloads/LXS_GB05_D.pdf (18.7. 2006).
[50] http://cohesion.rice.edu/centersandinst/cben/index.cfm (21.7. 2006).
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8 CONCLUSION

8.1 Conclusions related to the approach

The aim of the project is to give an overview of already used and conceivable applications of Nanotechnology (NT) in order to replace hazardous chemicals. In order to achieve this objective two main issues have to be addressed:

1. What is meant by the term Nanotechnology and how can it be distinguished from biology and chemistry respectively?
2. What is the meaning of ‘chemical substitution’ in relation to NT?

Concerning the first point, it has to be stated that there is **no clear definition of NT and that it is not possible to assign precisely an application to NT or to chemistry or to biology**. From the perspective of the overall aim of reducing risks caused by hazardous substances this is not important. But it is a major problem in respect to the focusing of the project which is explicitly oriented to NT.

The second point is linked with a crucial characteristic of NT which is in addition the reason why NT is ascribed such a huge potential: new functionalities. It is assumed that NT provides new effects which are not based on chemical properties of the related material but on the physical properties caused by its size and shape. Against this background the term chemical substitution in relation to NT has another meaning **Therefore in this report substitution is not restricted to the replacement of a hazardous substance by a less or non-hazardous substance. In this project a broader meaning of substitution is applied than it is the case in the chemical context.** NT can be used to develop completely different processes or different products which serve the same purpose but in a completely different way. Or it enables changing the properties of a material and achieves the intended functionality of the product as a whole by using a new and different approach.

The interviews and the comments of the experts during the validation workshop (see appendix 10.3 and 10.1) have shown that it is a delicate but necessary challenge to broaden the meaning of the term ‘substitution’ without losing its focus.

As a result of both points the relations of the applications to NT could vary considerably and are often very weak in the presented finding, discussed in detail in section 4.2.

As discussed in section 4, **substitution is not a straightforward endeavour**. To be sure that the substitute is really less hazardous than the original substance a lot of information has to be gathered about the substituting substance. This is the reason why the issue of toxicity of NT and nanoparticles (NP) dominated the comments and the discussion of the validation workshop. Here **it has to be mentioned that the assessment of the hazardous potential of the nanotechnological substitute itself was not objective of this study**[53.] The study concentrates on giving an overview of existing examples or perceived concepts and on the general background concerning NT in relation to chemical substitution.

[53] At present there are several projects and research activities addressing the issue of toxicity of nanoparticles, see for instance: Center for Biological and Environmental Nanotechnology (CBEN, http://cben.rice.edu/), NanoCare (http://www.nanopartikel.info/main.html), EMPA (http://www.empa.ch/plugin/template/empa/*/32939/---/l=2) to name only a few.

8.2 Conclusions related to the Findings

The investigations of this project show that the focus of this study is unique. There is no project which addresses the potential of NT for replacing hazardous chemicals.

Even though the list of identified examples where NT could reduce the use of hazardous chemicals seems to be long and even the applications seem to be mature[54] there are very few examples where research activities in the field of NT are directly focused on substitution. The only example to be found which is explicitly addressing substitution is the AMBIO-project. Aim of the AMBIO-project is to investigate nanotechnology-based coatings which could replace antifouling coatings usually based on TBT. The fact that there are very few research activities in the field of NT looking at substitution and the unique focus of this study were acknowledged by the experts during the validation workshop. In addition, the experts recommended continuing this work. They agreed with each other that this work is important and necessary.

Although the focus of this project was unique, considering the findings it can be concluded that **currently NT can not contribute in an exceptional manner to a large increase in substitution of hazardous substances**. Instead it revealed that the contribution of NT with respect to the reduction of hazardous substances is manifold but incremental.

This conclusion is restricted to nanotechnological products which are already on the market like self cleaning coatings or concepts which are assumed to be realisable in short or mid terms like nanocapsules for pesticides. NT which could lead to changes of entire production platforms, like printable or self-organisation-based nanoelectronics which could change the whole microelectronic industry were not subject of the analysis of this study. These cases were omitted because at present too many necessary data are not available and the analysis would have been based on highly speculative information.

Nevertheless, most of the interviewed or invited experts assign NT a considerable potential for substitution in future. For a comprehensive assessment of this potential, each identified example has to be assessed case by case and in more detail as it was performed in this project. For that, following aspects would have to be considered:

1. **Here, there is need to consider**
    - the toxicity of the concerned material which is to be substituted,
    - the amount of material which is used, and
    - the relevance of the material
      (Is the product or process crucial for society? Does it satisfy a basic need? Does it belong to a key technology? Is it part of a bigger essential system (water, energy supply, transportation)?
2. **Are there other chemicals which could substitute the concerned substance?**
3. **Of what quality is the suggested NT?**
    - To which extent is it able to replace the functionality of the hazardous substance or of the product the hazardous substance is used for?
    - When is it ready for market?

[54] The presentation of the examples suggests that the technologies are already developed. It has to be mentioned, that the functionalities promised by the producer and the nanotechnological origin have not been verified. It refers to what the producers themselves have claimed.

To evaluate the benefit of the new nanomaterial in relation to the conventional one a life cycle assessment (LCA) has to be performed. This kind of detailed assessment is only useful if there are some signs related to a special case of possible substitution that is worth evaluating this special case in detail.

The evaluation of the potential of NT for substitution in field where at present even no concepts are presented is even more challenging. An approach for capturing of applications of NT for substitution is sketched in second part of the outline.

Nevertheless, **two areas could be determined which are most promising to reduce the use of hazardous substances.** They are **coatings** and **catalysts**.

In both areas there are very different applications of NT with the potential for reduction of the use of hazardous substances, as is presented in section 7.1 and section 7.5. For example in the field of coatings there are tribological coatings, anti-adhesive coatings or biocide coatings, while in the field of catalysts there are ceroxide nanoparticles, photocatalysts.

Concerning the **field of catalysis** it has to be mentioned (see section 7.5), that:

- Research in this field was already in the dimension of nm therefore, it is **not clear to what extent further developments could be attributed to NT**.
- The development of new catalysts is seldom directly aimed at substituting hazardous substances. Instead, **in the development of new catalysts several objectives are pursued at the same time**. Therefore, substitution of hazardous substances in this field is often very indirect.
- The effect of catalysts on human health and the environment, if they are released, could be detrimental. **Their benefits and risks have to be balanced in detail.**

This field shows another aspect of the findings of the project:

At present, NT and nanotechnological concepts deliver a variety of mostly incremental improvements of existing bulk materials, coatings, or products. These improvements point in several directions and often are aimed at improving several properties at the same time. **With respect to substitution this means that nanotechnological approaches often cannot lead to direct substitution of a hazardous substance, but may lead in general to a more environmentally friendly product or process.**

The example of washing machines and clothes which are provided with silver nanoparticles make obvious, that the **use of NT does not automatically lead to positive effects.** And even if the product causes the reduction of use of materials or the reduction of the use of hazardous chemicals during its phase of use[55] it is not foregone that the overall effect of this special NT will still be positive if its production process and its deposits are taken into account.

In relation to environmental issues and hazardous substances research on catalysts especially in the field of NT is mainly related to filtering and remediation.

That means in conclusion, an analysis of the environmentally benign effect of catalysis should not be restricted to an analysis of avoiding the use or the production of hazardous substances during synthesis of products. The assessment of a new catalyst and its development should consider the entire range of benefits the catalyst could provide but including the analysis of potential problems which could be caused by the release of catalysts to the environment. In addition as an outcome of the workshop the use of rare materials and catalysts usually based on them should be carefully estimated in view of their limited availability on earth.

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[55] For example usage of cleaning agents which could be reduced due to easy to clean surfaces.

Another finding of the project which goes beyond the direct aim of the project is the observation, that **within research institutes as well as within the industry developing NT applications there is a lack of information about the problems existing in other production areas or with certain materials and substances.** Here, it seems promising to foster the exchange of information. It would be desirable for researchers dealing with applied science to know about the most prominent environmental and also technical problems of modern industry.

8.3 Outlook

Further research on the potential of NT for substitution points in two directions: detailed analysis of a concrete examples and a systematisation of as yet unknown fields of application of NT for substitution.

8.3.1 Detailed Analysis

As an outcome of the study, there are some examples which it would be desirable to assess in detail.

One example is of extraordinary interest because this application of NT is already on the market in the shape of widely used consumer products. It is the **use of silver nanoparticles as biocide in clothes, washing machines and other, medical, applications**. This example is also promising because it is paradigmatic for all catalysts in the form of nanoparticles.

A detailed assessment of these applications has to include:

- Analysis of the function and way of functioning
  Because the biocide effect of silver ions has been well known for a long time and is still widely used as a disinfectant for drinking water, it first has to be clarified whether the application in form of nanoparticles (NP) provides new functionalities and new effects.
- To include all effects of this application and to estimate its whole benefit a detailed life cycle assessment (LCA) has to be carried out.
  This LCA should also provide information about fields of applications where the most beneficial impacts could be assumed.
- Potential risks have to be identified and investigated.
  This assessment has to consider:
  1. The context of use: In which situation are these silver nanoparticles applied? Can man have contact with silver NP?
  2. What effect do they have on human heath (allergies) and what are their fate and effect in environment.

Even though this example is considered as important due to the fact that it is already widely used, it should be mentioned that the applications in washing machines and in clothes are not in the scope of the report. These kinds of applications do not replace hazardous substances nor is reasonable to assume that they will reduce the use of hazardous substances. These applications provide a common consumer product (washing machine, clothes) with additional functionalities from which the beneficial effect for the environment and even for the consumer is questionable.

8.3.2 Exploitation of unknown fields of application

The methodological approach of this project was to start with the analysis from the side of NT investigating which hazardous substances could be replaced. **Another approach** discussed at the workshop is to approach the identification of the substitution potential of NT by **focusing on the hazardous chemicals and to try to find applications of NT** which could lead to a reduction of these chemicals. Both these approaches reflect the challenges of this project. On the one hand there are a tremendous number of hazardous substances where a substitution would be desirable. How to select the most problematic ones has been described in section 4.3. On the other hand, there is huge variety of NTs. Each of them might lead to different applications and each application might be assigned to different stages of development. **The key question is: How is it possible to find a connection between a hazardous substance and a particular NT which could facilitate the substitution of this substance?** A first step in this direction was already suggested and discussed at the workshop. It is the **systematisation of the functions NT can provide** (see appendix 11). These functionalities could be **compared** with the **functionalities hazardous chemical substances provide**. Thus the question of which hazardous substances could be substituted by which NT is reduced to the question of which functionality of the hazardous substance could be provided by which NT. The systematisation of hazardous chemical substances by their functionality is more difficult than that of NT. At the moment it is still unclear whether the analysis of the chemical functionalities of the substance itself will lead to useful results, because the effects caused by a chemical in the material of a product are the result of a complex interaction with the other chemical substances involved. A less profound approach is to analyse the functionality of the products the hazardous substances are used for. This means, for example, that instead of analysing the functionality of organo-halogen compounds, the analysis will focus on the application of these compounds and on what the related products are used for. This approach is illustrated by the example of flame retardants mentioned in section 4.2. Instead of focusing on the chemical reaction processes during combustion and the role of brominated flame retardant, the focus is on the general question of how to slow down or even prevent the combustion process. One solution could be a thermal isolation coating with a quite different mode of functioning than brominated flame retardant.

On the other hand the systematisation of functions NT can provide could be used for an investigation of future application of NT to avoid hazardous chemicals. The discussion of this approach during the validation workshop shows that the attribution of functions is not as easy as it seems at first glance. Usually neither a chemical substance nor a certain NT serves a single function within a product or a material. Therefore, first it has to be shown in a preparatory study whether this approach will lead beyond the already identified fields of applications.

8.4 Recommendations

To **overcome the identified lack of exchange between scientists and industry** with respect to substitution in the field of NT it would be promising to organize **workshops and platforms** as they have already been installed in the field of green chemistry.

The focus of this study is unique and provides real new aspects and insights. This focus should be maintained. Further exploitation in this direction would be useful. But to end up with results going beyond this study **a more systematic approach would be necessary** (see outlook, section 8.3).

As a complement to the approach of this project **detailed case studies are necessary**. These studies which should **based on life cycle analysis** are necessary to generate **data for a well founded decision** base. In this respect it has to be kept in mind that successful substitution can only be realised when enough data about the substitute is available.

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10 APPENDIX

10.1 Summary and Results of the Validation Workshop

To **validate the findings** of the project nine **experts from different fields of NT** or chemistry with a nanotechnological background **were invited to the workshop at the European Parliament**: '**Validation Workshop on Nanotechnology for Chemical Substitution' -** Tuesday, September 19th - 14.00 – 18.00 p.m. - European Parliament, Brussels, PHS 7C050

The group of experts comprised representatives from industry, science, research management and NGOs. Prior to the workshop a summary of the preliminary results of the project (Deliverable No. 2: Input for the Validation Workshop) was sent to the experts. Some of the experts were invited to present a short assessment of the summary. The summary of the results and the opinions of the experts were the basis of the discussion. The workshop focused on the discussion among the experts but was open to Members of the European Parliament in order to give them the opportunity to give their views on the evaluation of the preliminary findings and related policy options. In addition the workshop was open to other persons active in the field of nanotechnology.

10.1.1 Participants of the Validation Workshop

Science

Dr. Tony Byrne

Head of the University of Ulster's photocatalysis research group of the

Nanotechnology Research Institute at University of Ulster, IR

Royal Society of Chemistry Local Section MRSC

Expertise: Semiconductor photocatalysis

Professor Dr. Graham Leggett,

Department of Chemistry

Centre for Biomaterials and Tissue Engineering

Royal Society of Chemistry

Sheffield University , UK

Expertise: nanometre scale surface chemistry and analytic chemistry.

Dr. Monica Ratoi

Electron Microscopy & Microanalysis Group

University of Oxford, UK

Expertise: Coatings and lubrications

Co-worker for the EU-project NanoSafe (Safe production and use of nanomaterials) which aimed at the development of risk assessment and management for secure industrial production of nanoparticles.

