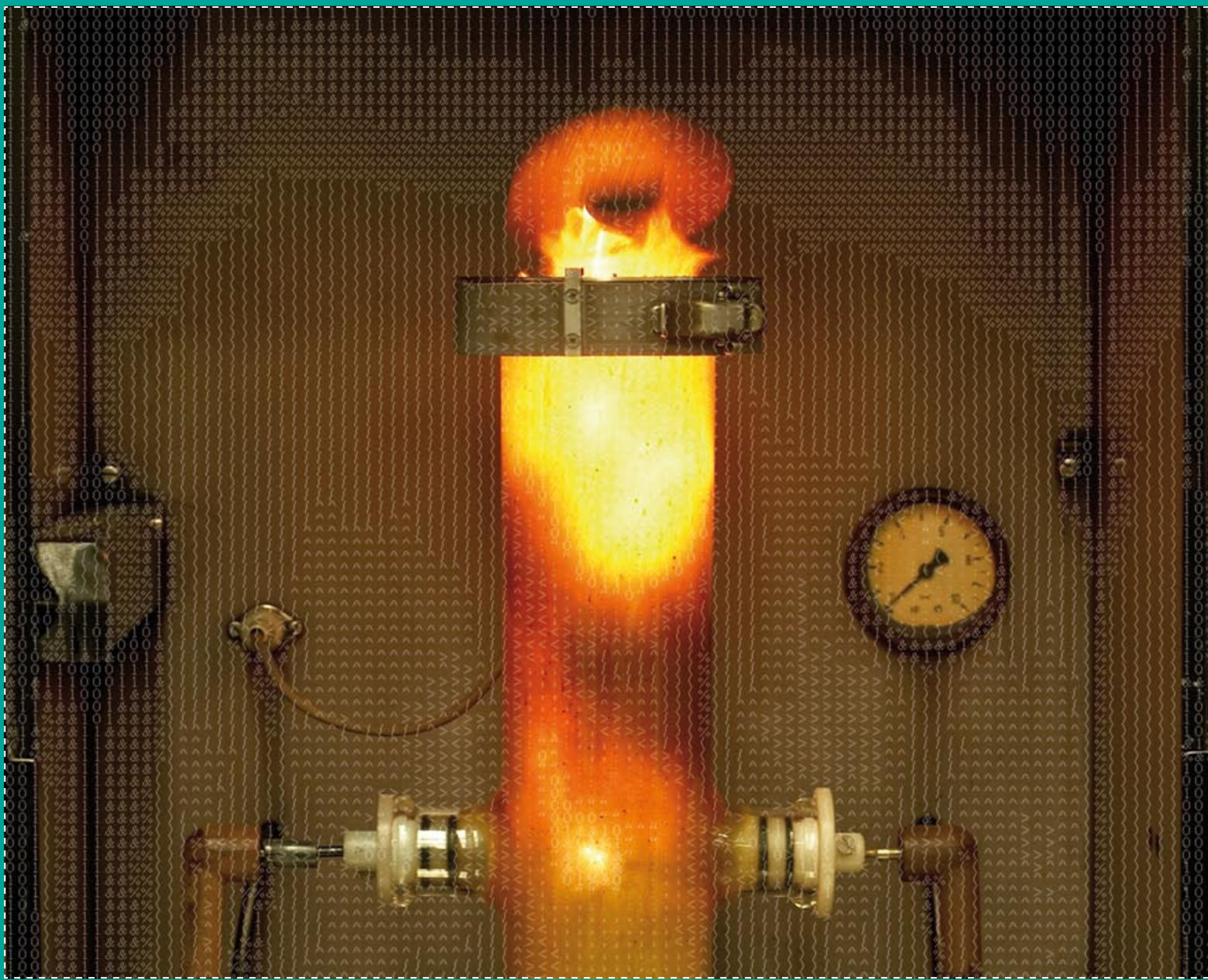
> Fire and explosion properties of synthetic nanomaterials

Initial investigations for major accident prevention



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> Fire and explosion properties of synthetic nanomaterials

Initial investigations for major accident prevention

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Authors
Marc Steinkrauss, Dr. Hans Fierz, Dr. Pablo Lerena, Dr. Georg Suter, Institute of Safety and Security, Basel

FOEN consultants
Dr. Martin Merkofer, Hazard Prevention Division (Project management)
Dr. Richard Bischof, Hazard Prevention Divison
Dr. Christof Studer, Substances, Soil, Biotechnology Division

Review
Dr. Harald Bresch, Federal Institute for Materials Research and Testing, Berlin
Dr. Anja Hofmann, Federal Institute for Materials Research and Testing, Berlin
Christoph Bosshard, suva, Lucerne
Dr. Hans Bossler, Department Chemical & Biological Safety, Canton Basel City
Dr. Marzio Giamboni, Department Chemical & Biological Safety, Canton Basel City

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Translation
Peter Case, 3615 Heimenschwand

Design
Ursula Nöthiger-Koch, 4813 Uerkheim

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> Abstracts

Nanotechnology is a rapidly growing research and development area with increasing importance for the economy, research and society. The present study addresses the question as to whether new criteria for the determination of the quantity thresholds quoted in the Ordinance on Protection against Major Accidents may result from new knowledge derived from hypothetical accident scenarios that take the fire and explosion properties of synthetic nanomaterials into account. The literature study carried out concludes that at present, insufficient fundamental data are available to draw final conclusions on this question. However, knowledge gained until now does not suggest a need for immediate specific regulations for nanomaterials to be included in the Ordinance on Protection against Major Accidents where their fire and explosion properties are concerned.

Keywords:
Major accident prevention,
nanotechnology,
synthetic nanomaterials,
fire- und explosion properties

Die Nanotechnologie ist ein rasch wachsendes Forschungs- und Entwicklungsgebiet mit zunehmender Bedeutung für Wirtschaft, Forschung und Gesellschaft. Die Studie befasst sich mit der Frage, ob sich aus den Erkenntnissen möglicher Störfallszenarien in Zusammenhang mit den Brand- und Explosionseigenschaften von synthetischen Nanomaterialien neue Kriterien für die Bestimmung der Mengenschwellen in der Störfallverordnung ergeben. Die durchgeführte Literaturstudie zeigt, dass zurzeit zu wenig Grundlagendaten für eine abschliessende Beurteilung dieser Fragestellung vorliegen. Bisherige Erkenntnisse geben aber keinen Anlass, sofort spezifische Regelungen für Nanomaterialien im Bereich der Brand- und Explosionseigenschaften in die Störfallverordnung aufzunehmen.

Stichwörter:
Störfallvorsorge,
Nanotechnologie,
synthetische Nanomaterialien,
Brand- und
Explosionseigenschaften

La nanotechnologie est un domaine de recherche et développement en rapide expansion. Son importance croît pour l’économie, pour la recherche et pour la société. L’étude cherche à déterminer si de nouveaux critères pour l’établissement des seuils quantitatifs de l’ordonnance sur les accidents majeurs peuvent résulter de nouvelles connaissances sur les scénarios possibles d’accidents majeurs liées à l’inflammabilité et à l’explosivité des nanomatériaux synthétiques. La recherche bibliographique réalisée montre que l’on ne dispose pas encore de données suffisantes pour évaluer cette question de manière définitive. Les connaissances actuelles ne fournissent cependant aucun motif d’inclure immédiatement, dans l’ordonnance, des réglementations spécifiques aux nanomatériaux en matière d’inflammabilité et d’explosibilité.

Mots-clés:
prévention des accidents
majeurs,
nanotechnologie,
nanomatériaux synthétiques,
inflammabilité et explosibilité

La nanotecnologia è un ambito della ricerca e dello sviluppo in rapida espansione, che riveste un'importanza sempre maggiore per l'economia, la ricerca e la società. Il presente studio cerca di determinare se, dalle conoscenze attuali relative a possibili scenari di incidenti rilevanti connessi con l'infiammabilità e l'esplosività di nanomateriali sintetici, risultano nuovi criteri per stabilire i quantitativi soglia nell'ordinanza sulla protezione contro gli incidenti rilevanti. Dallo studio della letteratura si evince che, al momento, non si dispone di sufficienti dati di base per valutare in modo definitivo tale questione. Tuttavia, sempre stando alle conoscenze attuali, non sussistono motivi che giustifichino l'inserimento immediato di norme specifiche in materia di infiammabilità e di esplosività dei nanomateriali nella suddetta ordinanza.

Parole chiave:
prevenzione contro gli incidenti rilevanti,
nanotecnologia,
nanomateriali sintetici,
infiammabilità ed esplosività

> Foreword

The purpose of the Ordinance on Protection against Major Accidents (OMA) is to protect the public and the environment from serious damage resulting from major accidents, which can occur during the operation of industrial facilities. The principal themes of the OMA include, among other things, the quantification of the risk to the public and the environment, which may result from the handling of substances, preparations, and special wastes. Where the enforcement of the OMA is concerned, the FOEN has the responsibility for overall control. In its control function, it monitors continuously developments involving chemical risks, lends its support to unified enforcement of the OMA in the whole of Switzerland, and prepares guidelines in cooperation with representatives of the responsible cantonal enforcement authorities, industry and science.

