



EUROPEAN PARLIAMENT

*Scientific Technology Options
Assessment*

S T O A

Galileo Applications

STOA Workshop Report

(Workshop held in Brussels on 13 September 2006)

TABLE OF CONTENTS

1	EXECUTIVE SUMMARY.....	ii
2	PRELIMINARY NOTES ON THE SUBJECT	1
3	WHAT IS NANOTECHNOLOGY?	3
3.1	Political background of NT	3
3.2	Technical definition of NT.....	3
3.3	Main characteristics of NT.....	5
3.4	What is NT in this project?	5
4	SUBSTITUTION.....	7
4.1	Background.....	7
4.2	What does substitution mean in respect to NT?.....	8
4.3	How to identify a hazardous substance?	10
4.4	List of hazardous substances.....	11
5	METHODOLOGY	14
5.1	Approach.....	14
5.2	Research strategy	14
5.3	Validation.....	15
6	CATEGORISATION OF THE FINDINGS	16
7	FINDINGS.....	17
7.1	Coatings	17
7.1.1	Self cleaning surfaces.....	17
7.1.2	Biocide coatings.....	19
7.1.3	Coatings for various purposes.....	20
7.2	Flame retardants.....	22
7.3	Flexibiliser	23
7.4	Substitution or reduction of solvents	23
7.5	Catalysts.....	24
7.6	Other examples	26
7.7	Remediation	28
7.8	NT as risk.....	29
8	CONCLUSION.....	30
8.1	Conclusions related to the approach	30
8.2	Conclusions related to the Findings.....	31
8.3	Outlook	33
8.3.1	Detailed Analysis.....	33
8.3.2	Exploitation of unknown fields of application.....	34
8.4	Recommendations.....	34
9	LITERATURE.....	36
10	APPENDIX.....	42
10.1	Summary and Results of the Validation Workshop.....	42
10.1.1	Participants of the Validation Workshop	42
10.1.2	Report on the Workshop	44
10.1.3	Discussion	52
10.1.4	Summary	54
10.2	List of functionalities of NT.....	54
10.3	Interviews.....	61
10.4	Reports Reviewed	83
10.5	Journals Reviewed	86
10.6	Experts	87
11	GLOSSARY	90

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 losing 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 inhibitor by absorbing oxygen. A similar effect could be realised by nanoparticles. If TiO₂, SiO₂, 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 2000³. 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).

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 NT⁵.

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 atom⁶. 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 fullerenes⁷ 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 size⁸.

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 effect⁹, 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 developed¹⁰. One of the consequences is that chemistry is one of the most regulated fields¹¹. 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 substance¹². 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: antibiotics¹³

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 nanostructuring 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 (Schering 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 made 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 found 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. phthalate)
- **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 substances¹⁷ 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), tetrabromobisphenol A (mostly used as reactive flame retardant) and hexabromocyclododecane (HBCD).

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

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 cerioxide 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 glues, 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 beer¹⁸). 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 dysfunctionality 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-Graffiti Painting]²³, Protectosil®²⁴, x-clean®²⁵ (NANO-X GmbH), [mpc coverax²⁶]).

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 conditions²⁷ (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 devices²⁸ (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 Perform³⁰ (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.**

²⁸ INM-Leibniz Institut für Neue Materialien gGmbH, http://www.inm-technology.de/kompetenzen/unternehmen/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).

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).