Professor Dr. Armin Reller

Head of the department of solid state chemistry of the Institute of Physics at

University of Augsburg, Germany

Member of the board of directors of Wissenschafts Zentrum Umwelt (WZU),

Augsburg, Germany

Editor of ‘Gaia’ and ‘Progress in Solid State Chemistry’

Professor Dr. Mark E. Welland

Head of the Nanoscience Centre at Cambridge University, UK

Editor-in-Chief of the Institute of Physics journal Nanotechnology

Author of the2004 report of the Royal Society on opportunities and risks of NT.

Industry

Dr John Hoskins,

Royal Chemical Society

Chair of the Royal Society of Chemistry Toxicology Group

Member the environment, health and safety committee of the RSC

Editor-in-Chief of ‘Indoor and Built Environment’

Dr. Elmar Keßenich

Department of Polymer Physics

BASF AG, Ludwigshafen, Germany

Responsibilities: Coordination of the R&D work and environmental health and safety issues in the new growth cluster NT of BASF, coordination of the activities European technology platform for sustainable chemistry, here part of the material and technology group.

Dr. Wolfgang Luther

Zukünftige Technologien Consulting at VDI-TZ GmbH, Düsseldorf, Germany

Working field: Funding strategy of NT for the federal ministry in Germany risk assessment and chances of environmental potentials of NT.

NGO

Dr. David Santillo

Greenpeace Research Laboratories

University of Exeter, UK

Main field of work: Chemical substitution

Also interest in potential of substitution but also potential risks of NT.

STOA Bureau

Malcolm Harbour

MEP for the Group of the European People's Party (Christian Democrats) and European Democrats

Vice-Chairman of STOA

Member of the

Committee on the Internal Market and Consumer Protection

Delegation for relations with Japan.

Substitute of the

Committee on Industry, Research and Energy

Subcommittee on Human Rights

Miklos Gyoerffi

Administrator of the STOA Secretariat

European Technology Assessment Group (ETAG)

Dr. Michael Rader

Institute of Technology assessment and Systems Analysis (ITAS)

Forschungszentrum Karlsruhe

Co-Coordinator of ETAG

Dr. Ulrich Fiedeler

Institute of Technology assessment and Systems Analysis (ITAS)

Forschungszentrum Karlsruhe

Project-leader of the project: “The Role of Nanotechnology in Chemical Substitution”

10.1.2 Report on the Workshop

In his welcome, Mr. Philippe Busquin (MEP) pointed out the relevance of the subject against the background of the development of ‘A new EU regulatory framework for the Registration, Evaluation and Authorisation of Chemicals’ (REACH), which was accepted by the EU Parliament in first reading on 17 November 2005. After a short self-introduction of the invited experts, the project leader, Dr. Ulrich Fiedeler, gave a short introduction to the project. Aim of the project is to identify and assess the potential of nanotechnology for replacing hazardous chemicals. At the end of his presentation he outlined the three main issues the preliminary results of the project should be evaluated by: completeness, relevance, and awareness.

At the beginning of the discussion, three experts gave their comments on the preliminary results of the project from three different perspectives: science, industry, and environmental perspective.

Comments from Prof. Mark E. Welland (Science)

In his statement from the scientific perspective, Prof. Welland underlined that the **approach of the whole project is important, particularly the specific focus** on substitution in relation to NT. He highlighted that the **subject of the project has not yet been addressed**.

He stated that the author had done an extremely good job in summarising this highly complex topic in the present report.

He pointed at the fact that the term 'chemical substitution' had a rather precise definition. In the present report, the term was used in a broader sense. It would probably help if a formal definition of chemical substitution was made up-front. In this respect, he recommended **not to widen the term of chemical substitution further than had already been done within the project**. Otherwise the project would end up with an ordinary all-encompassing list of potential benefits nanotechnology could provide with regard to human health and environment. The **interesting point of this project** was in the **specific and goal-oriented approach**.

The definition of NT seemed to be a general problem. However, it might be useful, because at the moment, the meaning of NT was rather unclear and ran the risk of loosing its momentum.

In this respect, it would be **useful to distinguish between applications where the nano-component simply increased the total surface area** (e.g. in catalysis, this issue is extremely important) and that ones **where a size or shape effect is actually used**. The question is, if we are trying to improve the catalytic efficiency simply by increasing the surface area or if we are looking for a sort of paradigm shift? The latter would mean that we might do something quite different based on the nanometre size or nanostructure.

In addition, the definitions often differentiate between natural NP and manufactured NP, which can sometimes be quite helpful.

These are some general aspects which could help to clarify the particular aims of the project.

Prof. Welland added some further general points.

An **important issue of NT** today are the **concerns about the toxicity of nanoparticles** (NP). Their behaviour in nature and especially in water is unknown. There are certain areas of nanoparticle applications were the toxicology of particles is unknown, ill-defined and perhaps not even measured. There are not even metrics for toxicological measurements of these particles.

Big companies are searching for NP for water remediation. If NP-based filters could be developed this would be very significant. However, this would lead to the release of NP into the water supply.

This also applies to silver nanoparticles. The **US Environmental Protection Agency (EPA) expresses concern** about or sees the need to take a closer look at silver **nanoparticles released by washing machines which are now on sale**. These particles are released into the environment during the use of the washing machine. The question is: what is the effect of introducing silver NPs into the environment?

In all examples listed in the report, a **Life Cycle Assessment (LCA) will be required** or would be appropriate.

Remarks concerning the evaluation criterion 'completeness'.

The only field Prof. Welland missed in the report is the field of clay-polymer composites that are currently being produced. Here, NPs of modified clays are used, which are chemically terminated so that they adhere to the polymer matrix and produce a composite. Possible applications are building materials and car bumpers. Polymer nanoparticle composites are not only used as structural materials but also for applications such as solar energy. Many solar cells and lithium batteries are based on NP.

Remarks concerning the evaluation criterion 'relevance'.

According to Prof. Welland the **question of the most relevant application** is scientifically quite **difficult to judge**.

As stated by the report, coatings based on NT are extremely important and already available on the market.

Remarks concerning the evaluation criterion 'awareness':

Presently, NT is in a crucial situation. If NT gets a bad press in one area, e.g. because of problems with a certain application of NT, this will be generalised and effect also other application areas.

Comments from Dr. John Hoskins (Industry)

Dr. Hoskins took up the point from Prof. Welland related to silver NP coated washing machines. In this respect, he pointed out a **problem with the definition of NT: In the field of NT, an old technology is often dressed up as new technology.**

At present, **industry is concerned** about **distinguishing between the bulk properties and the nano-properties** of materials, and tries to get the regulators to appreciate that these are two different things. The **physical and chemical properties of NP** are somewhere in **between those of pure chemical or pure physical objects**.

The bulk properties of carbon black, chalk or TiO2 do not cause problems, but in the shape of NPs they can lead to health problems.

At present, the bulk properties of materials are well regulated. In the field of NPs, however, there is a lack of regulation.

Dr. Hoskins drew attention to a **problem in determining the toxicity of NP**. Often, it is **not considered under which conditions** nanoparticles are used in a **specific application**. For example, in the work of Overdörster done in the United States he used uncoated TiO2, a material that is difficult to keep in nano-particle form because the particles tend to clump, but he managed to do so. In the real world, the best achievable result is coated TiO2. TiO2 in the form of uncoated NPs is not released into the environment. TiO2 – particles are not sold in pure form. For example, for cosmetics they are delivered in an emulsion or produced as slurry. Furthermore, in existing toxicological studies no differentiation is made between surface modified and non-surface modified material.

The **differentiation between bulk properties and nano-properties** has further consequences. A **material generally regarded as safe suddenly becomes a material classified as toxic**. Product **manufacturers** are **strongly worried** by this. For example, cosmetic manufacturers do not like to add materials to their cosmetics which are classified as toxic.

Another aspect pointed out by Dr. Hoskins was the **difference between risks and hazards.**

He criticised that so many **regulations are completely focused on hazards** while no thought is given to the risks. However, a **hazardous substance only becomes a risk after exposure**.

Therefore, the toxicity of nanoparticles and the question whether they are a good candidate for **substitution** of conventional chemicals has to be **evaluated in view of the application context.** An important issue in this respect is whether the nanoparticles might be released by the product or if they are bound into the product.

Furthermore, he claimed that it was an unfortunate fact that hazards provide regulators with a great scope for regulation because if they didn't like something they only had to look for its hazardous properties.

NT development will face a problem as it will be much more concerned with the risks of a material than with its hazards.

Comments from Dr. David Santillo (Environment)

The approach of Dr. David Santillo did not start from the side of NT but rather from the actual need, i.e. to replace hazardous chemicals. He agreed with Prof. Welland that the term 'chemical substitution' should be given a closer look. However, he also thought **we should bear in mind** that the **replacement of hazardous chemicals does not only include substitution** of one chemical by another but that it is necessary to **comprehensively examine the available alternatives**.

Remarks concerning the evaluation criterion 'completeness'

The **study provides a very good overview** of the current as well as some of the potential future applications of NT related to substitution. There has obviously been a broad consultation process based on a lot of expertise. But it is inevitable in an emerging field that some applications cannot be considered.

Dr. Santillo stressed that a lot of **information in this report comes from the developers** of the NT solutions. While this does not necessarily mean that we should not trust the information, we should be aware of the **fact that it comes from a side which has an interest in the development of these products.**

Therefore, he thought there is an urgent **need for more independent assessment** and that this report set the groundwork for that.

From the perspective of Dr. Santillo, there were two major barriers to such independent assessment. The first is the commercial confidentiality surrounding many nanotechnologies. The second barrier goes back to **huge disparities** between the amount of NT already put into practice and our **limited understanding** even of the most basic modes of action of these chemicals and materials, **including their toxicity.**

Around 200 consumer products using NT in one way or another are available on the market. Yet we are well behind in terms of researching the undesired impacts.

Although it can be seen from the description of tasks that it was beyond the scope of the document to look at the health and environmental effects of NT and NPs in particular, this was considered a substantial gap in the analysis. Assessing the potential of a material or substance to provide a less or non-hazardous alternative is hardly possible **without considering the context of the potential risks the nanomaterials may present.**

Especially in the field of NPs, Mr Santillo thought it was necessary to be much more aware of the risks because due to their properties NPs are quite different from what we are used to dealing with in toxicology in terms of the rates and immediacy of delivery to tissues. Particles may behave quite differently in different situations.

Remarks concerning the evaluation criterion 'relevance'

The most important question for him was: are there any other alternatives?

How far do we need to consider NT as a potential solution, or are we trying to be too clever?

And he went a step further. He argued that **before assessing the possible substitution** of chemicals by new complex and expensive technologies like NT **we should consider whether the related product is really needed**, or if there are already existing chemical substitutes.

What is the purpose of the product? What role does it play for society? Is this something what we really need, or can we find a much more elegant solution which is simply not to use this particular material or technology at all?

With regard to flame retardants he stated that replacing brominated and chlorinated flame retardants is still very important. But there are plenty of alternatives already available.

He considered it very important to look at potential substitutes for flexibilizers. Solvents are a big issue in terms of their environmental impact and it is worth looking for alternatives. There are some alternatives (e.g. supercritical CO2), but it seems to be primarily a question of costs. Lead-free solders are already available, but not for all applications.

Concerning nano-capsulated pesticides, he posed the question of what implications this might have for the persistence of pesticides and their availability to non-target organisms.

In case of **carbon nanotubes** (CNT) for displays, he recommended **comparing them with existing flat screens, rather than with ray tubes**.

Remarks concerning the evaluation criterion 'awareness'

The crucial question concerning the awareness of the role of NT for replacement of hazardous chemicals was for Dr. Santillo: How much do we need to know to make much sounder judgements? In his view, awareness is a major problem.

The information is coming in but relatively slowly compared to the speed of development.

It would be useful to have far **more information** on uses and on future applications **of NT from its manufacturers**.

This information is needed particularly to **understand and identify the real problems** and to distinguish them from those **which are rather problems of definition**.

There is a need to improve the availability and quality of information not only for the public but also for policy-makers. He recommended increasing the quality of information by **selecting** two or three **areas from the broad analysis for a much more detailed treatment.**

However, we have to recognise that when it comes to policy measures and risk assessments we never catch up with the rate of development and implementation of technology.

Perhaps we should focus on only **approving products that provide some guarantee**, some way of validating that there is **no release of particles** in their active phase to the environment. In other words, perhaps this is an occasion for us to **apply precaution**.

His last comment was addressed to the way NPs and nanomaterials should be treated in the new regulation on chemicals REACH. Should they be treated as new substances? The overall question is: how can we assure that the data gained for materials are actually sufficient to evaluate the facts.

Comments by the other experts

Dr. Tony Byrne

The **report seems reasonably comprehensive** given the impossibility to cover the whole field of NT.

The issues presented in the study concerning self-cleaning coatings and biocide coatings are well summarised.

Water purification should have been given more emphasis in the report.

Important issues are new membranes and new catalysts e.g. photocatalytic disinfection of water acts against bacteria which are resistant to chlorine or ozone.

A minor correction should be made in relation to photolysis. Photolysis is not the correct term. Water is not directly dissociated by light; instead TiO2 or another semiconductor is used as photocaltalyst.

(Remark of the author: This has been corrected, see chapter 7.)

In view of the toxicology of NT and particularly of NPs themselves, Dr. Byrne agreed that there was a general need for further research. On the other hand, he pointed out that NPs have already been used for a very long time. A problem in this respect is that **commercial products** do **not indicate** that they are **based on NT** but this doesn't mean that they do not contain nanomaterials. Therefore, **if consumer opinion turns against nano the word nano will disappear but the products won't disappear**. The question is: How can you deal with this?

A further point concerning the toxicity of NPs is a **lack of tools for monitoring nanomaterials.** The question is, how can you regulate products and production processes that involve nanomaterials without having the means to control them?

Dr. **Byrne agreed** with the general conclusion of this report **that NT is not considered important for substitution**. He argued that this is **actually true at the present time**. But in his view, NT will lead to the development of technologies for replacing hazardous substances.

Dr. Elmar Keßenich

Dr. Keßenich expressed his astonishment that the whole discussion is strongly dominated by the subject of toxicity of NT and NPs. From the scope of the report he had assumed that the potential of NT concerning substitution would be the dominant topic of the workshop. Therefore, he thought it would be **worth putting emphasis on the beneficial potential of NT**, e.g. reduction of the use of resources, the beneficial potential of self-cleaning paints and coatings, reduction of energy consumption. He concluded that we should focus on what is the benefit and what is the added value of NT.