Nanotechnology is a rapidly growing research and development area with increasing importance for the economy, research and society. Over and above the opportunities it offers, it is important to detect possible risks to humans and the environment in good time, and, where necessary, to take appropriate protection measures. As of 9 April 2008, the Federal Council approved the Action Plan on “Synthetic Nanomaterials”, whose purpose is to prepare the basis for a secure nanotechnology.

Part of the Action Plan is to investigate whether the hazard potential or hypothetical new accident scenarios make it necessary for specific regulations on nanomaterials to be included in the OMA. In the present study, the FOEN clarifies this question in connection with their fire and explosion properties. Although the presently available fundamental data are very limited, initial conclusions for protection against major accidents could be drawn, and perspectives on important future issues given. The FOEN hopes that the latter will be taken up by the research institutions, and will carefully follow national and international developments in this field in order to keep the information continuously up to date, to take measures if necessary, and in order to validate the knowledge gained.

We also would like to thank our reviewers for their useful remarks that have been taken into account or mentioned at the end of the study under the topic future perspectives.

Andreas Götz
Vice Director
Federal Office for the Environment (FOEN)

> Summary

The purpose of the Ordinance on Protection against Major Accidents (OMA)[1] is to protect the public and the environment against serious damage resulting from major accidents with chemical danger potential. The present study, which forms part of Switzerland's "Synthetic Nanomaterials"[2] Action Plan is concerned with the question of how nanomaterials, based on our current knowledge of their fire and explosion properties, should be taken into account when defining measures for accident prevention.

To clarify this question, it is necessary to determine whether the particular characteristics of substances in nanoparticle form make it necessary to classify them differently from the corresponding conventional powders, since the scope of the OMA depends on the classification of a substance together with the quantity threshold resulting from this. In designing the hypothetical accident scenarios with nanoparticles, their agglomeration and sedimentation behaviour, and their fire and explosion properties, are decisive. With these parameters, conclusions may be drawn and comparison made with accident scenarios for conventional powders.

The investigations carried out in the study have shown that at present very little fundamental data are available on the fire and explosion properties of nanomaterials. For this reason, the study concentrates mainly on the relatively well investigated aluminium and carbon nanoparticles. The initial conclusions in the field of fire and explosion show that no particular need for action appears to exist. However, insufficient fundamental data is available to enable final general conclusions to be drawn in this area.

Metallic nanoparticles may be pyrophorous. For example, aluminium has this property. Thus it begins to burn on contact with the air. That is to say that even small quantities represent a possible source of ignition that may trigger a fire, a deflagration or an explosion. Thus synthetic nanomaterials of this type must be assigned to Category AF (self-igniting substances), and therefore have a quantity threshold of 20 000 kg. Companies that store more than 20 000 kg of these nanomaterials are subject to the provisions of the Ordinance on Protection against Major Accidents. None of the non-metallic synthetic nanomaterials known to the authors have self-igniting characteristics.

Calculations of the agglomeration and suspension behaviour of nanoparticles indicate that the particles rapidly agglomerate. In this however, the average particle diameter increases only very slowly, and is likely to remain in the range of nm to µm. For this reason, sedimentation is negligible and the particles remain for long periods in the air. In case of dispersion, they are precipitated only very slowly.

1 Verordnung über den Schutz vor Störfällen, 27. Februar 1991 (Stand am 1. Juli 2008).
2 Synthetic Nanomaterials Plan of Action, Report of the Federal Council of 9 April, 2008..

Calculations were carried out in the present study to determine how the explosion overpressures and heat radiation doses of aluminium and carbon nanoparticles behave in comparison to the corresponding conventional powders and to the reference substances propane and hydrogen. The explosion overpressures for the two nanoparticles investigated, the corresponding conventional powders, and the reference substances propane and hydrogen are approximately equal.

A comparison between the heat radiation and the flame height based on the assumptions made in the report shows that a ground layer of aluminium nanoparticles behaves very similarly to a burning petrol pool. A ground layer of graphite nanoparticles, however, reacts much more slowly.

Conclusions of the study

Insufficient fundamental data are at present available on the fire and explosion properties to enable final general conclusions to be drawn. The knowledge gained to-date does not indicate any need for specific regulations for nanomaterials under the Ordinance on Protection against Major Accidents.

- The minimum ignition energy of substances at a nanoscale can differ from that of conventional powders. Moreover, metallic nanomaterials, in particular, may display pyrophoric characteristics. Such characteristics should be mentioned on the Safety Data Sheet.
- The effects relating to the explosion overpressure for the aluminium and carbon particles investigated are similar to those of the corresponding conventional powders or substances, which have the same quantity threshold based on their classification and labelling with respect to their fire and explosion properties.
- Concerning fire and explosion properties, there is no indication at present that the accident scenarios should differ from those for powders. Therefore the regulations applying to powders should also be used for nanomaterials.
- In Switzerland today, nanomaterials, which owing to their fire and explosion properties must be counted among the hazardous substances, are used or manufactured only in small quantities of several kg to a maximum of 1 tonne per year.
- The effects associated with the toxicological and ecotoxicological properties of synthetic nanomaterials and in what way these must be included in the Ordinance on Protection against Major Accidents must be clarified as soon as the necessary fundamental data become available.

> Résumé

L'ordonnance sur les accidents majeurs (OPAM)[1] a pour but de protéger la population et l'environnement des graves dommages résultant d'accidents majeurs présentant un danger potentiel chimique. Réalisée dans le cadre du Plan d'action «Nanomatériaux synthétiques»[2] établi par la Suisse, la présente étude cherche à savoir comment les nanomatériaux en raison de leurs propriétés d'inflammabilité et d'explosibilité doivent être pris en compte dans la prévention des accidents majeurs en se basant sur les connaissances actuelles.

Comme le champ d'application de l'OPAM dépend de la classification des substances et des seuils quantitatifs qui en découlent, il convient d'examiner si les substances présentes sous la forme de nanoparticules doivent être évaluées différemment des poussières conventionnelles correspondantes. Au moment d'étudier les scénarios possibles d'accidents majeurs impliquant des nanoparticules, les comportements d'agglomération et de sédimentation de ces particules constituent des indicateurs importants, tout comme leur inflammabilité et leur explosibilité. Ces informations permettent de formuler des conclusions et de faire des comparaisons avec les scénarios d'accidents majeurs impliquant des poussières conventionnelles.

Les travaux ont montré que l'on ne dispose, pour le moment, que de très peu de données fondamentales concernant l'inflammabilité et l'explosibilité des nanomatériaux. L'étude se concentre donc principalement sur les nanoparticules de carbone et d'aluminium, qui ont déjà fait l'objet de recherches plus étendues. Sur la base des premières constatations, il n'est pas nécessaire de prendre des mesures particulières pour la prévention des accidents majeurs dans le domaine des incendies et des explosions. Les données disponibles ne permettent toutefois pas de tirer dès maintenant des conclusions d'ordre général en la matière.

Les nanoparticules métalliques peuvent être pyrophoriques. L'aluminium, par exemple, présente cette propriété: il prend feu dès qu'il entre en contact avec l'air. Cela signifie que même de petites quantités peuvent constituer une source d'inflammation et provoquer un incendie ou une déflagration/explosion. De tels nanomatériaux synthétiques doivent donc être attribués à la catégorie AF (matières auto-inflammables), ce qui veut dire que leur seuil quantitatif est de 20 000 kg. Les entreprises qui stockent plus de 20 000 kg de ces nanomatériaux entrent dans le champ d'application de l'ordonnance. Les nanomatériaux synthétiques non métalliques connus des auteurs ne présentent pas de propriétés auto-inflammables.

Des calculs concernant le comportement d'agglomération et de suspension des nanoparticules laissent supposer que celles-ci s'agglomèrent rapidement. Le diamètre moyen des particules ainsi créées n'augmente toutefois que très progressivement et semble rester dans le domaine du nanomètre ou du micromètre. La sédimentation est

donc négligeable et les particules demeurent longtemps dans l'air. En cas de dissémination, elles ne se déposent que très lentement.

Dans le cadre de la présente étude, des déterminations mathématiques ont permis d'examiner comment se comportent des surpressions causées par explosion ainsi que les doses de rayonnement thermique des nanoparticules d'aluminium et de carbone, par comparaison avec les poussières conventionnelles et les deux substances de référence que sont le propane et l'hydrogène. Les surpressions sont similaires pour les deux nanoparticules étudiées, les poussières conventionnelles correspondantes ainsi que le propane et l'hydrogène.