Prof. Graham Leggett

First he pointed out that the **report was pretty well balanced and addressed** the issues in **good and sensible way.**

Then he came back to a problem already mentioned by Dr. Hoskins, which was the difficulty in evaluating a field like **NT and trying to identify what's really new and what's just a re-branding of existing technology.**

Of course, it is an obvious benefit if you need to paint your house less often. But the **crucial question** is how is it possible to perform a **realistic assessment of what happens over the whole lifecycle** of a particular product or material and to make sure that all relevant factors are taken into consideration. As an example he mentioned socks containing silver NPs. This could lead to reduced use of detergents and water consumption. But if the silver found its way into the waste water, complex problems would arise.

Concerning catalytic converters, he argued that they are the longest standing and successful example of NT, even though they are not classified as NT in the first instance.

Finally, he drew attention to another field of replacement: It is worth **thinking about the replacement of fossil fuels**, particularly because of the CO2 problem. In this field, NT provides many opportunities, e.g. energy storage, photovoltaic, and other alternative ways of energy production.

Dr. Wolfgang Luther

According to Dr. Luther, this was the **first time he had ever heard of this topic being addressed** in the field of NT. From this point of view, the **report is quite comprehensive**.

However, regarding substitution it is necessary to have the **appropriate measures to assess the risks** of the substitute. These measures are being developed, but **at present we cannot say that we are on the safe side**. This has to be kept in mind, especially in the case of open applications of nanomaterials.

Dr. Luther pointed out some **shortcomings** of the report. First he realised that the report concentrated on nanomaterial but it **did not consider the whole processes**. The question is whether just one substance is replaced or whether the whole production process is changed. **Really changing the technology platform involves the greatest potential of NT.**

As an example he mentioned the semiconductor industry: With NT (e.g. like polymer electronics) you can completely change this production platform (e.g. printing electronics with inkjet printers).

Here, another shortcoming of the report could be identified: The **report was concentrated on short-term applications** or applications available on the market. However, the **potential** for reducing or even avoiding hazardous chemicals would be revealed by looking a bit further and **considering the change of a whole technology platform** and not only the substitution of one chemical by a nanomaterial.

Dr. Luther thought that from the **methodological** point of view it would be a good idea to **approach the subject from the side of the toxic chemicals**: What substances are hazardous? Where are the big problems? In a next step, one could look where NT might contribute to replace processes. In this study it was the other way round.

Remarks concerning the evaluation criterion 'completeness'

NT is such a broad field that you cannot expect complete coverage. Maybe if one takes a closer look at the activities of the US Environmental Protection Agency (EPA) which had initiated many projects in the area of environmental issues in the context of NT, one can find some more examples related to the project subject.

(Remark of the author: This was done and added to the final version of the report.)

Remarks concerning the evaluation criterion 'relevance'

Coatings and surface modifications are the areas of major importance.

Also the **controlled release of pesticides is an important issue as well as catalysts** as mentioned several times before.

In relation to 'relevance', Dr. Luther addressed another **shortcoming** of the report: the **lack of quantitative data**. As a prime example he mentioned a study of the chemical industry in America that investigated the top fifty chemicals produced with catalysts. They identified 18 out of fifty applications of nanomaterials where NT could significantly contribute to avoiding by-products and saving energy, etc. With these catalysts, several billion US dollar can be saved per year by using nanomaterials.

Dr. Monica Ratoi

In general, Dr. Ratoi had a **positive view on the report**. She expected that it was not easy to go through such a vast amount of information and summarise the results so clearly.

Remarks concerning the evaluation criterion 'completeness'

Dr. Ratoi mentioned a few points that could have been included in the report. That is, a bit **more** could have been said **concerning drug delivery** and **diagnostics** and the use of NT in **cosmetics** as well as in energy. There is a huge potential of NPs in saving energy. This should be added.

Remarks concerning the evaluation criterion 'relevance'

To answer the question of **which kind of applications** are the **most promising** in terms of avoiding or substituting hazardous chemicals **still requires a lot of work.**

For instance, surface active layers have to be individually assessed for each application and each material.

Remarks concerning the evaluation criterion 'awareness'

Dr. Ratoi considered it **necessary to foster research on this subject**. At the same time, she recommended being careful **not to over-amplify the nano issue**. Future research should rather focus on the application of new chemicals and materials in unfamiliar areas.

In her last point she emphasised that **at present the exchange of ideas and concepts between academic scientists and industrial technologists was not very good**. There is quite a large deficiency in this field. Moreover, industrialists are rather used to working in large interdisciplinary teams which are actually needed in the field of NT, while academics usually still work in greater isolation. This is a pity, because there is a lot of very good research going on in the academic field which could be applied in industry.

Prof. Armin Reller

In his comment, Prof. Reller focused on a specific characteristic of the relation between chemistry and NT. **What do we expect by nanomaterials?** The answer is to **replace chemical functions of materials by physical functions based on shape and size** (see list of functionalities in appendix 10.2)**.**

Prof. Reller drew attention to the fact that the **present use of materials is irreversible.** This is a **huge problem if the materials are rare**. He illustrated this with the help of an example: A catalyst used in vehicles is platinum. When looking at the life cycle of platinum, we first realise that there are only four mines in the world.

Second, we realise that the platinum is released from the exhaust system of the vehicles. The platinum is mobilised and distributed. This is an example where the function is ok, the application is ok, but we have to be careful about the mobility of the material. We have to distinguish between mobile materials and immobile materials. As long as we can control the trajectories we are on the safe side. However, if the materials and particles are distributed we are faced with two main problems. First, we loose them, and second, they can have detrimental side-effects on the environment.

If we want the Chinese to use catalyst for their cars, the demand to develop substitutes for platinum will increase, simply because platinum resources are limited.

Therefore, the **replacement of platinum by ceramic is an important and challenging issue**. When we have distributed materials on earth, we can no longer benefit from them.

Against this background, substitution will be very important in the future from a quite different point of view as pointed out by Prof. Reller: the **need for substitution of rare materials** due to increasing demand and declining resources.

Consequently, we have to consider substitution of functions as the most important application of NT. This is also related to the **problem of classification of nanomaterials**. We cannot only talk about Ti or Pt as substances but we **have to give an idea of their shape and their function** and effects.

Lastly, he expressed his agreement with Mrs Ratoi and emphasised the **necessity of combining the knowledge of applied sciences and industrial science**. Therefore, he considered it very useful to have this type of meetings to exchange ideas and knowledge, but also to keep in mind the general idea of taking care of sustainable use of materials.

10.1.3 Discussion

At the beginning it was noted that the term ‘chemical substitution’ is quite specific. On the other hand in the report it was argued that the meaning of substitution in relation to NT must have a broader meaning. The question is: **How broad should the meaning of substitution be interpreted without losing the focus of this study.**

Prof. Reller suggested **going for a notion of substitution as substitution of functions**. At present our concepts are dominated by properties which we assign to substances. But in NT properties are less determined by chemical properties then by size and shape.

Prof. Welland highlighted that this **study got its value from its specific focus**. By broadening the notion too much the study would encompass every thing and would lose its informational benefit.

Indeed the crucial point behind this project was the idea that a benign substance acting in a nanotechnological way at a molecular level can replace toxic substance, Mr. Harbour, the initiator of this STOA-project commented.

Dr. Santillo pointed out that looking at potential benefit is not possible without having in mind possible risks. Both issues went together. **The assessment of the substitute is essential otherwise the attempt is pointless**. Concerning the question of gathering quantitative data he commented that both approaches are useful: a broad overview and specific case studies.

At present he thought that **detailed case studies are really needed** to bring the discussion down to earth. On the other hand he doubted that the outcome of one specific case study can be transferred directly to other applications of NT.

In line with this Prof. Welland argued, that it is inevitable to gather valid data for decisions. **Life cycle assessment seems to be difficult and tedious work but it is necessary to get quantitative data** for decisions.

Dr. Byrne raised the question, if there is a difference to **green chemistry**. He had the impression that NT in the sense of this project is directly in the line of the concepts of green chemistry.

Green chemistry was a **successful approach** especially in **raising attention to specific problems**, Prof Reller pronounced. In NT there is a lack of awareness of potential problems. This could be observed by looking at the **un-reflected way small enterprises tried to benefit from the term NT**. This behaviour can lead to a backlash, if **disappointment** arises and leads to a **bad image of NT**. Prof. Reller suggested, that **these problems could be reduced if a common declaration on nanomaterials is worked out.**

Prof Welland responded that **green chemistry does not** substantially **consider NT**. But a powerful tool in this field is the organisation of workshops bringing together researchers and industry for a focused discussion on related topics. This could be a model for NT. It would be promising to ask relevant actors in the field of green chemistry what they think about NT.

Prof. Leggett indicated that the **issues addressed in this study could not all be ascribed to green chemistry.**

Prof. Reller has the experience that the **green chemistry community does have NT in mind**. But he went back to the difference between chemical properties and properties based on size and shape. It would be promising if we could replace hazardous chemicals by nanomaterial which provides the same function by its size or shape instead of its chemical properties.

Dr. Ratoi would like to focus on the fact that there is a **difference** of the properties of **pure NP** in contrast to those after they have been **released to environment**. They will agglomerate, will adhere to other particles and surfaces and will change their properties. Especially she questioned in which way they will appear inside of human body.

Concerning the case of asbestos, Dr. Hoskins underlined that the material composition of these kinds of fibres did not influence their toxicity. Their toxicity is only determined by their shape, size and rigidity.

Concerning the **list of functionalities NT** can provide (see appendix 10.2) Dr. Welland pointed out that the increased efficiency of catalysts is mainly due to the **increased surface.** But this is **not a property which is related specifically to the nanometre size**. It is continuously scaleable. The interesting phenomenon arises from effects which are inextricably linked with the size, shape or surface effects of the materials.

Concerning this issue Mr. Harbour would like to know, **if it is possible to classify materials as those which really have size effects and those which just show continuous scaling effects.** The crucial question is, if there is material which even has a different functionality but with which one can achieve the same objective.

The question is if there is a step change in thinking in complete different terms of functionality, a rethinking of material performance but achieving the same effects. This question could not be answered during the workshop and is still open.

10.1.4 Summary

In summary, **all experts agreed** that the **results presented in the report are rather comprehensive and well summarised**, even though in the field of nanotechnology a complete overview of all possible approaches can never be given.

In addition, it was common sense that **further evaluation** of the potential of NT in chemical substitution **needs a detailed analysis of selected examples** for balancing benefits versus problems. Therefore, parallel to the broad approach as it was applied in the project, it is **necessary to perform Life Cycle Analysis (LCA) of specific concepts** of substitution to get valid data for legitimating action. Well based data were considered from all participants of the workshop as important and crucial.

Astonishingly, the discussion very quickly turned into the direction that NT is perceived as risk rather than as benefit. Especially the focus of the project – the substitution of hazardous substances by NT – has often been ignored.

Another approach to **estimate the potential of NT in chemical substitution** which was discussed **starts from the functionalities** of both the nanotechnological concepts and the chemical substances. Even though **all experts agreed that this approach is worth following**, it is **not clear to which extent this will be realisable**.

A **major challenge** which was seen in the context of evaluation of NT for chemical substitution is the **evaluation of the impact of NT** and especially of nanoparticles on human health and environment. Here, in contrast to the conventional evaluation of new substances, **shape and surface effects have to be taken into account**. As an **important step** in this direction **an international nano-material declaration** was considered by the experts.

In his concluding remarks, Malcolm Harbour, the initiator of this project, expressed the view that the preliminary results of the project and the discussion of the experts showed that the project addressed an important issue which should be followed-up.

10.2 List of functionalities of NT

Input *(List of functionalities)* for the

'Validation Workshop on Nanotechnology for Chemical Substitution'

Tuesday, September 19th

14.00 – 18.00 p.m.

European Parliament, Brussels, PHS 7C050

Identification of further applications of NT for substitution

Since most NTs are at an early stage of development and due to the fact that NT is an enabling technology there are only a few publications and only very few research projects directly addressing the substitution of hazardous substances by NT. Therefore, the challenge of this project is to estimate a potential that has not yet been explored yet.

A way how to cope with this challenge in a systematic manner is to approaches the issue from two perspectives. On the one hand side there is a tremendous number of hazardous substances where substitution would be desirable. On the other hand, there is huge variety of NTs. Each of them might lead to different applications and each application might be assigned to different stages of development. The key question is: How is it possible to find a connection between a hazardous substance and a particular NT which could facilitate the substitution of this substance? A first approach to answer this question is given the connection of both by their functionality.

This means, on the one hand, that NT provides several functionalities. These functionalities could be compared with the functionalities hazardous chemical substances provides. Thus the question of which hazardous substances could be substituted by which NT is reduced to the question of which functionality of the hazardous substance could be provided by which NT.

I would like to start with this systematic connection by filing a list of functionalities NT could provide. A list of most relevant hazardous substances which should be substituted and their functionalities would be the second step.

I do not claim that the following list is comprehensive. It is only an attempt to structure the various functionalities which are the reason why the field of application of NT is so broad and NT is expected to be so important.

In the first row the functionalities are listed. Both further rows (material, application) are of less importance and should only regard as examples to clarify which kind of functionality in the first row is meant. To have a better differentiation the list is subdivided in to for categories: coatings, bulk material, particles and nano-systems.

While composing this list I realise that in most applications not one but the combination of different functionalities together are the crucial reason why a certain NT-based material or coating is more appropriate as conventional materials. Perhaps here we find the first weakness of the above mentioned approach, because the list is focused on single functions instead of sets of functionalities. Especially the last category, nano-systems, shows the difficulties how to identify for a certain nano technique its crucial functionality. The other weakness could be possibly found in the fact, that the functionalities are oriented on physical rather than on chemical properties. A question is, if we compare this list of functionalities with that one hazardous substances provide.

Coatings

Properties	***Materials (examples)***	***Applications(examples)***
enhanced reactivity	Metal carbide, carbide-oxides	substitute for Pt catalysis material
	nano scaled zeolites	catalysts, oxidation in cat ion exchanger, reduction of NOx, photo catalytic disintegration of organic compounds
selective reactivity		selective and specific catalyst
chemical stability / inertness		anti-corrosion, material withstanding aggressive agents
corrosion protection **and** tribology	DLC, carbon nitrides	hard drives
adjustable tribological properties, high hardness	carbides, nitrides, Oxides (Al2O3, SiO2, ZrO2, TiO2-nanoparticles), DLC	super hard coatings, reduction of friction, grease free bearings
high hardness on soft material	Oxides (SiO2)	mechanical protection layers on wood, paper, textiles
thermal insulation	aero gel	
thermal stability		
thermo insulating and high hardness		
thermo insulating and transparent		transparent thermal insulating fire doors
electric conductivity		
biocide coatings	polymers, oxides (SiO2)	anti fouling, disinfecting
biocompatible coatings	carbides, DLC, TiO2, Al2O3-Ca	inflammation reduction of implants (medical)
anti fog coating	polymers, tensides, oxides (TiO2)	
self cleaning/ anti adhesive	DLC-F, flouro-hydrocarbons, ZrO2	anti fouling, anti-graffiti, reduction of cleaning agents, windows
	TiO2, ZnO nanoparticles	Self-cleaning surface by photo catalytic disintegration of dirt
adjustable adhesion		gluing, synthetic gecko foot-hair, micro/nano-structures as dry adhesives
adjustable transparency/reflexivity	meso-porous Si,	antireflexion coatings, Transparent UV-protection (sunscreen, in materials and coatings), optical filter
transparent **and** conductive	ITO (ZnO...), polymers (PMMA), CNT	antistatic, IR-absorbance

Continued overleaf

Table cont.

Properties	***Materials (examples)***	***Applications(examples)***
self adjusting transparency	polymers, oxide (WO3)	Sunglasses changing their transparency depending on brightness
enhanced brightness	TiO2, silicates	paper industry, substitute for bleaching agents
coloring/color effects	nano pigments	Textiles, paints etc.
separation/selective filtration	polymers nano-composites	membranes in fuel cells (proton exchange membrane, PEM)
	carbon nanotubes (CNT)	nano-filtration
diffusion barriers	Ti-nitrides, oxides (SiO2, TiO2...)	chip industry, PET bottles, food packaging, tennis balls etc.
ultra flat surfaces	abrasives, TiO2-nanoparticles	chemical-mechanical polishing (CMP) e.g. for hard discs, microelectronics, ultra high precision optics
coatings with combined properties		
smart coatings		e.g. sunglasses changing their transparency depending on brightness, monitoring of substances by changing of colour
coatings which could switch between different properties (optical, adhesion...) (triggered by electrical, magnetic, chemical, thermal influences)		
self-healing coatings	ormocere	

Bulk material

Properties	***Materials (examples)***	***Applications (examples)***
thermal conductivity	CNT, carbon nanoparticles as fillers	chip packaging
electric properties (conductivity, insulating, dielectrics)	CNT, carbon nanoparticles as fillers, PEO-ZrO2 nanocomposite	conductive polymers, polymer electrolytes for batteries, ionic conductivity of polymer electrolytes
adjustable optical properties (transparency, high dielectric constants, specific diffraction properties)	photonic crystals, oxides (ZrO2, Ta2O5, (Ba,Sr)TiO3)	opto-electronics, LASER-diodes etc.
colour	Ag nanoparticle	adjusting of colour of glass, labeling of products or even substances
hardness	nano composites/ceramics	
stiffness		
avoid to be brittle	nano composites/ceramics	
chemical stability / inertness		anti-corrosion
thermal insulation	aero gels	fire resistance **and** transparent
thermal stability	nano composites/ceramics	
super plasticity	nano composites/ceramics	
improvement of various kinds of mechanical properties	Al and Mg alloys, Ti and Ti alloys with nm-grain size	
biocompatibility		tissue engineering
optimising abrasion, friction and adhesion	Carbon black	tyres, UV-protection
increased tensile strength	CNT, artificial silk	fibres with enhanced properties
switch-able materials	polymers	organic semiconductor
self-healing materials		
surface to volume ratio	nano porous material, CNT, metal hydrides (Mg)	enhancing surface to volume ratio for higher efficiency of catalytic reactions, batteries, super capacitors, hydrogen (butane, methane) storage
high diffusion rates for hydrogen and increased solubility limits	metal hydrides (Mg)	hydrogen (butane, methane) storage
combination of different properties like thermo insulating and high hardness		
flame retardant, light weight, stable	nanocomposite from inorganic clays and organic polymers	plastics with enhanced performance
low density, high strength and good corrosion resistance	Al-based bulk nanomaterials, Magnesium alloys	
corrosion resistance is biocompatible, with low density and good mechanical properties	Ti-based alloys	

Particles

Properties	***Materials (examples)***	***Applications (examples)***
selective reactivity	Fe(bimetal)-nanoparticles, MgO	cleaning by catalytic reduction of organic/inorganic contamination (e.g. Per chlorates chromate VI)
enhanced reactivity	ceroxide	catalyst for enhance the efficiency of the combustion process in engines
electron acceptor	fullerenes	solar cells
Solubility		NP as dispersion agents
Fluidity		colloidal systems
reducing friction	MoS_2-fullerenes, metal nanoparticles (Cu)	additives for lubricants
changing specific properties (of the bulk material or in handling properties)	oxides (SiO_2)	aggregates for construction materials (concrete)
Absorption	cyclodextrine	ordure reducing textiles
antibacterial	Ag nanoparticles	
		cleaning of water by initiated precipitation
switch able fluids	ferrorfluids	
Abrasives	TiO_2	chemical-mechanical polishing (CMP)
	CNT, carbon fillers	ion exchanger, desalination
	dendrites	
optical properties/colour	nano pigments	cosmetic products
	unorganic nanoparticles (TiO_2, CdS...)	medical tracer, contrast agents, optical application
	Carbon black	
	nano layered silicates	
	layered carbon nano particles	
		functionalised nanoparticles (by coatings)
		labeling of products or even substances
biodegradability		drug carrier/drug delivery system
	Fe_3O_4 nanoparticles	hyper term therapy

Nano-Systems

Properties	***Applications (examples)***
high sensitivity to specific agents	sensors, bio-sensors
new generation of computing and memory performance	spintronics
	Molecular electronics, DNA-computing
Separation of chemicals on molecular level	ultra fine filter systems
new generation of computing and display technique	Microelectronic, LED, OLED
new generation of computing	quantum computing
new display technique	CNT-displays, flexible displays
ubiquous analytic	lab on a chip
	bio-molecular engines
new generation of computing and memory performance	contribute to further miniaturisation in microelectronics
	micro-mechanical systems
	Integration of mechanical electrical and sensorial elements
	analytics (measurement in nm precision)

10.3 Interviews

Due to the fact that research in the field of NT for chemical substitution has not yet been established, interviews are as important to explore the potential of NT in chemical substitution as literature research, or even more important. The aim of the interviews was to explore the field and to identify relevant questions which have to be addressed during this project. The interviews allowed identifying research groups and industrial development activities as well as individual researchers. Nevertheless, the quality and quantity of the outcome of the interviews shows a great variety. This is due to the fact that the contacted researchers are involved in the subject of the project with different intensity. Most of them are specialised in a certain research field, but the application of NT for chemical substitution needs an interdisciplinary approach. They often did not consider themselves as experts in the sense of the project, even though being experts in a certain field of NT and mostly also in chemistry, surface physics, biology, and even having experience in the field of substitution.

The intention of the minutes of the interviews performed in the framework of this project is to document the estimations and assessments of the interviewed experts concerning scope, concept and subject of the project. Therefore, the minutes of the interviews do only contain the main statements in a summarised manner.

The interviews were performed at the beginning of the project. Consequently, the minutes encompass all suggestions of interviewees, even though not all of them are in the line of the project and therefore not all of them have been considered. The issues and examples discussed in the interviews are incorporated in the final report. Some examples mentioned in the interviews are not listed in the chapter on the project results, because the relation to NT is not clear or because they fall out of the range of substitution as considered in this project.

Interviewee:

A. von Gleich, M. Steinfeld	08.02.2006, Bremen,	p. 51
D. Oertel	20.02.2006, (phone),	p. 55
A. Reller, M. Erlemann	21.02.2006, Augsburg,	p. 57
W. Döring	23.02.2006, (phone),	p. 61
M. Pridöhl	13.03.2006, Karlsruhe,	p. 62
Q. Zhao	18.05.2006, (phone),	p. 65
B. Watermann	30.05.2006, (phone),	p. 66
B. Liedberg	30.05.2006, (phone),	p. 67
G. Bachmann, W. Luther	13.06.2006, Düsseldorf,	p. 68
E. Keßenich	19.06.2006, (phone),	p. 71
M. Fichtner	06.07.2006, Karlsruhe,	p. 73

Interview with M. Steinfeldt and A. von Gleich, 8 February 2006, Bremen

Prof. Dr. Arnim von Gleich

University of Bremen

Forschungszentrum Nachhaltigkeit

Enrique-Schmidt-Straße 7

D-28359 Bremen

Mail address:

Postfach 33 04 40, D-28334 Bremen

e-mail: gleich@uni-bremen.de

Expertise:

Coordinator of the research field: *"Nachhaltigkeitsorientierte Technikentwicklung und Technikbewertung"* at the University of Bremen.

Long experience in the field of chemical substitution (participant of the Enquete Commission *"Schutz des Menschen und der Umwelt – Bewertungskriterien und Perspektiven für umweltverträgliche Stoffkreisläufe in der Industriegesellschaft."*

Co-worker in the project SubChem and co-author of the book "*Hazardous Chemicals in Products and Processes"* (Ahrens 2006).

Working since several years in the field of environmental impact of NT.

Co-author of the report *"Nachhaltigkeitseffekte durch Herstellung und Anwendung nanotechnologischer Produkte."*

Michael Steinfeldt

e-mail: michael@familie-steinfeldt.de

Expertise:

Co-author of the report *"Nachhaltigkeitseffekte durch Herstellung und Anwendung nanotechnologischer Produkte."*

Problem of distinguishing NT from chemistry

The interviewees acknowledged that the term NT is vague. For example, chemists of colloidal chemistry assign themselves to chemistry rather than to NT. But they think that this is not a severe problem. One knows what is meant by NT while one is talking about it.

Related to NT, Mr. Steinfeldt has the impression that chemistry of biomolecules and microsystems (microreactors) will play an important role in the future, while Prof. von Gleich expects the main impact of NT in terms of chemistry in the field of self-organisation and in the fact that NT will lead to co-operation between different disciplines.

Existing approaches

In the field of catalysis, there are some examples of realised substitution, e.g. the substitution of the heavy metal containing catalyst by another one in the synthesis of styrene (see case study 2 in Steinfeldt 2004).

Clarifying the term "hazardous substances"

In the discussion during the interview it was made clear that the hazardous potential of nanoparticles has not been assessed yet, even though there are several projects concerning this issue (see footnote on page 41). It might turn out that nanoparticles are as hazardous as the substances to be substituted. Therefore, a case-by-case analysis is required for each case of substitution considered.

Several characteristics of the substance have to be considered when assessing the hazardous potential of a substance. In terms of environmental issues, the persistence of the chemical in the environment is crucial. Concerning safety at work, the chemicals are assessed by their carcinogenic, mutagenic potential, and their toxicity to reproduction (CMR).

In Germany, the handling of hazardous substances is regulated by “Technische Regeln für Gefahrenstoffe” (TRGS). They include a detailed description of hazardous substances. Furthermore, the hazardous potential of chemicals is listed in the so-called “MAK-Liste” (Maximale Arbeitsplatzkonzentration – maximum workplace concentration).

Besides these kinds of hazardous substances there are substances that are not toxic but hazardous due to their effect on the environment because of their potential for climate change, such as CO2 and chlorofluorocarbon (CFC). These substances are also called Rio-substances. The name is related to the UN Conference on Environment and Development (UNCED) in Rio de Janeiro 1992, where these substances were subject of negotiations related to the Agenda 21.

General understanding of the role of halogens in chemistry

Halogens are fluorine, chlorine, bromine, and iodine.

Halogenated organic compounds often cause environmental and health problems. Dioxins are only one example. Dioxins consist of benzene rings functionalised by a chlorine group.

A halogen used in flame retardants is bromine.

Some notes to the background of the role of halogens in chemistry:

Benzenes are very reactive. With the help of chlorine this reactivity could be suppressed. Thus, it is possible to produce polymers with long chains and increased durability. But on the other hand, this longevity leads to persistence in the environment. The importance of chlorine for chemistry becomes obvious if one considers that it has been used since 1869 for the synthesis of aniline by the BASF (Badische Anilin- und Soda-Fabrik). The purpose of chlorine was to control the velocity of reactions. It is used to increase the reactivity in the process. Also in the semiconductor industry chlorine plays an important role. It is used for the extraction of silicon (chlorine silane). Furthermore, chlorine is used in the metal industry.

Accomplishment

During the interview, Mr. Steinfeld and Prof. von Gleich recommended that the study should start with well-known hazardous substances. Based on these chemicals a prioritisation could be developed, e.g. flame retardants (halogenated organic compounds in general) are of particular importance.

According to their advice, a further step in the study could be the investigation of the context of use. Here, a systematisation in open (e.g. pesticides), semi-open (e.g. coatings, lubricants), and closed (e.g. certain production processes, dry cleaner) systems would be useful.

Instead of listing cases of substitution realised through NT, Mr. Steinfeld and Prof. von Gleich suggested that it would be more desirable to construct a matrix where functions of the hazardous substances are connected with functions and applications of NT.

Possible contexts of use

The following fields of application, where substitution by NT might reduce hazardous substances, are promising:

- coatings
- cooling liquids
- lubricants
- flame retardants
- pigments

Pigments often contain heavy metals:

- yellow → Cd
- red → Cd
- green → Cu, Zn

It would be useful to have only one substance to produce different colours depending on its size (like gold particles which are used for colouring glass or CdS particles which emit fluorescent light of different colour depending on their size).

Another conceivable application is the use of functionalised nanoparticles as delivery system for pesticides.

In the field of washing and cleaning agents, substitution on the basis of NT is conceivable, too, e.g. tanning agents are a problem due to their chromium content.

The disposal of flame retardants in an environmentally friendly way is not easy because they have to be re-extracted from the plastics. The problem with flame retardants is that dioxin is produced in case of burning. In the field of fire protection, there are already applications of NT, e.g. highly porous transparent heat resistant insulations.