La comparaison du rayonnement thermique et de la hauteur de flamme, sur la base des hypothèses mentionnées dans le rapport, montre qu'un déversement de nanoparticules d'aluminium adopte un comportement similaire à celui d'un feu de flaque d'essence. En revanche, les nanoparticules de graphite déversées réagissent de manière bien moins dynamique.

Conclusions de l'étude

Pour l'instant, les données dont on dispose en matière d'inflammabilité et d'explosibilité ne permettent pas de procéder à une évaluation générale définitive. Les connaissances actuelles ne justifient pas que l'on réglemente les nanomatériaux de manière spécifique dans le cadre de l'ordonnance sur les accidents majeurs.

> L'énergie minimale nécessaire pour enflammer des substances à l'échelle nanométrique peut différer de celle mesurée pour les poussières conventionnelles. De plus, les nanomatériaux métalliques, en particulier, peuvent présenter des propriétés pyrophoriques. Ces informations doivent figurer sur la fiche de données de sécurité.
> En ce qui concerne la surpression causée par explosion, les conséquences – pour les nanoparticules d'aluminium et de carbone – sont similaires à celles constatées pour les poussières ou substances conventionnelles correspondantes, qui sont soumises au même seuil quantitatif, sur la base de leur classification et de leur étiquetage en matière d'inflammabilité et d'explosibilité.
> Il n'existe pas à l'heure actuelle d'indice laissant supposer que les scénarios d'accidents majeurs des nanomatériaux se distinguent de ceux des poussières conventionnelles en ce qui concerne l'inflammabilité et l'explosibilité. Les prescriptions en vigueur pour les poussières doivent donc aussi être appliquées aux nanomatériaux.
> Les nanomatériaux que l'on doit compter parmi les substances dangereuses en raison de leur inflammabilité et de leur explosibilité ne sont actuellement produits ou utilisés en Suisse qu'en petites quantités, allant de quelques kilogrammes à une tonne au plus par an.
> En ce qui concerne les propriétés toxicologiques et écotoxicologiques des nanomatériaux synthétiques en lien avec l'ordonnance sur les accidents majeurs, leurs effets devront encore être évalués lorsque les données nécessaires seront disponibles.

1 > Introduction

1.1 Introduction and Questions Covered

Ordinance on the Protection against Major Accidents

The purpose of the Ordinance on Protection against Major Accidents (OMA)[1] is to protect the public and the environment against serious damage resulting from major accidents. Establishments are subject to the provisions of the OMA if substances are stored on their premises in quantities exceeding the quantity thresholds for substances, preparations or special wastes covered by the OMA. The quantity thresholds for substances and preparations can be determined from the list of criteria contained in Annex 1.1 item 4 OMA on the basis of their characteristics, or (for certain substances and preparations), directly from the list of exceptions. In this, the determination of the quantity thresholds is based on an approach that sets the characteristics of a substance in relation to the mass. Establishments subject to the provisions of the OMA must submit a summary report to the enforcement authorities containing, among other things, an estimate of the extent of possible damage. According to Handbook I of the OMA[3], the estimate must be based on accident scenarios. In selecting these, the type of establishment, the danger potential present in the individual installations in the company, as well as the possible accident causes and sequences of events based on a reasoned assessment. Where substantial damage to the public (more than 10 fatalities outside the company premises) or to the environment cannot be excluded, the enforcement authorities must require the owner of the establishment to submit a quantitative risk study based on accident scenarios.

The OMA differs from the regulations on workplace and consumer safety in that it protects the public and the environment from serious damage through exceptional events. In this, only persons outside the premises of the establishment are taken into account.

Synthetic Nanomaterials Plan of Action

Nanotechnology is a rapidly growing research and development area with increasing importance for the economy, research and society. It is therefore important to investigate possible risks comprehensively and if necessary to take measures to protect humans and the environment. The current discussion on the risks involved is concentrated on the synthetic nanomaterials used in nanotechnology. The purpose of the "Synthetic Nanomaterials" Action Plan[2] is to prepare the basis for the safe use of nanotechnology.

Question considered in the study

In the present study, a literature study and calculations are performed to determine in what way the fire and explosion properties of synthetic nanomaterials should be considered in the accident prevention measures, and thus whether this makes new accident scenarios necessary for nanomaterials. In a subsequent study, similar questions con-

3 Gay B. et al 2008: Handbook I of the Ordinance on Protection against Major Accidents.

cerning the toxic and ecotoxic characteristics will be considered in due course if necessary, and when sufficient fundamental data are available.

To clarify these questions, an investigation must be made whether the characteristics of substances in nanoparticle form must be assessed differently from the corresponding substances in powder form, since the quantity threshold and thus the scope of the OMA depend on the classification of a substance. In determining the hypothetical accident scenarios for nanoparticles, their agglomeration and sedimentation behaviour and their fire and explosion properties represent important parameters. On the basis of the above information, conclusions can be drawn and comparisons made with accident scenarios for powders.

1.2 Definitions

Nanomaterialien

Nanomaterials consist of very small particles with a size of 1–100 nm (nanometre). A distinction is made between the following types[4]:

> *Nanoparticles:* All three dimensions of nanoscale.
> *Nanofibres:* Two dimensions of nanoscale.
The third dimension is significantly larger.
> *Nanotube:* Tube type, hollow nanorod.
> *Nanoplates:* One dimension on a nanoscale.
The other two dimensions are significantly larger.

Agglomeration und aggregation[4]

> *Agglomeration:* Cluster of loosely bound particles in which the resulting surface area is of similar magnitude to the sum of the surface areas of the individual particles. The agglomerates are held together by weak forces, as for example Van der Waals forces.
> *Aggregation:* Cluster of particles in which the resulting surface area is significantly smaller than the sum of the surface areas of the individual particles. The aggregates are held together by strong forces, as for example covalent bonds or forces, which arise from sinter processes.

Deflagration, Explosion and Detonation[5,6]

> *Deflagration:* Combustion without confinement, with only limited effect. Speed of expansion 0.1–1 m/s, low pressure rise.

4 ISO/TS 27687 2009: (Technical Specification ISO/TS 27687, Nanotechnologies – Terminology and definitions for nano-objects – Nanoparticle, nanofibre and nanoplate, corrected version 2009-0201).
5 Bartknecht W. 1993: Explosionsschutz, Grundlagen und Anwendungen, Springer-Verlag: S. 52/195/265.
6 ATEX-Produktrichtlinie 94/9/EG (www.druckgeraete-online.de/seiten/frameset10.htm).

- *Explosion:* Rapid combustion, speed of expansion below the speed of sound, 1–333 m/s (speed of sound), peak overpressure up to approx. 10 bar.
- *Detonation:* Strong explosion, speed of expansion above the speed of sound, mostly above 1000 m/s, peak overpressure up to approx. 10 bar.

1.3 Nanomaterials used in Switzerland

Where the investigation of the fire and explosion properties is concerned, oxidable organic and metallic nanoparticles must be taken into account. Already oxidised nanoparticles, such as Al_2O_3, ZnO or TiO_2 are not relevant to the present study and are not considered further. Among the nanomaterials relevant to the study, fullerenes, carbon nanotubes (single und multi-walled), silver, iron, soot, polystyrene and dendrimers (repeatedly branched organic molecules) are the most widely distributed on the market.

By extrapolating the results taken from studies by Schmid et al.[7,8] on the use of nanoparticles in Switzerland, it can be concluded that approx. 600 companies employ nanomaterials. The greater part of these companies work with non-oxidable nanomaterials.

Nanomaterials are used in the following sectors of the economy:

- Chemical industry
- Paints
- Cosmetics
- Watches/optical apparatus
- Microelectronics, sensors
- The trades
- Milling industry
- Textile industry
- Cleaning agents
- Plastics industry
- Plating and surface treatment
- Suppliers of car parts, tyre industry
- Foodstuffs and food packaging
- Metal working (surfaces)
- Ceramics and glass
- Paper and printing industry
- Pharmaceutical industry
- Others

The study performed by Schmid et al[7,8] indicates that most companies store, process or produce significantly less than 1 tonne of nanomaterials that are relevant to this study. Certain companies, which work with organic pigments or carbon black have a turnover of approx. 100 tonnes per year.

Owing to the fact that the nano industry is a growing branch of industry, it is anticipated that the quantities will tend to increase.

[7] Schmid K., Riediker M. 2008: Use of Nanoparticles in Swiss Industry, Env. Science & Technology, Vol. 42 No. 7.
[8] Schmid K., Danuser B., Riediker M. 2008: Swiss Nano-Inventory, Final Report.

1.4
International developments

Major efforts are underway worldwide to quantify the risks of nanomaterials to health and the environment. Furthermore, international organisations and national authorities are working intensively on questions of regulation. Efforts are concentrated at present mainly on the preparation of fundamental data.