Functions of NT

- In the field of catalysis, NT can help to find highly selective and specific catalysts.
- Solubility could be changed by adding nanoparticles or by covering the walls of the reactor with functional coatings. This is especially important for the concepts of microreactors.
- Reactivity could be changed (nanoparticles as catalyst).
- Transitions in phase diagrams could be changed by decreasing the size of the particles, e.g. for changing the properties of ceramics or metals.
- Optical properties (colour) might be changed by variation of the particle size or structure.
- Magnetic and electronic properties could by adjusted.

Further source of information

The SubChem project (Ahrens 2006).

The project on flame retardants initiated by the Umweltbundesamt (UBA, Germany) in 2000.

(Title: *"Erarbeitung von Bewertungsgrundlagen zur Substitution umweltrelevanter Flammschutzmittel"* Report No. UBA-FB 000171/1)

The Deutsche Bundesstiftung Umwelt (DBU) and the UBA has financed some projects on antifouling (http://www.limnomar.de/conthtml/ger/mp2_prevprojects_af.htm):

Title: *"Untersuchungen zu den Haftmechanismen von Balanus improvisus (Darwin) auf nicht-toxischen Antihaftbeschichtungen"*

Title: *"Weiterentwicklung der Produktinnovation Chitosan für den Bereich der ökologischen Naturfarben (Lacke, Lasuren und Sportbootantifouling)"*

Title: *"Machbarkeitsstudie für neue Umweltzeichen in Anlehnung an*

ISO 14024 für biozidfreie Antifouling-Produkte" (UBA RAL/UZ project)

Contact person mentioned by the interviewees

Participants of the working group on nanomaterials of DECHEMA

(Head Dr. Prof. Rüdiger Iden [BASF]), e.g. Rüdiger Iden, Martin Möller (RWTH-Aachen).

Further contact persons:

Dr. Andreas Kicherer (BASF AG),

Dr. Franz Saykowski (Bayer AG),

Dr. Vollmerhaus (Henkel KGaA),

Marcus Wagner (Wacker-Chemie GmbH),

Dr. Stefan Spiekermann (SusTech),

Karl-Otto Henseling (UBA).

Interview with D. Oertel by phone, 20 February 2006

Dr. Dagmar Oertel

Büro für Technikfolgen-Abschätzung beim Deutschen Bundestag (TAB)

(Office of Technology Assessment at the German Parliament)

Neue Schönhauser Straße 10

D-10178 Berlin

Expertise:

PhD in chemistry.

Long experience in the field of Technology Assessment

(since 1996 research officer at the Office of Technology Assessment at the German Parliament).

Co-author of:

Paschen, H.; Coenen, C.; Fleischer, T.; Grünwald, R.; Oertel, D.; Revermann, C.:

"Nanotechnologie in Forschung, Entwicklung, Anwendung. Stand und Perspektiven".

Springer Berlin (2004).

Two main questions have to be considered:

What are hazardous substances?

How is it possible to distinguish between NT, Biology, and Chemistry?

Background:

Bionics considers NT as a rival "label". Bionicists are usually not very interested in relating their work to NT. They feel occupied by NT. A prominent example is the Lotus effect. It stems from bionics but was then taken as a vivid and effective example for NT.

Similarities exist in so far as the subjects of bionics are often also regular structures in the scale of nm. They are developed, as partly in NT, with a bottom-up approach. However, there is also a tendency to merge the fields of nano and bionics: nanobionics.

Antifouling paints are a thematic complex of bionics mainly concerned with investigating the growth of algae, barnacles, and other biotic systems.

The main scientific subject underlying antifouling paints are the conditions of adhesion and non-adhesion.

Dr. Oertel mentioned some areas where antifouling plays a role:

- Ship hulls (flow resistance, ballast, cleaning costs)
- Oceanic measuring instruments
- Locks, pumps, and other mechanical machines for marine application
- Pipes for water/liquid supply (laboratories, clean rooms)
- Inner walls of reactors, water filter systems, etc.

General discussion of the project approach:

According to Dr. Oertel, it is not useful to approach the subject from the perspective of hazardous substances. First, the following issues need to be clarified: What is meant by substitution, what is NT, and how can both be linked together? The most important questions in this context must be identified, structured and explained in the final report. This will be the main part of the project. Subsequently, a current state analysis is required. This analysis should include the field of remediation.

Furthermore, the political classification should be performed, particularly in relation to REACH. How are hazardous substances identified within REACH? Here, the amount of material used plays an important role.

Special attention should be given to the complex of substitution. A successful substitution is not only characterised by the identification of an adequate substitute. There are other reasons why some substitution processes are successful and others not. A key question is whether the substitute, e.g. nanomaterial, is less harmful than the material used at present (example: chlorofluorocarbon [CFC]).

To clarify the notion of substitution in the field of NT, the following examples are useful: self-cleaning surfaces, biocide coatings (for surgery tools, operating rooms), functional textiles used in sports.

An issue Dr. Oertel suggested to consider is the distinction between process and product.

Often, the requirements and regulations concerning the conditions of production are so sophisticated that the handling of hazardous substances meanwhile hardly presents a problem in this area. An example is chemical cleaning. Today, the chemical cleaning systems are closed and the requirements are high. The solvents, that have previously caused problems, are hardly used anymore. Today, the textiles are easier to clean, e.g. with water, although being made of synthetic fibres.

Problematic, however, is the user side. This applies e.g. to solvents.

It is difficult to find criteria which allow to exclude some chemical fields and concentrate on others. For example it might be argued that the function of chemicals in flame retardants is performed by the binding of the molecules and therefore could not be fulfilled by nanoparticles. But this is not true. It cannot be categorically excluded that flame retardants might be substituted by nanomaterials. For instance, it is perceivable that nanoparticles might also lead to an increase in ignition temperature. Moreover, it cannot be excluded that nanotechnological coatings might allow avoiding the use of common flame retardants. The same is valid for flexibiliser, which is an important topic in the field of substitution.

Contact person mentioned by the interviewee

Expert in research on antifouling at the FH Bremen:

Mrs. Prof. Kesel

FB Bionik

0421/59052731

www.bionik-hs.bremen.de

Interview with A. Reller und M. Erlemann, 21 February 2006, Augsburg

Professor Dr. Armin Reller

Universität Augsburg

Lehrstuhl für Festkörperchemie

Universitätsstrasse 1

D-86159 Augsburg

e-mail: armin.reller@physik.uni-augsburg.de

Expertise:

Head of the department of solid state chemistry of the Institute of Physics at University of Augsburg, Germany.

Member of the board of directors of Wissenschaftszentrum Umwelt (WZU), Augsburg, Germany.

Editor of *"Gaia"* and *"Progress in Solid State Chemistry."*

Martina Erlemann

Wissenschaftszentrum Umwelt

Building: innocube

Universitätsstrasse 1a

D-86159 Augsburg

e-mail: erlemann@wzu.uni-augsburg.de

What is special about NT?

First, NT is defined by a value of size – it is a geometric dimension. It thus crosses the established disciplines. This is a chance, because it could help to break with disciplinary habits of thought and could help searching for innovative solutions.

Here, the main starting point is a turn to a concept of functionality. Rather than focussing on the substances or their composition, in the future one should concentrate on the functionalities a chemical product or composition could provide. We have to pass from the history of materials to the history of functions (compare appendix 10.2).

Concerning NT from the perspective of chemistry it is new that the substance is no longer in the foreground but the geometric form. We are learning that the form of the material is related to its effects.

A further different is that in conventional chemistry, the strong chemical bonds play the decisive role, while in NT the focus is rather on the weak Van der Waals bonds. This is similar with surfaces science. Here, too, the weak bonds play the decisive role.

In addition, NT helps to develop a new form of material efficiency.

However, concerning the environment nanomaterials, e.g. nanoparticles, are linked to an enormous mobility. The mobilisation of metals is a particular danger. The history of materials, the Life Cycle Assessment (LCA), is gaining importance. An example is the platinum released from catalysts. Similarly, it is conceivable that adding ceroxide to the fuel would mean the fine distribution of another rare metal into the environment.

In this context, we can observe the general trend that we exploit rare elements as natural resources occurring in relatively high concentrations and distribute them irreversibly to the earth’s surface. Besides the related unforeseeable consequences, the exploitation conditions are extremely problematic, in particular of platinum.

Because of the characteristic of NT, which is that the form or structure is more decisive than the substance, it will be more difficult to identify hazards. The causal connections do not fit into the dominant analytical pattern. At present, chemistry is good at analysing the composition which can be determined up to the ng range, but there are no instruments to determine the form and its related effects. However, this can be decisive as the example of asbestos shows.

Objective

The aim is to substitute problematic chemicals by simple but complexly structured substances that can assume the function of the chemicals. Ideally, this would be substances that already occur in large quantities in nature and that are inherently harmless, e.g. SiO2, TiO2.

Subject: Catalysts

The development of catalysts has always been in the nanoscale. Here, the focus is on developing a specific design of the catalysts.

Surfaces, mostly of metals, serve as catalysts in heterogeneous catalysis. This is related to the fact that surfaces have another work function, which means another electrochemical potential, due to the disordered crystal structure at the surface. The chemical potential can also be changed by the surface topology. The aim is to increase the selectivity or stereo-selectivity of the catalytic material. However, topology is rather about the fact that only certain molecules, the reacting agents, reach the surface and “see” the changed work function while the other molecules are kept away from it. Furthermore, the reacting agents must meet at the surface. The background is that just feeding the reactants into the reactor is not enough. This is because besides them, there are too many other molecules (from the solvent or the transportation gas in CVD[56] systems) in the reactor, so that the probability of the reactants meeting each other is too low.

Therefore, other approaches are under investigation. For example, one approach is to use materials with a specific topology, so that only the intended reactants are able to meet at the surface of the material. The principle is similar to enzymes which are also characterised by their specificity. This approach is called template chemistry, and zeolites are an example of that kind of materials. In general, for template chemistry one searches for mesoporous materials with a pore size through which only certain molecules, the reactants, can pass (practically, this means that the reaction takes place under high-pressure conditions).

An important point is to realise that chemical processes take place in the space and that they are dynamical. At present, this can not be controlled in practice and even not modelled theoretically.

[56] CVD Chemical Vapour Deposition, a process technology common in NT.

Nevertheless, simulation has been developed so far, that in certain cases pre-selection is performed in pharmaceutical industry via simulation (pre-screening). Here, it is possible to consider the geometry of the site where the reaction takes place, but e.g. not the influence of the water molecules in the solution.

Discussion of hazardous substances and their substitution possibilities

- *Biocide coatings*

  One field of application of nanomaterials are biocide coatings. Silver nanoparticles are widely used for this purpose. However, the biocide effect is less related to the topographic properties of the particle, but the particles serve as source for silver ions entering the solution (see for example Mikropur).

  In a similar way, Cu is used as biocide, e.g. as contraceptive loop.

- *Flame retardants*

  Bromine is used for absorption of O2, which leads to reaction inhibition. A similar result can be achieved with certain NP. If substances are mixed with MgO or TiO2 particles, the oxygen accumulates during combustion and forms an oxide layer around the residues of the respective material. An oxide layer is formed, similar to the anti-corrosion layer with the oxidation of aluminium. This oxide layer prevents further (exothermal) reaction.

- *Softeners*
  The function of softeners is to increase the elasticity of the cross-links between the polymer chains. If these are firmly linked together, the material becomes brittle. It is conceivable that nanotechnology could be used to provide such effects; similar effects of NP are presently used for car tyres.

- *Chromium*
  Chromium is used in a similar way as chlorine to trigger a specific oxidation (bleaching). However, it is supposed not to affect the basic material, which in this case is leather. Chromium is used in tanning agents. In various oxidation stages (chromium IV, chromium III), chromium is toxic.

- *Chlorine*
  Chlorine is produced from common salt and is almost unlimitedly available in nature. Therefore, it is very cheap. It is used for the formation of radicals, as reaction accelerator or to start reactions. Other halogens are not as suitable for this. For example, reactions with iodine are very difficult to control.

  The use of chlorine is extremely manifold. On the one hand, it is used for oxidising, i.e. for bleaching in the paper industry (whether chlorine or chromium is used depends on the basic material). On the other hand, the Cl-C bindings are of the same strength as the C-O bindings. Compared to other halogen bindings like F-C the Cl-C binding is weaker. Therefore, bindings with fluorine are stable against oxidation. This is the reason for the inertness of chloroflourocarbon (CFC).

Fields of application of NT

An important field is the cleaning and detoxification of water.

A problem in filter technology is that the filters clog. However, they can be cleaned with a reverse wash system. Decisive in this respect is that the materials filtered out do not adhere to the filter material. This is less often the case with ceramics (Al2O3) since this material is rather inert. A coating based on NT can further reduce this adherence.

Furthermore, it is conceivable that the surface of the filter is coated with a catalyst. This would allow to combine filtering and transformation processes e.g. decomposition of the substances in the solution.

When using pesticides in agriculture, the main problem is the dosing; the pesticides themselves are very effective. The problem is that due to the weather (rain, wind) they are washed out of the soil too quickly and thus leave their site of action.

It is conceivable that the dosing could be improved with NT, similar to drug delivery systems which are investigated for medical applications. For example, it might be possible to encapsulate pesticides in nanocapsules so that they continuously release their agent.

It is also conceivable that the specifity of toxins could be increased with NT. However, all in all this does not seem to be a realistic and practical field of application because of the costs involved.

General problems of substitution:

Production processes must be changed, which implies additional costs.

In general, the question is whether the benefit of nanotechnology can offset the costs. If the substitution by NT is primarily motivated by ecological reasons, the question is how this can be financed and integrated into the market.

It also has to be considered that due to globalisation high environmental requirements will lead to a transfer of “dirty” chemistry to other countries. In terms of NT, the same situation will develop as we have already discussed with platinum: platinum is mined under catastrophic conditions in less developed countries in order to clean our air here with catalysts.

Conclusion:

Are there criteria for deciding when and when not to substitute toxic chemical substances by NT?

There are no general or comprehensive criteria concerning this matter. However, there are signs indicating whether a substance or a process can be substituted or whether this is unlikely. Substitution becomes difficult if:

- the reaction centres are distributed (at the molecular level like tanning with chromium compounds),
- processes are concerned where the whole material is transformed.

Since the chemical processes depend on the architecture, the space and motion and the dynamics, these factors must be considered in the analysis of the substitution potential.