1.5
Major accidents

The authors have no knowledge either of releases of larger quantities of nanomaterials nor of major accidents affecting the public or the environment outside of the premises of an establishment, such as specified in Chapter 1.1. However, certain industrial accidents involving nanomaterials have been documented in the literature[9,10,11].

9 Kemsley J.N. 2008: Chemical & Engeneering News. (http://pubs.acs.org/cen/news/86/i09/8609news3.html)
10 Song Y., Li X., Du X. 2009: Eur. Respir. J. 34: 559–567.
11 ISO/TR 12885: 2008 Nanotechnologies – Health and safety practices in occupational settings relevant to nanotechnologies.

2 > Properties of nanoparticles

2.1 Agglomeration and sedimentation of nanoparticles

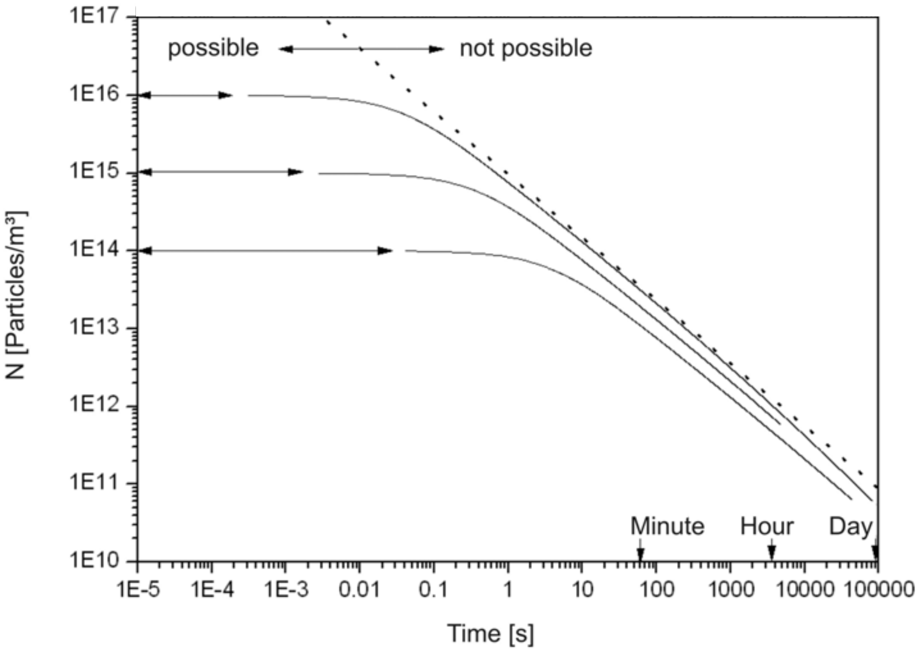
In the course of its investigations on the dispersion behaviour of nanoparticles, the Safety Institute entrusted the University of Applied Sciences Northwestern Switzerland with a study on the agglomeration and sedimentation behaviour of nanoparticles[12]. In assessing the danger to the public, the residence time of nanoparticles in the air is very important. In connection with the fire and explosion properties, the residence time determines the duration of the existence of an explosive atmosphere and in connection with the human toxic characteristics, it determines the duration of exposure of the public. To determine the residence time, it is of fundamental importance to know the relationship between the particle diameter and the sedimentation speed. In general, the sedimentation speed increases sharply with particle diameter. With particle diameters in the nanometre range, the sedimentation rate has a value of approx. $7 \cdot 10^{-8}$ m/s, and is therefore negligible. Particles with a diameter ≤ 1 µm can persist for hours up to days in the air, if their removal takes place solely through sedimentation.

The agglomeration of nanoparticles is a very significant, spontaneous phenomenon, leading to a reduction of the particle number in a given volume (and thus also of the particle concentration), whilst the sedimentation speed increases with increasing agglomeration. The agglomeration rate is proportional to the square of the particle number, that is to say that in a system with a large number of particles in a volume, the agglomeration takes place very rapidly, but with a low number of particles, only very slowly. In these considerations, other important parameters such as the material, the temperature and the humidity were not individually taken into account. In a monodispersive system, in which all particles have approximately the same diameter, agglomeration takes place more slowly than in a polydispersive system, in which coarser foreign particles still remain. This may be explained by the fact that agglomeration also takes place with the coarser foreign particles, and, since these represent larger “targets”, the nanoparticles are more likely to strike these than the smaller particles. Fig. 1 illustrates the agglomeration of nanoparticles having a diameter of 20 nm against time for three different initial concentrations. This system is initially monodispersive, but owing to the different agglomeration rates of the particles in time becomes polydispersive.

12 The study can be obtained from the FOEN.

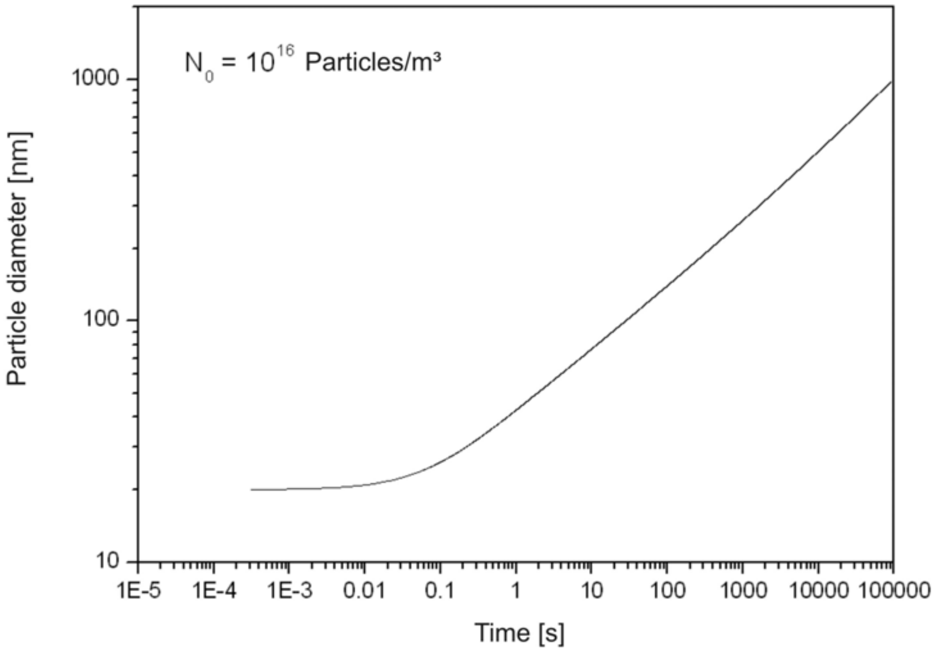
Fig. 1 > Particle concentration as a function of time for various initial concentrations in a monodispersive system

Dashed line: agglomeration limit.



With high initial concentrations, the agglomeration proceeds very rapidly, since the probability of collision is relatively high. After approx. 10 seconds, the particle number is still 10^{14} nanoparticles/m³, and after one hour, 10^{12} nanoparticles/m³. With low particle concentrations, agglomeration has practically no influence. The sedimentation rate also depends on the variation of agglomeration with particle diameter. Fig. 2 demonstrates that even for the release of very large concentrations of nanoparticles, agglomeration leads only to a very slow rise in the mean particle diameter, so that the role of sedimentation in removing particles from the air can be ignored. Owing to their small size, nanoparticles therefore remain much longer in the gaseous phase than traditional powders.

Fig. 2 > Mean diameter of the aggregated nanoparticles for an initial concentration of 10^{16} particles/m³



The rapid agglomeration of nanoparticles in the initial phase has also been demonstrated by G. Kasper[13]. In his work, he performed the following series of experiments. In a 2 m³ container filled with air, nanoparticles of platinum (diameter 10 nm) were injected. The agglomeration behaviour of these was then measured. After 3 minutes, the particle concentration was already heavily reduced.

Certain nanomaterials are specially treated to prevent agglomeration (see Chap. 2.4). How this treatment alters the fire and explosion behaviour is largely unknown. Investigations on this are necessary, particularly when these substances are manufactured on the scale of tonnes.

2.2 Oxidation sensitivity of nanoparticles

The oxidation sensitivity of nanoparticles is important in connection with serious accidents, since it has a decisive influence on the fire and explosion properties of the particles. It is related not only to the surface area, but also on whether or not the surface is covered by a protecting layer, as for example with aluminium. Furthermore, metallic and non-metallic nanoparticles display differing oxidation sensitivity, as described below[14].

[13] Kasper G. 2008: The life cycle of airborne nanoparticles, KIT Universität Karlsruhe, Paper given at the Nanosafe Konferenz Grenoble.
[14] Eisenreich N. 2008: Safety aspects and approaches for fire hazard classification of metal nanopowders, International Annual Conference of ICT: S. 55/1 bis 55/8.