Contact person mentioned by the interviewee

The participants and speakers of the Matforum 2004, Augsburg, e.g.

Mr. Hunger (Bundesministerium für Bildung und Forschung – BMBF, Germany),

Mr. König (Daimler Chrysler)

Mr. Presting (Daimler Chrysler),

Viki Colvin (Center for Biological and Environmental Nanotechnology – CBEN, USA)

Relevant Journals:

Nanotoday (Elsevier)

www.nanotoday.de

Journals in the field of "Green Chemistry", e.g. *Chemosphere, Green Chemistry* or *Environmental Science and Technology.*

Interview with M. Döring by phone, 23 February 2006.

Prof. Dr. Manfred Döring

Head of the Department of Technical Catalysis and Polymer Additives at the Institute of Technical Chemistry (ITC-CPV), Forschungszentrum Karlsruhe

Hermann-von-Helmholtz-Platz 1

D-76344 Eggenstein-Leopoldshafen, Germany

e-mail: manfred.doering@itc-cpv.fzk.de

Expertise:

Research priority, among others, is the investigation of halogen-free flame retardants for polymers.

Flame retardants

In the field of flame retardants, nanoparticles (NP) do not play an important role. There are other solutions which are more useful. Nevertheless, NP are added to polymers, but for other complex purposes.

Halogenated flame retardants are attractive because they are cheap and can fulfil various functions at the same time. But there are already alternatives. And it has to be taken into account that not all halogenated flame retardants have the same hazardous potential. In addition, European regulations are currently strongly aimed at reducing the amount of halogenated flame retardants. In the USA, such regulations do not exist. Therefore, problems related to halogenated flame retardants will become more acute in the USA.

To conclude, from the technical point of view the problems with flame retardants are solved.

Interview with M. Pridöhl, 13 March 2006, Karlsruhe

Dr. Markus Pridöhl

Coordinator Nanotechnology

Advanced Nanomaterials,

Degussa AG, Hanau.

Chair DECHEMA/VCI-Arbeitskreis Responsible

Production and Use of Nanomaterials

e-mail: markus.pridoehl@degussa.com

Expertise:

Chair DECHEMA/VCI working group *"Responsible Production and Use of Nanomaterials."*

Hazardous substances

One approach to handle the problem of the huge number of hazardous substances and the problem of distinction between hazardous and less hazardous substances is the orientation towards the German catalogue on handling hazardous substances (TRGS, Technische Regeln für Gefahrstoffe). To concentrate on the top 100, especially on those marked with T+ (extraordinary toxic), should be more than sufficient for the first approach. Further distinction criteria are the mutagenic and carcinogenic potential and persistence.

A further step would be to look for products containing these substances and to identify potential NT to substitute these products or the functionality of the products. It does not make sense to concentrate on processes where toxic substances are used. For example, the pharmaceutical industry often uses highly toxic substances in the processes. But these processes are well-controlled and do not represent a risk.

At this point, a differentiation should be made between hazard and risk. A hazardous substance is not necessarily a risk. A hazardous substance represents a risk in case of potential exposition. A risk is the product of toxicity (hazard) and probability of exposition. For example, polyvinyl chloride (PVC) is not a hazardous substance. PVC only becomes a risk when burnt, because in this case dioxin is produced and released to the environment. In contrast to this, gasoline soot is exhausted during the combustion process. This represents a risk because it is toxic *and* is released. Therefore, its hazardous potential is acute.

Coatings

Degussa has finished a project last year. Objective of the project was to develop a self-cleaning coating with reduced adhesion on the basis of NT for ships and boots.

The lotus effect is realised at Degussa by SiO2 nanoparticles coated with a hydrophobic layer. In nature, the lotus effect results from a microstructure with a nanostructure on top. The main challenge for transparent applications is to guarantee the adhesion of the coating. In toilets these kinds of coatings are already used. The enterprise selling these products is Nanogate.

Another issue in respect of coatings and paints is the use of SiO2 nanoparticles aimed at reducing the overall thickness of the coating. In this way, material and energy can be saved. Detailed information on the amount of energy and material needed for each kg of resin can be found in Steinfeldt 2004.

Coatings can be used to reduce abrasion, e.g. in ball and floating bearings. This can reduce the use of lubricants and leads to reduced heavy metal release.

A problem with the use of coatings for various purposes on the basis of polymers is their instability under ultra-violet (UV) radiation. At present, organic molecules are used as UV absorbers. With inorganic materials like ZnO less material is needed; these kinds of coatings are also interesting for outdoor applications, such as wood sealing.

Catalysts

Due to higher selectivity, new catalysts can help to reduce the production of by-products. In case of NT, the field of interest is heterogenic catalysis, e.g. catalysts for cars.

Heterogenic catalysts have been at the nano-level right from the beginning. However, improved analytic tools will help to understand when, for example, desorption of H2 takes place at the surface of metal X and not of metal Y.

An important field of application are membranes combined with catalysts.

A catalyst which could be of great importance in the future is ceroxid. The idea is to incorporate ceroxid particles into the fuel so that they can act in the burning chamber of the engine. This would reduce the production of carbonised by-products like gasoline soot and facilitate the cleaning of the soot filters.

In general, catalysts are used to enable oxidation (reduction) at lower temperatures. These processes are described in all standard references. It is important, for example, for the synthesis of polyethylene.

Photocatalysts could be used to destroy organic compounds for self-cleaning or pathogenic germs for disinfection. The use of disinfectants in clinics could be reduced by the latter application.

Drug targeting

In the medical area, NT will play an important role in the field of drug targeting.

Gluing

A special application where NT could help to speed up processes is the addition of magnetic nanoparticles (ferrite) to heat up hardening adhesives. With the help of AC magnetic fields it is possible just to heat up the adhesive instead of heating the whole components. Degussa produces such kinds of particles. The product is called MagSilica® and is used by the enterprise Sustech.

NT for solar cells

An example not leading directly to the reduction or avoidance of hazardous chemicals are NT-based anti-reflecting coatings for solar cells or NT for Grätzel solar cells. However, due to their contribution to the energy supply, the emission of combustion residues could be reduced. The development of light-weight material points in a similar direction. Its use in means of transport like cars or airplanes can reduce energy consumption.

Sensors

An example which also indirectly contributes to the reduction of hazardous substances is the development of new sensor systems on the basis of NT (e.g. lambda testing probe on the basis of zirconium oxide). These systems can help to optimise process technology and can thus reduce emission or consumption of hazardous substances.

Flame retardants

Silica particles are already used as flame retardant additive in plastics. They could influence the dropping properties of the burning plastic, e.g. reduce wicking (the development of wick-like structures increases the evaporation of the polymer and thus accelerates burning).

A concept especially for wooden elements is to add silica nanoparticles (silane) to the resin which forms a ceramic-like layer under heat exposure. This layer has a heat insulating effect and prevents oxygen exchange between air and wood and in addition reduces fume generation.

For transparent applications, nanotechnological aerogels which are also produced by Degussa are used as insulators for glass doors (see for example in: elements 2006). But these aerogels are very expensive and at the moment only useful for niche applications.

Energy storage / fuel cells

Nanomaterials are developed to increase the capacity of lithium ion batteries thus saving material. The capacity of the batteries can be increased by using specially treated nanoscaled silicon particles with higher specific storage capacity for lithium ions.

New membranes for fuel cells based on NT are developed. This is an example of substitution in the sense that other energy supply methods, that are linked with a higher release of hazardous substances, are substituted. Another development linked to fuel cells is the development of H2 storage material. So-called “cubes” – a material consisting of molecules in the shape of a cube – are developed by BASF.

Replacing a lead-containing battery by a fuel cell or by a lithium-ion battery reduces the use of lead. Currently, the polymeric separation layer in Li-ion batteries is not very temperature stable. This lack of stability can be overcome by substitution with a flexible ceramic membrane made from nanostructured particles. Thus, Li-ion batteries will become suitable for use in automobiles. This would allow the replacement of the lead-containing batteries used at present. The membrane, called SEPARION® is produced by Degussa[57]

Further examples pointing to the reduction of energy consumption are:

- Tyres with nanostructured fillers for reduced rolling resistance, i.e. ECORAX® from Degussa.
- Increase in the flow ability of transported material, e.g. in extinguishers, but also of other transported materials, in order to reduce energy demand.
- Reduction of the sinter temperature of ceramics.

Pesticides

With the help of functionalised nanoparticles it could be possible to immobilise pesticides or fertilizers.

How could NT contribute to substitution in processes?

A field where NT will change process technology is the use of membranes for the separation of different substances. Here, it is conceivable that such membranes could reduce the use of hazardous substances used for separation purposes.

It might be possible to avoid or reduce the use of chromate by new anti-corrosion coatings. One example is given in Steinfeldt (2004). A company delivering such coatings is NTC-Coatings.

Powder coatings could reduce the use of organic solvents.

Carbon-based nanoparticles as additive in plastics could be a way to substitute metals, e.g. soldering, which is based on heavy metals like Zn and Sb.

General remark

In some cases, it is not so easy to distinguish between nanomaterials and chemistry, e.g. with fullerenes like C60. This is a nanoparticle but also a molecule. Usually, in cluster chemistry the discrimination level between molecules and particles is gold 55 (consisting of 55 gold atoms), which is assigned as particle.

Interview with Q. Zhao by phone, 18 May 2006

Dr. Qi Zhao

Department of Mechanical Engineering and Mechatronics

University of Dundee, Scotland, UK

[57] http://www.creavis.com/site_separion/de/default.cfm?content=about/about (26.Oktober 2006)

Expertise:

Biomedical Engineering, Surface Modification, Anti-microbial Materials & Coatings, Anti-fouling surfaces, AMBIO-Partner.

Biofilms/Antifouling

The main research interest is in the growth of biofilms. Biofilms are present on every surface exposed to air or water. The objective is to understand growth and adhesion of these films with the aim to control adhesion: either to prevent it in case of biofouling or enhance it in case of implants or tissue engineering. Important issues are surface energy, surface structure, etc.

There are different approaches to prevent adhesion or to reduce the toxic components in the coatings. The lotus effect is one approach.

The concept used in the AMBIO project is based on NT.

There are several fields of application: Medical applications (as mentioned above), coatings of the inner wall of tubes for water supply, cooling systems or oil pipelines. The aim is to prevent the growth of a biofilm inside the tube. This example is explicitly mentioned in the AMBIO project.

Interview with B. Watermann by phone, 30 May 2006

Dr. Burkard Watermann

Bei der Neuen Münze 11,

D-22145 Hamburg, Germany

e-mail: watermann@limnomar.de

www.limnomare.de

Expertise:

Head of Limnomare, a private aquatic research laboratory, co-author of the WWF study *"Alternativen zu TBT"* (2001) (engl.: *Alternatives to TBT*).

Antifouling

None of the NT-based coatings were good.

Why is it so difficult to develop alternative antifouling coatings?

The problem is that the investigations cannot be carried out in the laboratory. The results obtained in the laboratory are not transferable to natural environments. Therefore, only long-term experiments in natural environments can lead to the desired knowledge. This takes time which the companies usually cannot or are not willing to invest, particularly as it is unknown which substances will be prohibited in future.

Nanostructures do not seem to be very useful, since in water proteins very quickly accumulate at the surface and cover the nanostructure.

Relation to NT

Holmenkol (cooperation with Nanogate) and Nanogate (former Colloid Surface Technologies GmbH) have claimed to use NT-based products.

Alternatives to TBT-containing coatings

There is a multitude of coatings for niche applications. The most effective and most distributed coatings are based on silicone (approx. 10% market share).

Contact persons mentioned by the interviewee

Ralf Lieder (Dep. Bionik, Hochschule Bremen)

Christof Bauer (Alfred Wegner Inst.)

Ninja Reinike (Former project leader of the WWF project on Alternatives to Conventional Biofouling Coatings (see Watermann 2001).

Interview with B. Liedberg by phone, 30 May 2006.

Prof. Dr. Bo Liedberg

Head of the Molecular Films and Surface Analysis Group

Laboratory of Applied Physics

Department of Physics and Measurement Technology

Linköping University

S-581 83 Linköping, Sweden

e-mail: bolie@ifm.liu.se

Expertise:

Professor for surface chemistry and physics, co-worker in the AMBIO project.

Antifouling

What is the relation of antifouling coatings to NT?

Topography and chemical composition are important factors for antifouling coatings. Both factors have to be combined. A further element is the softness of the coating. However, its influence is rather on the nanoscopic than on the microscopic level.

Application areas

There are a lot of application areas where biocide coatings are useful, e.g. for medical applications. Non-adhesive coatings could also be used in several fields of application such as house paint. With such coatings, buildings have to be painted much more seldom. Consequently, a lot of paint and other chemicals such as cleaning agents could be saved.

A further important field of application of antifouling coatings are heat exchangers, especially in power plants or air-conditioning systems and other industrial processes where filter systems should be prevented from clogging.

If we can realise antifouling coatings that do not release toxic agents, an important application of such coatings will be in the field of food production, e.g. for milk pasteurisation, where protein sticking is a cost-intensive problem.

Contact persons mentioned by the interviewee

Experts in the field of antifouling are Mr. Callow (project leader of the AMBIO project) and researchers in the field of toxicology.

Interview with G. Bachmann and W. Luther, 13 June 2006, Düsseldorf.

Dr. Gerd Bachmann

Verein Deutscher Ingenieure (VDI)

Technologiezentrum
Graf-Recke-Straße 84
D-40239 Düsseldorf

E-mail: bachmann@vdi.de

Expertise:

Technology analysis studies in the field of nanotechnology since 1998.

Dr. Wolfgang Luther

Verein Deutscher Ingenieure (VDI)

Technologiezentrum
Graf-Recke-Straße 84
D-40239 Düsseldorf

E-mail: luther@vdi.de

Expertise:

Since 2003 coordination of innovation accompanying activities of the VDI-TZ in the field of NT for the Ministry of Research and Education.

Catalysis

Goals of the development of catalysts are the reduction of energy consumption, increased efficiency, reduction of educts, and cost reduction.

The key issue is selectivity. This can be achieved by adjusting the binding energies with the help of alloys.

In this respect, functionalised nanoparticles play a crucial role. Nanomaterial plays an important role as host or carrier structure (e.g. zeolites which are already used in the petrol industry for cracking oil).