2.2.1 Metallic nanomaterials

Minimum ignition energy

Metallic nanoparticles, e.g. aluminium, magnesium and titanium are pyrophorous, that is, they ignite on contact with the air. The minimum ignition energy for aluminium nanoparticles depends on the particle diameter, having a value less than 1 mJ for a particle diameter of 100 nm and approx. 7 mJ for a particle diameter of 200 nm[15]. Thus owing to their oxidation sensitivity even very small quantities of nanoparticles (in comparison to their non-pyrophorous powder counterparts) represent a possible source of ignition that can trigger a fire, a deflagration or an explosion. That metallic nanoparticles are not generally pyrophorous, is shown, for example, by nanosilver, which does not display this characteristic. For other metals used in nanotechnology, such as molybdenum, tantalum or tungsten, the pyrophoricity must still be experimentally clarified[16,17].

Nanoparticles freshly manufactured in an inert atmosphere display a significantly higher sensitivity to oxygen. This property can manifest, for example, through the following observations: self-heating and explosion, strongly reduced ignition temperatures and ignition energies, as well as increased speed of combustion[14].

Explosion overpressure

As shown by the maximum explosion overpressures in Tab. 1, aluminium nanoparticles tend to react somewhat less violently than the corresponding powders, but slightly more violently than non-metallic carbon nanoparticles. Possible reasons for the more sluggish behaviour of aluminium nanoparticles in comparison to aluminium powder could lie in the increase in the particle diameter caused by the rapid agglomeration of the nanoparticles in an already oxidised and inertised surface of the nanoparticles, and in the reaction mechanism of the combustion reaction (Chap. 2.3). Aluminium nanoparticles are often already agglomerated in their containers. Furthermore, agglomerates can form on filling them into the test apparatus.

2.2.2 Non-metallic nanomaterials

None of the non-metallic nanoparticles known to the authors display pyrophorous properties. In a comparison between multi-walled carbon nanotubes and carbon black powder, Vignes et al.[18] demonstrated that carbon nanoparticles react only slightly more violently than carbon powders. The reason for the similar behaviour of powders and nanoparticles probably lies in the rapid agglomeration of the nanoparticles and in the reaction mechanism described in Chap. 2.3.

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15 Bouillard J. 2008: Vortrag Nanosafe Konferenz Grenoble, Afsset Rapport No 2006/006.
16 Reuse P. 2007: Nanosafe II, Behaviour of nanopowder in the closed Hartmann tube and determination of the MIE, Institut for Safety and Security.
17 Reuse P. 2007: Nanosafe II, Comparison of the chemical reactivity of aluminium nanopowder Part I and Part II, Institut for Safety and Security.
18 Vignes A. 2007: Nano vs Micro: Estimation and modelling of the dust explosion sensitivity and severity, IChem Symposium Series No. 153.

2.3 Explosion properties of nanoparticles

2.3.1 Non-metallic nanomaterials

The work of Pritchard[19] and Bartknecht[20] shows that for organic particles both the maximum explosion pressure and the rate of pressure increase with decreasing particle diameter, but appear to level out for particle diameters of < 50 µm. This "plateau" effect is explained by the reaction mechanism of a fire reaction. In the case of a powder explosion of carbon powder or other organic materials, burning is always preceded by pyrolysis or devolatisation in the homogeneous gas phase. The particle size below which the combustion rate of the powder cloud no longer increases depends on the three reaction speeds of (a) pyrolysis or devolatisation, (b) gas phase mixture and (c) combustion of the gas phase. Below a sufficiently small particle diameter, combustion in the gas phase becomes the determining phenomenon for the combustion rate. Thus despite smaller particle diameters, and rising rate of pyrolysis, the combustion reaction can no longer be accelerated.

The "plateau" effect for organic powders from a particle diameter of approx. 50 µm described by Pritchard or Bartknecht is confirmed by measurements in the BIA report[21]. When the particle size decreases, the maximum explosion overpressure for methyl cellulose, polyethylene and flour increases up to a plateau of approx. 50 µm (Fig. 3). When the particle size decreases further, the maximum explosion overpressure increases only slightly. Denkevits et al. have also demonstrated the plateau effect for graphite powder[22].

The variation of the maximum explosion overpressure as a function of particle size for PVC, however, differs markedly from the other substances investigated (Fig. 3). For large particles > 150 µm, no explosion overpressure is detectable. Between 150 µm and approx. 50 µm, the increase is almost linear, but remains substantially below the niveau of the other three substances. When the particle size decreases further, the maximum explosion overpressure continues to increase. This behaviour shows that caution is needed in making statements about particles in the nanometre range, i.e. general conclusions cannot be drawn from isolated examples.

For carbon nanoparticles, the plateau effect probably applies, too, to particle sizes in the nanometre range. Data on the maximum explosion overpressure of carbon particles[15] with a diameter of 3 nm and 7.2 bar show that this is smaller still than that of carbon powder with a diameter of < 63 µm and a maximum explosion overpressure of 8.2 bar[5]. As the above-mentioned example for PVC with particle sizes in the µm range shows, all substances must be investigated experimentally for a possible plateau effect in the µm range.

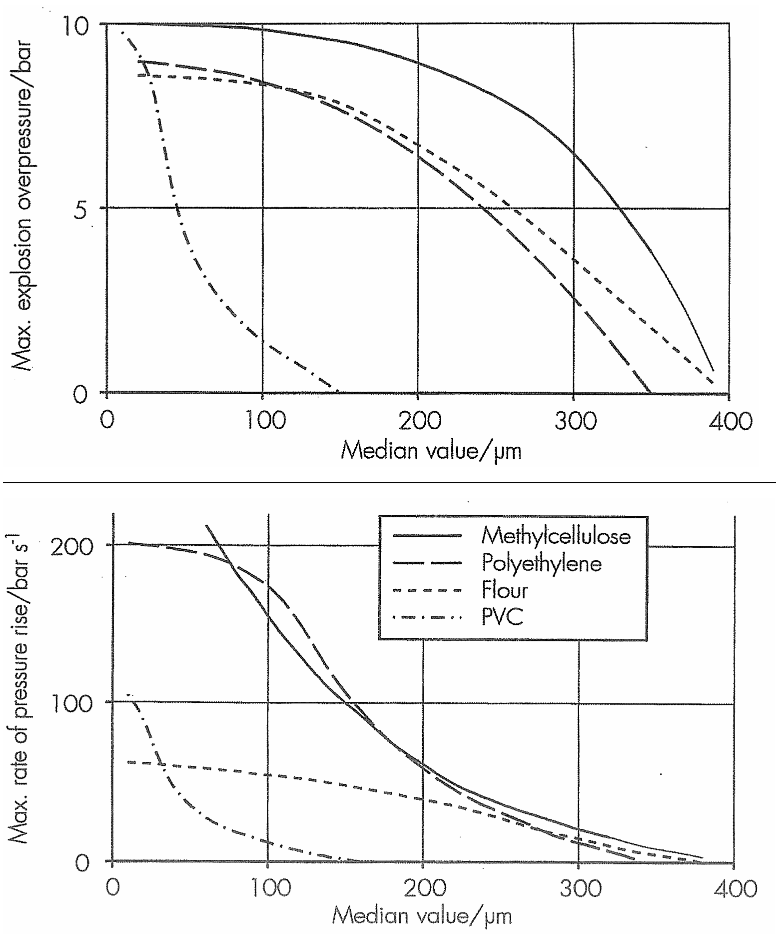
19 Pritchard D.K. 2004: Literature review: Explosion hazards associated with nanopowders, HSL.
20 Bartknecht W. 1993: Explosionsschutz, Grundlagen und Anwendungen, Springer-Verlag, S. 266.
21 Beck H., Glienke N., Möhlmann C. 1997: BIA-Report, Combustion and explosion characteristics of dusts, Berufsgenossenschaftliches Institut für Arbeitssicherheit.
22 Denkevits A., Dorofeev S. 2006: Explosibility of fine graphite and tungsten dusts and their mixtures, Journal of Loss Prevention in the Process Industries, Vol. 19: 174–180.

2.3.2 Metallic nanomaterials

In the case of metal powders such as aluminium and magnesium, a plateau effect must be anticipated at smaller particle diameters than for organic powders according to Pritchard et al.[19]. No experimental values could be found in the literature. Based on computations, however, Pritchard et al. were able to show that the plateau effect should occur for aluminium at a specific surface of 6.5 m^2/g. This would correspond to a particle diameter of 0.34 µm. Mechanistically, since metal powder explosions proceed unlike powder explosions with organic particles, the process stage that determines the combustion rate is different, so that the particle diameter at the point where the plateau effect occurs appears to become smaller.

For aluminium nanoparticles, the plateau effect probably applies, too, to particle sizes in the nanometre range. A comparison of experimental values confirms, for example, that the maximum explosion overpressure of aluminium nanoparticles with a diameter of 100 nm (8.2 bar) and 200 nm (9.5 bar)[15] does not increase in comparison to that for aluminium powder with a diameter of < 63 µm (12.5 bar)[5]. On the contrary, it actually decreases further. Here, too, it must be experimentally investigated whether this phenomenon generally applies to metallic nanoparticles.

Fig. 3 > Dependence of the maximum explosion overpressure on particle size[21]



2.4 Specially treated nanomaterials to prevent agglomeration

Until today, the following methods for preventing the occurrence of agglomeration have been known:

> *Coating of metallic nanoparticles with organic substances:*
  This method is only used in solution. Today, the quantities manufactured are very small.
> *Electrostatic charging of (metallic and/or organic) nanoparticles:*
  Static charging of nanoparticles can prevent agglomeration. In practice, when the nanomaterial is sprayed on a surface, the particles are charged, for example using electro spray methods. In this, only particles directly in the path of the spray jet are charged. For systemic reasons, no great quantity of charged material arises that can no longer agglomerate.

3 > Effects of explosion and fire

3.1 Explosion overpressures for nanoparticles, powders, propane and hydrogen

The effects of the accident scenarios described in Chap. 4 include overpressures caused by an explosion. In this section, a comparison is made of the overpressures that occur through an explosion of nanoparticles, powders, propane and hydrogen. For this, the bursting pressures of a sealed vessel of 20 m³ are calculated for explosions of fuel/air mixtures, and the maximum overpressures occurring recorded. The masses of fuel on the assumption of a stoichiometrically proceeding reaction are given in brackets.

> Explosion of a stoichiometric mixture of hydrogen and air (0.75 kg H_2).
> Explosion of a stoichiometric mixture of propane and air (1.65 kg C_3H_8).
> Explosion of a stoichiometric mixture of carbon nanoparticles (Printex XE2, 3 nm) and air (2.25 kg C).
> Explosion of a stoichiometric mixture of aluminium nanoparticles (100 nm) and air (6.75 kg Al).
> Explosion of a stoichiometric mixture of carbon powder (< 63 µm) and air (2.25 kg C).
> Explosion of a stoichiometric mixture of aluminium powder (< 63 µm) and air (6.75 kg Al)

The maximum explosion overpressure (p_{max}) in the vessel is reached immediately following bursting of the vessel. During the explosion, a small part of the energy is emitted in the form of heat radiation. Since an explosion proceeds extremely rapidly (in milliseconds), the heat radiation is likewise of only short duration. For this reason, the effects of the heat radiation are negligible in comparison to those of the overpressure. Tab. 1 shows the p_{max} values and the corresponding TNT equivalents of the energy released for the various substances.

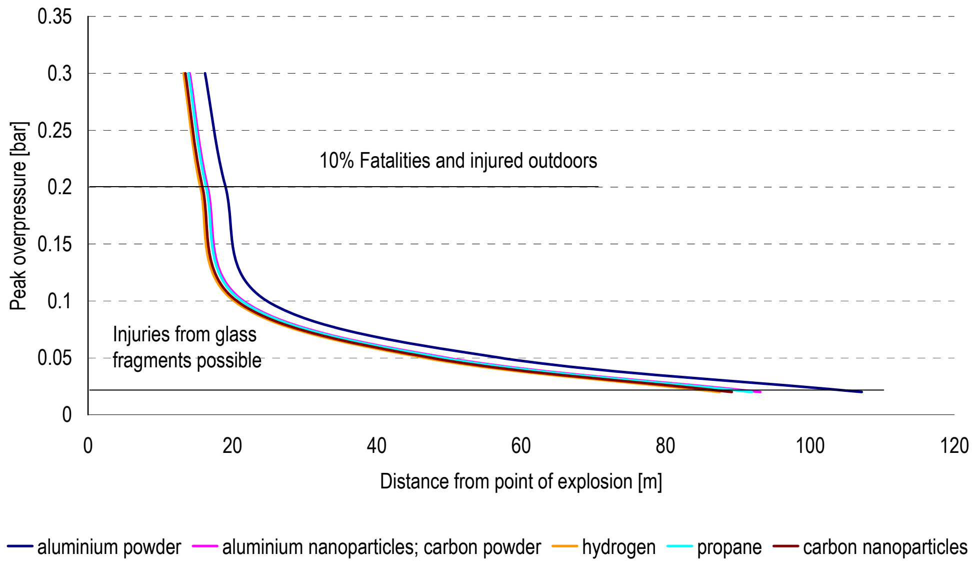
The equivalent quantity of TNT is determined based on the reference explosion energy of TNT of $4.69 \cdot 10^6$ J/k

Tab. 1 > Conversion of the maximum explosion overpressures in TNT equivalents of the energy released following bursting of a 20 m³ vessel

Substanz	Max. overpressure p_{max} [bar]	TNT equivalents [kg M_{TNT}]
aluminium powder, particle size < 63 µm[5]	12.5	13.5
aluminium nanoparticles, particle size 100 nm[15]	8.2	8.9
carbon powder, particle size < 63 µm[5]	8.2	8.9
carbon nanoparticles, Printex XE2, 3 nm[15]	7.2	7.8
hydrogen[5]	6.8	7.3
propane[5]	7.9	8.5

Starting with the maximum overpressures, the overpressures were calculated as a function of the distance from the point of explosion using figure 5.6 of the Yellow Book of TNO[23]. The results of this estimate are shown in Fig. 4.

Fig. 4 > Peak overpressures for bursting of a 20 m³ vessel with various substance-air mixtures



As shown in Fig. 4, the curves for all substances compared lie very close. In the present case of a 20 m³ vessel, fatalities must be anticipated up to a distance of approx. 20 m from the point of explosion, should persons be present within this distance. Injuries from glass fragments are possible up to a distance of approx. 90 m.

23 TNO, Methods for the calculation of physical effects, CPR14E, 3rd Ed. Revised, 2005.

3.2 Heat radiation for aluminium nanoparticles, graphite powder and petrol

The calculation[24] of the heat radiation (fire simulation), was based on the assumed ignition of 250 kg petrol, 250 kg graphite powder and 250 kg aluminium nanopowder. A pool fire of 250 kg petrol (density 780 kg/m³), with a depth of 0.1 m gives an area of 3.2 m². To obtain comparable results, this area was also used for the other substances.

For petrol pool fires (burning liquid), very well-established characteristic values are available, and these were used in the calculation. The combustion of graphite powder (burning solid) and aluminium nanopowder differs fundamentally from a liquid fire. As no values for the combustion rates for these two substances could be found in the literature, assumptions based on expert estimates made by the authors were used.

In the case of graphite powder and aluminium nanopowder, a smoothed equivalent surface (in this case the ground area of 3.2 m²) was used. No relation to the actual surface was made. The use of suitable simulation models to do so, the experimental determination of the necessary material characteristic values, and the modelling of the nanoparticles would have exceeded the scope of the study.

Tab. 2 > Summary of the simulation results

Product	Radiation Part	Combustion rate [g/m² • s]	Calorific value [MJ/kg]	Density [kg/m³]	Heat radiation [MW]	Flame height [m]	Distance for safety of persons (2.5 kW/m) [m]
Benzin	0.3	55	43.7	780	2.3	5.1	8.2
Graphit-Pulver (< 63 µm)	0.3	10 (assumption)	32.8	2200	0.3	2.3	2.6
Al-Nanopulver (100 nm)	0.3	80 (assumption)	31.5	2700	2.4	5.2	8.3

On the basis of the assumed combustion rates in Tab. 2, aluminium nanopowder shows a heat radiation comparable to that of petrol, i.e. approx. 2.3 MW, although the calorific value of aluminium is approx. 30 % lower. Furthermore, the flame heights of an aluminium nanopowder and a petrol fire are thus very similar. By contrast, graphite powder reacts much more sluggishly. The combustion rate was assumed to be lower, so that the heat radiation and the flame height are also lower.

The following effects can arise from the heat radiation, depending on the duration of exposure:

[24] For simulation model and assumptions, see Annex

Tab. 3 > Heat radiation and ist effects[25]

Heat radiation [kW/m²]	Duration of exposure [min]	Effect
2.5	0.5	Painful aching of the skin (criterion for safety of persons)
10.0	1.0	Spontaneous ignition of newspaper
20.0	1.0	Spontaneous ignition of furniture

It is noted at this point that in the case of dust eddying of nanomaterials in an unconfined environment, these can also burn as a ball of fire.