Self-cleaning coatings

There are already several products on the market using silver particles as biocide. For example, the enterprise Sarasko provides a hygienic spray designed for clinics in order to reduce the cleaning effort.

Further enterprises are Biogate and Samsung. Samsung delivers washing machines with silver nanoparticle coated washer drums.

Further products are silver nanoparticle coated textiles, or textiles which are provided with cyclodextrin. Cyclodextrin is used as odour absorber.

The relation to the project is the reduction of water consumption and washing agents.

Further self-cleaning coatings are based on TiO_2 nanoparticles used as photocatalysts (producer: NanoX, Saarland).

Anti-adhesive coatings

There are several coatings based on the Lotus effect. One product is called Lotosan. The problem of abrasion has not yet been solved. Self-generation of the surface structure, as performed by the lotus flower, cannot be technically reproduced.

Anti-adhesive coatings based on Teflon are already on the market, e.g. for barbecue foils or coatings for ovens. They are also used in the field of heat exchangers, e.g. in cooling towers, to avoid adhesion and clogging.

Enterprises providing hydrophobic agents are Nanogate or Nanozentrum Fulda.

A self-cleaning coating for windows, called “Sidolin Nanoprotektor”, is provided by Henkel. The producer of this coating is ItN Nanovation GmbH.

Tributyltin (TBT) substitution:

The “Alfred Wegner Institut” has been working on an imitation of the dolphin’s skin, with a fine structure allowing to store grease and oil in order to reduce adhesion.

Hard coatings and coatings with special tribological properties

Hard coatings, e.g. based on diamond-like carbon (DLC), could lead to a reduction in lubricants, an increase in service life, and a reduction of material consumption.

A leading institute in this field is the Fraunhofer Institut für Werkstoffmechanik (Fh-IWM).

Another application of such coatings is the coating of surgery tools.

The Institut für Angewandte Verschleißforschung GmbH, Karlsruhe is active in this field. They are especially working on the processes related to tribomutation.

Ferrofluide (Producer: Degussa) could be used to hold lubricants at the site of action.

Dry coating

Dry coating or powder coating has the advantage that no solvents are required during the coating process. A precondition is, however, that the material to be coated is electrically conducting. Therefore, there are attempts to develop conductive polymers, e.g. by introducing carbon nanotubes (CNT) or other carbon nanoparticles. With these additives, polymers could be coated by powder coating.

Colour effects

Nanocoatings are being investigated in terms of their ability to provide special optical effects like diffraction and pearly shine.

Industries which are working in this field are BASF Coatings, Merck (Coating), PPG-Lacke.

Under the name “NanoCotta”, an enterprise offers a spray to prevent calcification of clay pots.

At present, research is being carried out on nanocoatings for the inner walls of PET bottles to reduce both CO2 emissions and biofouling. This would allow to store beverages such as beer much longer, also without cooling. The Carlsberg Brewery follows this approach.

Corrosion protection

Steel sheets are covered with SiO2 coatings, e.g. by chemical vapour deposition or using a sol-gel procedure (Institute of New Materials INM, Saarbrücken) to protect them against corrosion (see Luther 2006). This is used for electric irons, but here not as anti-corrosion coating but to enhance the ironing performance (producer: Engineered nanoProducts Germany (EPG), a start-up of the INM)

Another institute working in this field is the Fraunhofer Institut für Silikat Forschung und Keramik (Fh-ISC). Even tough concentrating on nanoceramics, they have developed a new nanomaterial which is called Omyceere and also used as corrosion protection.

Flame retardants

An alternative approach to avoid halogenated flame retardants is followed by Bayer. They add a catalyst to the plastics which produces even at relatively low temperatures a carbon-based coating on the surface of the product. This coating prevents further combustion.

The enterprise “Südchemie” produces silicate additives (alumina minerals) which are used by Bayer as flame retardant additives.

The Institut für Neue Materialien (INM) has developed a transparent and thermal insolating coating which can be used for transparent fireproof doors or windows.

In the field of construction, SiO_2 is added to material consisting of wood shavings, which increases the inflammability.

TiO_2 nanoparticles are used as UV protection for wood instead of FeO_2. Wood covered with TiO_2-based UV protection is easier to recycle and produces less toxic substances in case of burning (producer: Sachtleben).

Herbicides, fungicides, insecticides

With electrospinning it is possible to produce fibres with cavities in the nm range. The concept is to deposit pesticides in these cavities. When these fibres are spread on the field, the fibre structure slowly decays while continuously releasing the pesticides. It is thus possible to extend the effect of the pesticides and to prevent them from being washed off prematurely by rain.

The Swiss manufacturer NanoSys GmbH provides wood preservatives under the name Nano-Profi.

Further sources of information recommended by the interviewees

A good collection of existing products containing or based on NT can be found on the homepage of the Woodrow Wilson Center www.nanotechproject.org.

A really comprehensive overview of all activities, especially of enterprises and SME in the field of NT in Germany, can be found at: www.nano-map.de

The Center for Biological and Environmental Nanotechnology (CBEN) provides useful information concerning environmental benefits of NT.

The International Council on Nanotechnology (ICON) database provides information on health aspects of chemical substances as well as of nanomaterials: http://icon.rice.edu

Contact persons mentioned by the interviewees

Experts in this field of catalysis:

Mr. Ferdie Schüth, (MPI für Kohleforschung, Mühlheim)

Mr. Schlögl, (Fritz-Haber-Institut, Berlin)

Mr. Besenbacher, (University of Aarhus)

Fraunhofer Institut Chemische Technolgien in Pfinztal

perform research in the field of catalysis.

Expert in the field of self cleaning coatings:

Mr. Hanselmann (Sarasko, Saarland)

Expert in the field of textiles which are enhanced by NT:

Mr. Knittel (Deutsches Textilienforschungszentrum Nord-West – DTNW)

Expert in the field of antifouling:

Mr. Bohrmann (Geesthacht/FH Harburg)

Experts in the field of corrosion protection:

Mr. Mennig (INM, Saarbrücken)

Mr. Haas (Fraunhofer Institut für Silicatforschung – Fh-ISC)

Expert concerning the potential of substitution in the field of microelectronics:

Mr. Gessner (Zentralverband Elektrotechnik- und Elektronikindustrie e.V. – ZVEI)

Expert concerning hazardous substances:

Mr. Dubbert (Umweltbundesamt – UBA, Dessau).

Interview with E. Keßenich by phone, 19 June 2006

Dr. Elmar Keßenich

Department of Polymer Physics

BASF AG, GKP/N-B1

D-67056 Ludwigshafen, Germany

Expertise:

Coordination of the R&D work and environmental health and safety issues in the new growth cluster NT of BASF; coordination of the activities of the European technology platform for sustainable chemistry, here part of the material and technology group.

Basic problem:

Chemical products shall usually combine a lot of characteristics (e.g. special flow properties, defined drying time, desired processing behaviour, special colour effects). Therefore, it does not make sense to confine oneself to substitution when analysing the application area of NT in chemistry. Especially the benefits for the environment can be realised in manifold ways by NT, or a certain NT can be developed for many different reasons. Substitution is only one of them.

Examples: flame retardants

In the substitution of flame retardants, brominated hydrocarbons are replaced. However, in most cases it is not possible to reproduce exactly the same properties. On the other hand, the substitution is often aimed at other purposes for instance to increase the heat resistance of polymers or the heat transportation capacity for packaging material in the chip industry.

Supplier is for example the Bayer company. The name of the product is BAYmedur.

Application area is the use in plastics for cases of electronic devices.

The relation to NT is given by the SiO2 particles the product is based on.

Example: quick drying house paints

The aim is to develop a product that contains less organic solvents while still drying quickly after processing. Additional functions to be realised with NT in the products are self-cleaning effects (product by Bayer).

The relation to nano is given by solid particles which are embedded in a matrix.

Example: pesticides

The aim is to control the release of pesticides at the site of action in order to reduce the overall use of pesticides.

This is to be realised via “microencapsulation” in combination with an increase in the surface through which the agent is to be released. These microencapsulations are produced using the mini-emulsion process. There is still no product on the market. At present, it only exists as a concept. However, it is comparable to the product F500 of the Bayer company.

Catalysts

In principal, with the help of NT it is possible to specifically develop new catalysts, i.e. no longer by a trial-and-error procedure.

At present, the main problem related to the development of catalysts is to translate the concepts working at the laboratory scale into the scale of industrial production. In this area, great expectations are placed on NT, due to the combination of homogenous (large surface) with heterogeneous (surface effects) catalysis. In this way it will be possible to realise three-dimensional (nanoporous) carrier material with large surface and small volume.

An example of an innovative catalyst is the concept of Oxonica. Here, ceroxid particles incorporated into the fuel are acting as catalysts in the burning chamber of the engine. This reduces the production of carbonised by-products, such as gasoline soot, and facilitates the cleaning of the soot filters.

Further potential areas in the field of catalysis are dendrimers and so-called Janus particles.

Contact persons mentioned by the interviewees

Dr. Harald Pielartzik (BAYER MaterialScience AG)

Andreas Förster (Dechema, Working group: Surface Chemistry)

Prof. Mühlhaupt (Univ. Freiburg)

Interview with H. Fichtner, 6 July 2006, Karlsruhe.

Dr. Maximilian Fichtner

Institute of Nanotechnology (INT), Forschungszentrum Karlsruhe

Hermann-von-Helmholtz-Platz 1

D-76344 Eggenstein-Leopoldshafen, Germany

e-mail: fichtner@int.fzk.de

Expertise:

Responsible for the field of nanostructured materials in the Department of Nanomaterials I of the Institute of Nanotechnology, Forschungszentrum Karlsruhe.

Spokesman of the HyTecGroup at the Forschungszentrum Karlsruhe.

Catalysis

NT has given a new impetus to research on catalysis. The main reason for this may lie in the interdisciplinary approach of NT. In general, new catalysts may make it possible to follow other paths of synthesis.

Before NT was perceived as an own research area research on catalysts in this field had been assigned to heterogenic catalysts consisting of a carrier material (e.g. AlOx, or special ceramics) covered with metal particles, e.g. platinum particles with a diameter of 2-20 nm.

There are several aspects related to the nanometer size that play an important role in this field. First, by enhancing the surface of the carrier material the whole catalyst can be reduced in size and weight without loosing efficiency. Reducing the size of the catalytic particles saves expensive material like platinum. Crucial is the dispersion factor (ratio of the number of surface atoms to the number of all atoms).

Presently, oxide mixtures are being investigated to avoid the use of expensive material, e.g. platinum.

Another approach is the use of zeolites. Here, small cavities prevent the molecules from getting in touch with each other. Only certain molecules can react with each other. This principle has been used in petrochemistry (for cracking) for a long time. Another example is the ammonia production by the Haber-Bosch process.

Coatings

Scratch resistant resins could reduce the use of polishing agents.

Special coatings are developed to reduce the growth of fungi, e.g. in sanitary areas.

Self-cleaning coatings could be used to reduce cleaning agents.

Biocide coatings may reduce the use of disinfectants.

Gluing

Nanoparticles of iron are used to change gluing. The particles are set in motion by microwaves and thus only produce heat at the location of the surfaces to be glued. This method makes it possible to save energy, reduce the use of solvent, and glue less heat-resistant materials.

Flame retardants

Compressed wood boards have already been impregnated by silicates to increase the flame resistance. But the resulting silicon particles are not necessarily in the dimension of nm.

Textiles

Dirt-repelling coatings for textiles are already used. They are mostly based on Teflon.

Silver NP are used for disinfecting purposes and for catalytic decomposition of organic compounds, e.g. to reduce odour.

Drug delivery

By targeted drug delivery, only a fraction of drugs would be required to get the same result. The body of the patient is less strained and less drugs are released to the environment.

Wear resistant coatings

Nanotechnology-based hard coatings could be used to reduce material and energy consumption and lubricants.

Perception – Is there a need to increase the awareness on the subject of the project?

From the perspective of the interviewee the contact to industry is strong and well developed. In this respect, ideas for applications often come from industry. They address researchers in this field, asking what could be realised with a certain NT, or what NT could be applied to a certain problem.

Journals recommended by the interviewee

Journals in which articles on this subject may be found are:

Technology Review,

Materials Today,

Nature Materials,

Advanced Materials,

Advanced Engineering Materials,

Journal of Nanoscience and Nanotechnology.

A further source of information is the Institut für Neue Materialien (INM, Saarland) and their related work in the Competence Cluster NanoChem.

10.4 Reports Reviewed

Allianz

Small Size that Matter: Opportunities and Risks of Nanotechnologies

Report in co-operation with the OECD International Future Programme

Ahrens, A.; Braun, A.; von Gleich, A.; Heitmann, K.; Lißner, L.

Hazardous Chemicals in Products and Processes: Substitution as an Innovative Process

Physica-Verlag, Heidelberg (2006)

Bergeron, S.; Archambault, E. (Science Metrix)

Canadian Stewardship Practices for Environmental Nanotechnology

Environment Canada, Quebec (2005)

BMBF 2003

Produktion von und mit Nanomaterialien – Untersuchung des Forschungs- und Handlungsbedarfs für die industrielle Produktion.

Report on the Project: NanoProduction

Fraunhofer – ISC, PT-Production und Vertigungstechnik, Fraunhofer-ISI

Chemical Industry Vision2020 Technology Partnership, USA

Nanomaterials and the Chemical Industry

Preliminary Results on R&D Roadmap Workshop, September 30, October 1 and 2 (2002)

Jørgensen, M. S.; Andersen, M. M.; Hansen, A.; Wenzel, H.; Pedersen, T. T.; Jørgensen, U.; Falch, M.; Rasmussen, B.; Olsen, S. I.; Willum, O.

Green Technology Foresight about Environmentally Friendly Products and Materials. Challenges from Nanotechnology, Biotechnology and ICT

Department of Manufacturing Engineering and Management, Technical University of Denmark (2005)

Chemical Industry Vision2020 Technology Partnership, USA

Chemical Industry R&D Roadmap for Nanomaterials By Design (2003)

Department of Trade and Industry (DTI), Office of Science and Technology, UK

New Dimensions for Manufacturing – A UK Strategy for Nanotechnology

Chair: J. M. Taylor (2002)

Environmental Protection Agency, USA

Proceedings

EPA Nanotechnology and the Environment: Applications and Implications STAR Progress Review Workshop

28.-29. August 2002, Arlington, Virginia (2002)

Environmental Protection Agency, USA

Nanotechnology White Paper (External Review Draft)

December (2005)

European Commission, Community Health and Consumer Protection

Nanotechnologies: A Preliminary Risk Analysis

Brussels: European Commission (2004)

European Commission

Integrated Pollution Prevention and Control

Draft Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics

Study performed by the IPTS-JRC, Seville (2005)

Hessen Agentur GmbH (ed.)