Tab. 4 > Classification and properties of nanomaterials and reference substances

	Aluminium nanoparticles (100 nm)	Carbon/Graphite nanoparticles (Printex XE2, 3 nm)	Petrol[26]	Propane gas	TNT	Hydrogen[26]
Quantity used[27]	B: 250kg E: 6.75 kg	B: 250kg E: 2.25 kg	B: 250kg E: ---	B: --- E: 1.65 kg	B: --- E: ---	B: --- E: 0.75 kg
Classification acc. to SI	AF	(HF)	F+	F+	E 1	F+
Quantity threshold OMA	20 000 kg	20 000 kg	200 000 kg	20 000 kg	2000 kg	5000 kg
Explosion overpressure	8.2 bar	7.2 bar	--	7.9 bar	--	6.8 bar
TNT equivalent	8.9 kg	7.8 kg	--	8.5 kg	--	7.3 kg
Heat radiation	2.4 MW	0.3 MW	2.3 MW	--	--	--
Boundary for safety of persons with fire	8.3 m	2.6 m	8.2 m	--	--	--
Lethality radius 10 % (Explosion)	ca. 20 m	ca. 20 m		ca. 20 m		ca. 20 m

25 SFPE Handbook of fire protection engineering, third edition 2002.
26 Substances and preparations with specified quantity thresholds (list of exceptions)
27 Quantities adopted in the calculations/simulations: B = fire; E = explosions (stochiometric relationship to 20 m³ air)

4 > Hypothetical accident scenarios with nanomaterials

Using the following scenarios, the object is to investigate whether accident scenarios with nanomaterials differ fundamentally from those of powders. Owing to the lack of fundamental data, as for example on explosion limits, a detailed treatment, as needed for example in an enforcement guidance document, was not yet possible.

4.1 Warehouse fire

Scenario

Breakout of a fire in a warehouse containing 1 tonne of metallic nanomaterial (pyrophorous) and 1 tonne of non-metallic nanomaterial. Through the rapid combustion of the metallic nanomaterials, a large fire breaks out. The resulting cloud of smoke possibly contains toxic nanoparticles.

Possible effects of the scenario on third persons

The cloud of smoke resulting from a fire can contain burnt and unburnt toxic nanoparticles. However, it must be expected that these nanoparticles agglomerate with the much larger smoke particles. Following this, deagglomeration of the particles can take place, for example, after their being washed by the rain into surface waters, leading to renewed release of the nanoparticles. To assess the effects, it would be necessary to take the human and eco toxicity of the oxidised nanoparticles into account in an additional study; for this, however, no fundamental data are at present available.

Measures to avoid the serious accident

Warehouses containing pyrophorous nanomaterial must be equipped with fire protection systems under warehouse regulations. In accordance with the applicable provisions, these substances must be stored in a separate fire sector[28].

Measures to limit the effects when an outbreak occurs

The company must have a contingency plan for the case of fire. The local fire service should be informed about the stored quantities, the type of chemicals, and about the measures required to combat the effects of the accident. Furthermore, it must be ensured that in the case of a serious accident, the public is given instructions on how to act.

[28] Lagerung von gefährlichen Stoffen, Leitfaden für die Praxis, Umweltfachstellen AG, BL, BS, BE, SO, TG, 2008.

4.2 Deflagration

Scenario

During the manufacture of metallic nanomaterials a deflagration occurs in the apparatus. A sizeable quantity of nanomaterial is emitted to the environment via the pressure release duct. The resulting cloud of nanoparticles is self-ignited. A secondary explosion results, leading to the formation of metal oxides in the form of nanoparticles. Depending on the weather conditions and the wind speed, these metal oxide nanoparticles can be further dispersed.

Possible effects of the scenario on third persons

Even when the opening of the pressure release duct lies directly on the periphery of the company premises, it may be assumed that neither further persons nor buildings are at risk from the resulting flame jet. The existing standards prohibit pressure release in areas in which persons or sensitive goods are present. As soon as the necessary fundamental data are available, the effects on humans and the environment resulting from the dispersal of the metal oxide nanoparticles must be investigated as part of investigations on human and eco toxicity.

Measures to prevent the serious accident

The production of this type of nanomaterials must take place under inert conditions. The inertisation must be monitored through technical measures.

Measures to limit the effects when the event occurs

If the inertisation cannot be assured with a high degree of reliability, the plant must be constructed to resist pressure. Pressure release systems should be avoided to prevent the release of toxic nanomaterials and reaction products.

4.3 Explosion

Scenario

During manufacture of metallic nanoparticles (normally under inert conditions), air finds its way into the production vessel. The pyrophorous particles ignite spontaneously, and an explosion occurs. The vessel suffers a burst, leading to the ejection of debris and release of oxidized nanoparticles.

Possible effects of the scenario on third persons

The overpressures can be estimated by a comparison with the results of the calculations of the effects, e.g. for hydrogen. As soon as the necessary fundamental data are available, the effects on humans and the environment resulting from the dispersal of the metal oxide nanoparticles must be investigated as part of investigations on human and eco toxicity.

Measures to reduce the danger potential

The quantity manufactured must be limited.

Measures to prevent the serious accident

The inertisation must be assured and monitored by effective technical measures.

Measures to limit the effects on occurrence of the event

Structural measures to prevent the release of nanomaterials or of oxidised reaction products must be considered in particular:

> Decoupling through technical anti-explosion measures
> Increased safety distances to neighbouring plant and to the periphery of the plot must be observed.
> Pressure-resistant construction
> Limitation of the release of oxidised nanoparticles

4.4 Comparison to existing scenarios

The above scenarios differ only slightly from those adopted in the chemical industry in the manufacture/processing of correspondingly active substances.

5 > Principal Results and Conclusions

5.1 Principal Results

The principal results are as follows:

Minimum ignition energy: Since the minimum ignition energy for metallic nanoparticles can be substantially lower than for powders, metallic nanoparticles might have to be differently classified and labelled. It must therefore be ensured that the data used to classify the fire and explosion properties are not simply taken from those for powders, but that separate tests are performed and that it is stated on the Safety Data Sheet to which particle diameters the classification and labelling given apply.

Explosion: In respect of their explosion properties, carbon and aluminium nanoparticles do not behave substantially differently to the corresponding powders. Experimental investigations must be performed to assess whether this is also true of other nanomaterials.

Fire properties: The heat radiation for aluminium nanoparticles calculated based on the assumptions given in the Annex can be compared with a pool fire of petrol. The heat radiation released on combustion of the same quantity of carbon powder is, however, much smaller. It must likewise be assessed here whether this conclusion also applies to other nanomaterials.

Tests required to provide the data for the Safety Data Sheet (SDS): Current knowledge suggests that the existing tests (for powders) are also applicable to nanomaterials. However, the test equipment and methods must be adapted to the properties of the new materials.[29] A particular problem in tests with nanomaterials is the rapid agglomeration of the particles and the resulting increase in the particle diameter. Owing to this, it is not the true properties of the nanoparticles, but instead those of the larger agglomerated particles that are measured. At present, investigations are in progress at international level under ISO and the OECD to determine whether the existing tests for chemicals may be used for the determination of the physico-chemical, toxicological and ecotoxicological properties, or whether these must be modified for nanomaterials. To permit classification and labelling of the substance, the following tests must be carried out under combustion and explosivity aspects, and the results noted in the Safety Data Sheets:

[29] Owing to the possible toxic properties of the nanoparticles, workplace protection must be considered in the tests.

– Determination of the particle size and statement on their agglomeration behaviour
– Explosion test
– Pyrophoric Behaviour
– Minimum Ignition Energy
– Explosion limits

5.2 Conclusions of the Study

Too few fundamental data are available on the fire and explosion properties of nanomaterials to enable final general conclusions to be drawn. The knowledge gained until now does not suggest a need for specific regulations for nanomaterials to be included in the Ordinance on Protection against Major Accidents.

> The minimum ignition energy of substances at a nanoscale can differ from that for conventional powders. Furthermore, metallic nanomaterials in particular can display pyrophoric properties. This data should be mentioned on the Safety Data Sheet.
> The effects associated with the explosion overpressure are similar to those of the corresponding conventional powders or substances, which, based on the classification and labelling in connection with the fire and explosion properties have the same quantity threshold.
> At present, there is no indication that the accident scenarios associated with the fire and explosion properties should differ from those for powders. Therefore the provisions applying to powders should also be used for nanomaterials.
> Nanomaterials, which owing to their fire and explosion properties must be assigned to the hazardous substances are manufactured or used today in Switzerland only in small quantities of several kg to a maximum of 1 tonne per year.
> The effects associated with the toxicological and ecotoxicological properties of synthetic nanomaterials must be clarified as soon as the necessary fundamental data are available, and before including them in the OMA.

6 > Future Perspectives

In the course of preparing the literature study, and during the review process of this study, further interesting questions have arisen, whose treatment was beyond the scope of the present study. They are listed here for the purposes of possible future research work.

> In Chap. 2.1, the agglomeration behaviour was investigated as a function of time and particle concentration for (initially) monodispersive nanoparticles. Further relevant factors, as for example material dependency, temperature dependency and air humidity were not considered. To obtain more precise results on dispersal behaviour, these factors must be determined and considered.
> The results obtained in the study for aluminium and carbon nanoparticles are based on the diameters quoted in the literature. To what extent the surface structure and coating may affect the properties was not found in the literature and must be investigated.
> To obtain generally valid results on the extrapolation of the explosion behaviour of powders to the nanometre range, further investigations must be performed. The question as to whether there is a relationship between the particle size and the maximum explosion overpressure cannot be conclusively answered based on existing research results.
> The model used to calculate the peak overpressure as a function of the point of explosion is based on the TNT explosion model, which is well-established in the field of overpressure calculations in accident prevention. The pressure-related processes involved in a TNT explosion differ, however, from those in a powder explosion. To what extent this has an influence on the peak overpressures as a function of the distance from the point of explosion must be assessed when more detailed models are available.
> The model used to calculate the heat radiation in Chap. 3.2 is based on a smoothed equivalent surface. To what extent an actual surface that takes the specific properties of nanoparticles more precisely into account would influence the results must be investigated. For this, more exhaustive models are required.
> Certain parameters for the calculation of the heat radiation are based on expert estimates, since fundamental data for this are not available. To obtain more precise results, and to verify the results, experimentally determined values must be obtained.
> Whether existing fire protection regulations for the storage of flammable substances are adequate for the storage of pyrophorous nanomaterials must yet be established.
> No data could be found in the literature on explosion limits of nanomaterials. This data is essential for the development of accident scenarios.

Following the release of nanoparticles from a container, these are dispersed in the air. As a result, their concentration, the agglomeration rate and the sedimentation rate are reduced. The nanoparticles persist over a longer period in the air. As the effect on humans depends on the exposure time and the toxicity of the nanoparticles, it must be investigated to what extent and for which limiting toxicity values the longer residence time in the air may have negative effects on humans.

> Annexe

Fire Simulation

FDS Software

The FDS simulation model (Fire Dynamics Simulator)[30,31,32] Version 5.2 (July 2008) is a member of the family of CFD programs (Computation Fluid Dynamics). It was developed by the US National Institute of Standard and Technology (NIST) and is in continuous development. Contrary to the zonal models, a CFD code has the facility to calculate the fire dynamics based on the classical Navier-Stokes equations. By this means, the equations of fluid dynamics can be more precisely solved than with zonal models. FDS solves the equations for mass, momentum and energy conservation for an ideal gas at low Mach numbers. Turbulent eddies are calculated using the LES (Large Eddy Simulation) based on the Smagorinsky method. The integrated combustion model is based on the assumption of an instant and temperature-independent combustion reaction at the calculated injection rate of fuel and oxygen. As shown by the latest comparisons with experiments, the FDS prediction gives values comparable to those of experiments for all decisive parameters, the differences lying within the range of mathematical uncertainty[33].

General

The Safety Institute has been mandated by the Federal Office for the Environment to calculate (using fire simulation) the heat radiation for a fire of 250 kg petrol, 250 kg graphite and 250 kg aluminium nanopowder.

The calculation of the heat radiation was performed using the FDS program (Version 5.2). For petrol pool fires (liquid fire), very well-established input parameters are available. These are used in the simulation.

> The combustion of graphite (solid fire with assumed particle size < 63 µm) differs fundamentally from a liquid fire, since the combustion behaviour is much more difficult to determine (pyrolysis) and is also dependent on the constellation, point of ignition and source of ignition.

30 McGratten K. et al. 2008: Fire Dynamics Simulator (Version 5), Technical Reference Guide, NIST Special Publication 1018-5, NIST, U.S. Department of Commerce, Washington DC (USA).
31 McGrattan K. et al. 2008: "Fire Dynamics Simulator (Version 5), User's Guide", NIST Special Publication 1019-5, NIST, U.S. Department of Commerce, Washington, DC (USA).
32 Forney G. 2008: "Smokeview (Version 5), User's Guide", NIST Special Publication 1017-1, NIST, U.S. Department of Commerce, Washington, DC (USA).
33 NUREG 1824 – Verification and Validation of Selected Fire Models for Nuclear Power Plants, U.S. Nuclear Regulatory Commission Office of Nuclear Regulatory, 2007.

> With a fire of aluminium nanopowder (assumed particle size 100 nm), the process depends not only on the chemical reaction kinetics, but also on the constellation, point of ignition and source of ignition.

Heat radiation

The following effects can result from the heat radiation (Tab. 5):

Tab. 5 > Heat radiation and its effects

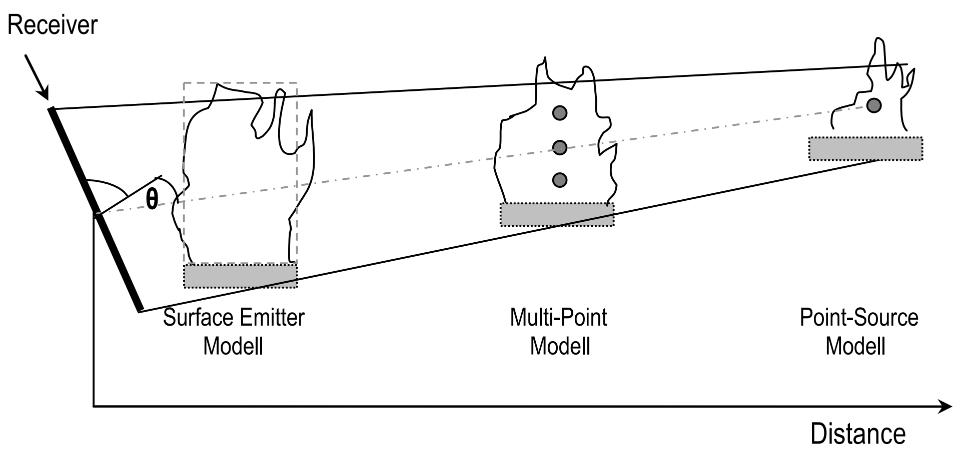
Heat radiation [kW/m²]	Duration of exposure [min]	Effect
2.5	0.5	Painful aching of the skin (Criterion for safety of persons)
10.0	1.0	Spontaneous ignition of newspaper
20.0	1.0	Spontaneous ignition of furniture

Calculation method

There are 3 methods to calculate the heat radiation on a receiver, depending on the distance from the receiver (Fig. 5) and on the complexity of the problem:

Fig. 5 > Models for the calculation of the heat radiation on a receiver, dependent on the distance from the receiver

Point source model (at right), multi-point model (at centre) and surface emitter model (at left)



Point-source model

Simplest model

$$\dot{q}'' = \frac{\dot{Q}_r \cos\theta}{4\pi r^2}$$

Multi-point model

For distances > 5D (D = fire diameter)

Surface emitter model

The heat radiation is calculated over an area and transferred to a receiver using a view factor.

The heat radiation Q_r for a point source model (generally used for liquid fires) is calculated as follows:

$$\dot{Q}_r = \tau X_r \dot{Q} = \tau X_r \dot{m} \Delta H_c A_f$$

The following tables give the available values and the assumptions made:

> The **emissivity** τ is normally set to 1.0:

Petrol	1.0
Graphite	1.0
Aluminium	1.0

> The factor X_r is the **radiation part:**

Petrol	0.3–0.6 (**0.3**)
Graphite	0.3 (**0.3**)
Aluminium	assumption **0.3**

> The factor $\dot{m}$ gives the **combustion rate** of the substance [unit g/m²s]:

Petrol	**55.0** g/m²s (Gasoline)
Graphite	Polypropylene 18.0 g/m²s (assumption **10.0** g/m²s)
Aluminium	assumption **80.0** g/m²s

> The combustion rates for solids are very difficult to determine (pyrolysis). Furthermore, they are also dependent on constellation, point of ignition and source of ignition.
> The **calorific value** ΔH_c of these substances is known:

Petrol	43.7 MJ/kg
Graphite	32.8 MJ/kg
Aluminium	31.5 MJ/kg

> The area A_f (**fire area**) is chosen to be equal for all substances (for comparison purposes), i.e. for graphite and aluminium, it must be assumed that the entire area immediately catches fire.

Petrol	Pool fire (density 780 kg/m³) 3.2 m² ground area with a depth of 0.1 m, giving 250 kg.
Graphite	Ground layer (density 2200 kg/m³) 3.2 m² ground area, giving a depth of 0.04 m at 250 kg. (Caution: regarded in the calculation as a compact solid body.)
Aluminium	Ground layer (density 2700 kg/m³) 3.2 m² ground area, giving a depth of 0.03 m at 250 kg. (Caution: regarded in the calculation as a compact solid body.)

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Abbreviations

p_{max}
Maximum explosion overpressure in bar

M_{TNT}
TNT equivalents in kg

Q_r
Heat radiation in MW

τ
emissivity-factor (normally set to 1.0)

Xr
Radiation part (factor)

$\dot{m}$
combustion rate in g/m²*s

Hc
Calorific value in MJ/kg

A_f
Fire area in m²

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