Einsatz von Nanotechnologie in der hessischen Umwelttechnologie

Wiesbaden (2005)

ICSTI (Irish Council for Science, Technology, and Innovation)

ICSTI Statement on Nanotechnology

The study was performed by Forfás (2004)

Hoffknecht, A. et al.

Nutzung der Nanotechnologie für sicherheitspolitische Anwendungen

VDI-Technologiezentrum, Düsseldorf (2006)

Lohse, J.; Wirts, M.; Ahrens, A.; Heitmann, K.; Lundie, S.; Lißner L.; Wagner, A.

Hazardous Chemicals in Products and Processes

Report compiled for the Directorate General Environment, Nuclear Safety and Civil Protection of the Commission of the European Communities

Contract No B3-4305/2000/293861/MAR/E1, Final Report 2003

Luther, W. et al.

Nanotechnologie als wirtschaftlicher Wachstumsmarkt

VDI-Technologiezentrum, Düsseldorf (2004)

Luther, W. et al.

Industrial Application of Nanomaterials – Chances and Risks

VDI-Technologiezentrum, Düsseldorf (2004)

Malanowsky, N.

Vorstudie – Nanotechnologie

VDI-Technologiezentrum, Düsseldorf (2004)

Ministerium für Umwelt und Verkehr Baden-Württemberg

Zukunftspotenziale der Mikro- und Nanotechnologie als Schlüsseltechnologie für die Umwelttechnik in Baden-Württemberg

Stuttgart (2004)

Malsch, I. (ed.)

Benefits, Risks, Ethical, Legal and Social Aspects of Nanotechnology

4th Nanoforum Report (2004)

Nanoforum

Nano & the Environment

Workshop organised by Nanoforum and the Institute for Environment and Sustainability, JRC Ispra, 30. and 31. March (2006)

http://www.nanoforum.org/nf06~modul~searchevents~eventid~1292~.html?action=longview&moreaction=&idauswahl=& (18.7. 2006)

Paschen, H.; Coenen, C.; Fleischer, T.; Grünwald, R.; Oertel, D.; Revermann, C.

Nanotechnologie in Forschung, Entwicklung, Anwendung. Stand und Perspektiven,

Springer Berlin (2004)

Royal Society & Royal Academy of Engineering

Nanoscience and Nanotechnologies: Opportunities and Uncertainties

Royal Society, London (2004)

Royal Society

Environmental Applications and Impacts of Nanotechnology

Summary of evidence presented to nanotechnology working group (2003)

Hett, A.

Nanotechnology – Small Matter, Many Unknowns

Swiss-Re (2004)

Steinfeldt, M. et al.

Nachhaltigkeitseffekte durch Herstellung und Anwendung nanotechnologischer Produkte

Schriftenreihe des IÖW 177/04

Berlin, November (2004)

INTECH (Institute for new Technologies)

Bartzokas, A.; Yarime, M.

Technology Trends in Pollution-intensive Industries: A Review of Sectoral Trends

The United Nation University, Discussion Paper (1997)

Wood, S.; Jones, R.; Geldart, A.

The Social and Economic Challenges of Nanotechnology

Economic and Social Research Council, Swindon, UK (2003)

10.5 Journals Reviewed

The relevant literature was identified by following criteria:

- Reports from governmental departments, research institutes, industrial associations, and other stakeholder groups which addresses NT and environmental issues. The considered reports are listed in appendix 10.3.
- Journals, carrying “Nano” in their titles.
- Certain journals in the field of applied chemistry.
- Journals addressing chemistry and environmental issues (e.g. Green Chemistry).
- broad keyword based searches in several data bases

The specific journals are reviewed differently. **Recent issues of journals specialised on NT are examined manually title by title.** The same applies to journals on chemistry which focus on environmental issues. **Other issues of these journals and the other journals** are examined with the help of **keyword-based research**. Concerning the subject of the journal, either the keyword ‘nano*’ (all words starting with ‘nano’) is used (for journals with an environmental background) or the combination of the keywords ‘nano*’ together with keywords like ‘substitution’ ‘hazardous’, and ‘replacement’ are used. Subsequently, the results are examined manually title by title.

This keyword based search was performed in

– journals of the American Chemical Society (ACS)

– journals covered by Science Direct

Journals on applied chemistry:

Angewandte Chemie

Chemical Processing

Chemical Engineering

Chemical Engineering and Technology

Chemical Engineering and Processes

Chemie in unserer Zeit

Chemie – Ingenieur – Technik Wiley

Chemie Technik

Chemistry of Materials

Industrial & Engineering Chemsitry

Journal of Materials Chemistry **(RSC-Publishing)**

elements **(Degussa research newsletter)**

Journals carrying the prefix Nano in its title:

Journal of Nanoparticles Research

Journal of Nanoscience and Nanotechnology

Nanotechnology

Nano Letters

Journals addressing chemistry and environmental issues

Chemosphere

Green Chemistry

Environmental Science and Technology

Environmental Science and Technology A-Pages

Other important journals on chemistry:

Chemical Reviews

Journal of the American Chemical Society

10.6 Experts

The following list summarises all experts who have been contacted for this Report. The contact is differentiated between face-to-face interview partners (FF-interview), telephone interview partners (phone interview), face-to-face conversation (FF-talk) and mail correspondence (mail).

Name	Surname	Organisation	Expertise	contacted by
Allan	Dr. Jacqueline	Forfás, Dublin, Ireland	NanoMaterials Background Paper 2005	mail
Anselmann	Dr. Ralf	Degussa AG, Marl, Germany	Head of Science to Business Center Nanotronics	mail
Bachmann	Dr. Gerd	VDI-Technologiezentrum, Düsseldorf, Germany	author of several studis on nanotechnology	FF-interview
Byrne	Dr. Tony	Nanotechnology Research Institute University of Ulster's	Head of the photocatalysis research group	WS
Callow	Prof. James .A.	University of Birmingham, UK	AMBIO-Projecleader	phone
Croucher	Dr. Terrence G.	Polymere Laboratories Ltd, Church Stretton, UK	Deputy Chairman Operations Director	phone
Dobson	Prof. Peter	Department of Engineering Science, University of Oxford	Academic Director of the Oxford University Begbroke Science Park	phone
Döring	Prof. Manfred	ITC, Forschungzentrum Karlsruhe, Germany	Technical Catalysis and Polymer Additives	phone
Dubbert	Dr. Wolfgang	Umwelt Bundes Amt, Dessau, Germany	Biotechnology, Substitution, Catalysis	phone
Fichtner	Dr. Maximilian	INT, Forschungzentrum Karlsruhe, Germany	Nanostructured Materials	FF-interview
Gerhard-Abozari	Dr. Eva	PTJ, Forschungszentrum Jülich GmbH	Contact person of the BMBF-Initiative NanoChem	phone/mail
Gutsch	Dr. Andreas	Degussa AG, Marl, Germany	CVD of Nanoparticles	mail
Hoskin	Dr. John	Royal Chemical Society	Chair of the Royal Society of Chemistry	WS

			Toxicology Group	
Hullmann	Dr. Angela	European Commission DG-Research, Unit G4:	Nanoscience and Nanotechnologies	mail
Iden	Prof. Rüdiger	BASF AG, Ludwigshafen, Germany	Head of Polymer Research at BASF	FF-talk
Keller	Dr. Harald	BASF, Ludwigshafen, Germany	Functional Polymers	mail
Keßenich	Elmar	Department of Polymer Physics, BASF AG, Ludwigshafen, Germany	Coordination environmental health and safety issues for NT at BASF	phone/WS
Kranz	Carolin	BASF, Ludwigshafen, Germany	Corporate and Governmental Relations for Environmental Issues	phone
Leggett	Prof. Graham	Centre for Biomaterials and Tissue Engineering Sheffield University	nanometre scale surface chemistry and analytic chemistry	mail
Lambkin	Dr. Imelda	Forfás, Dublin, Ireland	NanoBiotechnology Background Paper 2005	mail
Liedberg	Prof. Bo	Linköping University, Sweden	Surface Chemist / Physicist AMBIO-Partner	phone
Lipworths	Dr. Steven	Health, Safty and Environment Officer Royal Society of Chemistry	Policy Adviser, specific field: REACH	mail
Luther	Dr. Wolfgang	VDI, Düsseldorf, Germany	Economic Potential of Nanotechnology	FF-interview/WS
Masciangioli	Dr. Tina	Woodrow Wilson Center, Washington, USA	Environmental Technologies at the Nanoscale, 2003	mail
Maynard	Dr. Andrew	Woodrow Wilson Center, Washington, USA	Senior Research Associate, Project on Emerging Nanotechnologies	phone
McLaughlin	Prof. James	School of Electrical and Mechanical Engineering University of Ulster	Director - Nanotechnology & Advanced Materials Research Institute	mail
Oertel	Dr. Dagma	Office of Technology Assessment at the German Parliament (TAB)	co-author of Nanotechnologie Herbert Paschen et al. 2004	phone
Parr	Dr. Douglas	Greenpeace, London, UK	Chief scientist	FF-talk
Peter	Dr. Ralf	PTJ, Forschungszentrum Jülich GmbH	Head of the department Chemistry / Polymeres	phone

Pridöhl	Dr. Markus	Degussa	R&D Manoger at Degussa Advanced Nanomaterials	FF-interview
Ratoi	Dr. Monica	Department of Materials, Oxford University, UK	Characteration of Nanomaterials, Participation in NANOSAFE2	Phone/WS
Reller	Prof. Armin	Univeristät Augsburg, Germany	Solidstate chemstry, Nanomaterials, Editor of Gaya	FF-interview/WS
Rip	Prof. Arie	University of Twente, NL	Technology assessment of NT, NanoNed,	phone
Santillo	Dr. David	University of Exeter, UK	Greenpeace Research Laboratories School of Biosciences	Phone/WS
Steinfeldt	Michael		Study: Effects fo Sustainabillity by production and application of nanotechnological products (BMBF)	FF-interview
Steingrobe	Dr. Bernd	PTJ, Forschungszentrum Jülich GmbH	Material research and Nanotechnology	phone
Vielfort	Dr, Annette	Verband der Chemischen Industrie, Frankfurt, Germany		FF-talk
von Gleich	Prof. Arnim	artec, Universität Bremen, Germany	Sustainable development and NT	FF-interview
Watermann	Dr. Burkard	WWF, Hamburg, Germany	Co-author of WWF-Study: 'Performance of biocide-free antifouling paints' 2001	phone
Welland	Prof. Mark E.	Nanoscience Centre, Cambridge, UK	Head of the laboratory	Phone/WS
Zhao	Dr. Qi	University of Dundee, Scotland,UK	Anti-fouling surfaces, AMBIO-Partner	phone

11 GLOSSARY

AMBIO	(Advanced Nanostructured Surfaces for the Control of Biofouling) is an Integrated Project funded by the European Commission under its Sixth Framework Programme. The project is at the crossroads between nanosciences and marine biology, environment and high technology and is devoted to the knowledge-based development of antifouling coatings that function through their nanoscale physico-chemical properties, without the release of biocides which may damage the environment. http://www.ambio.bham.ac.uk/about/what%20is%20biofouling.htm
Biofouling	Biofouling or biological fouling is the undesirable accumulation of microorganisms, plants, algae, and animals on submerged structures, especially ships' hulls. Individually small, accumulated biofoulers can form enormous masses that severely diminish ships' manoeuvrability and carrying capacity. Fouling causes huge material and economic costs in maintenance of mariculture, shipping industries, naval vessels, and seawater pipelines. Governments and industry spend more than US$ 5.7 billion annually to prevent and control marine biofouling. (Source: Wikipedia)
Bionic	(also known as biomimetics, biognosis, biomimicry, or bionical creativity engineering) is the application of methods and systems found in nature to the study and design of engineering systems and modern technology.
Carbon nanotubes	are tubes consisting of a rolled up mesh.like configuration of carbon atoms. The geometry of the rolled graphite sheets affects their properties.
cefic	European chemical industry council
CFC	Chlorofluorcarbon
CMR	Carcinogenic, mutagenic, or toxic to reproduction
DDT	Dichlorodiphenyl trichloroethane (insecticide)
EDC	Endocrine disrupting chemicals
EPA	Environmental Protection Agency
Fullerenes	are a carbon configuration where the atoms form more or less spherical cages also known as Buckminster-fullerenes or as ‘Bucky Balls’. C60, consisting of 60 carbon atoms, in pentagon and hexagonal arrangement is the best known fullerene but there are a several other fullerenes with e.g. 20 or 70 carbon atoms.
Halogens	Halogens are fluorine chlorine, bromine and iodine.
HBCD	Hexabromocyclododecane (flame retardant)

Heterogeneous catalysts	Heterogeneous catalysts are solids which facilitates the reaction. In contrast to homogeneous catalysts, which are molecules the catalyst could not be dissolved in the solvent.
ICT	Information and communication technology
LCA	Life Cycle Assessment Analysis and assessment of the fate of the material components of a product and the material used during the usage of the product in respect to the amount of material and energy consumption and its related environmental load.
Lotus effect	The Lotus effect in material science is the observed self-cleaning property found with lotus plants. Their microscopic structure and surface chemistry mean that the leaves never get wet. Rather, water droplets roll off a leaf's surface like mercury, taking mud, tiny insects, and contaminants with them. This is known as the Lotus Effect.
MAK	German abbr for Maximale Arbeitsplatzkonzentration (maximum workplace concentration)
nm	Nanometre = 10-9 metre
NP	Nanoparticle(s)
NT	Nanotechnology
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether (flame retardant)
PCB	Polychlorinated biphenyls
phtalate	a certain flexibiliser for plastics
POPs	Persistent organic pollutants
PVC	Poly vinyl chlorine
TBT	Tributyltin
VCI	German chemicals industry association
VOCs	Volatile organic compounds