Nouryon Pulp and Performance Chemicals
PSRA

Our position regarding colloidal silica and nanoparticles

Bohus, Sweden, November 2021

- Nouryon fully recognizes the opportunities nanomaterials present and understands that, as is the case with all new technologies, health and safety issues must be fully considered as part of the innovation process when developing new products containing them. Safe use of all chemicals, including nanomaterials, is one of Nouryon' s top priorities.

- We have conducted an extensive testing program on various forms of colloidal silica covering inhalation toxicity, dermal penetration, sensitization and mutagenicity. The results of these studies demonstrate that colloidal silica can be used safely when handled as recommended by Nouryon.

In use for decades

Colloidal silica meets the size definition for nanoparticles and is manufactured using technology based on chemical understanding and techniques that date back to the early 1950s. Colloidal silica products have been widely used in a variety of industries since then. It is a proven technology that Nouryon masters since decades.
Engineering improvements made over the years allow much better control over the manufacturing process and thus much better product control. In addition, chemical innovations developed over time now allow us to devise and manufacture surface-modified colloidal silica that meet specialized customer requirements.
Modern "nano" colloidal silica products are designed to have enhanced properties compared to bulk silica and represent the continuation of decades of development.
Overall, production of colloidal silica is based on an old technology which has been improved to produce modern products, differing from the old ones in certain technical aspects, but comparable with respect to the absence of toxicological hazards.

Amorphous colloidal silica

All colloidal silica dispersions are nanoparticles per definition, otherwise they would not be sols (stable colloidal dispersions). On the other hand, when dried, these small particles irreversibly aggregate into much larger aggregates and agglomerates in the micrometer range.
The 100 % amorphous nature of colloidal silica has been extensively assessed through X-ray diffraction, SEM and TEM images. Analytical reports are available for a variety of colloidal silica grades.

Inhalation studies

Nouryon has commissioned acute inhalation toxicity studies with various colloidal silica products. The studies were performed according to OECD testing guideline 403 and GLP. As required, testing conditions were carefully chosen to ensure the material could reach the lungs by delivery as a respirable liquid aerosol with droplet size less than 4 micrometer MMAD (Mass Median Aerodynamic Diameter). Measures were taken to prevent, as much as possible, the silica nanoparticles would form larger-than-nanosized aggregates.
Under these conditions, the acute 4-hour $LC50^2$ values of the four tested colloidal varieties were all higher than 5000 mg/m3 (dry silica weight). This means that these materials are not considered hazardous or dangerous to health by inhalation, according to standards accepted worldwide.
Recently Nouryon has performed a 90-day inhalation toxicity study on colloidal silica, with a non-exposure (recovery) period of 3 months and under GLP conditions. The study was performed at concentrations of 0, 1,

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5 and 25 mg/m^3 of a liquid aerosol of silane modified silica (Levasil CC301). Two other types of colloidal silica (non-surface modified, and aluminate treated) were also tested at 25 mg/m3. The results of this study indicate that animal exposure to this colloidal silica resulted in local, transient pulmonary inflammatory reactions but not to chronic conditions as findings were clearly reduced at the end of the recovery period. The No Observed Adverse Effect Concentration (NOAEC) was 1 mg/m^3**.** These results are in line with other subchronic and chronic studies with different amorphous silica (Groth et al. 1981; Reuzel et al. 1991; McLaughlin et al. 1997; Johnston et al. 2000; Warheit 2001; Merget et al. 2002; Greer and Goldsmith 2007) in which it took more than 90 days and up to one year of non-exposure to obtain (almost) complete recovery (Reuzel et al., 1991). Also, even after a 5-day inhalation exposure period, full recovery was not obtained at the higher exposure levels within 90 days (Arts et al., 2007). The fact that pulmonary changes are transient is probably partly due to amorphous silica being weakly soluble in biological fluids and thus slowly disappearing from the lungs.

The acute and sub-chronic inhalation toxicity tests described above represent worst-case scenarios; Nouryon is confident that under normal conditions of spray application uses, such as hard surface cleaning, the aerosol droplet size will not reach respirable dimensions in sufficient amounts. The concentration of respirable particles in air will therefore be significantly lower than 1mg/m^3. In addition, epidemiological studies do not indicate that amorphous silica have any relevant potential to induce lung fibrosis in exposed workers (ACGIH 2001). Therefore, Nouryon believe that the use of our colloidal silica products in every application we recommend is safe when handled as recommended.

Other studies

Dermal
Skin exposure to colloidal silica may occur when handled and used in various applications. An in vitro study performed by Nouryon on four different types of colloidal silica (including unmodified and modified silica) showed that the dermal absorption of silica from any of these formulations was negligible.

Sensitization
A Local Lymph Node Assay (OECD 429) performed on a silane surface modified silica showed that the substance is not a skin sensitizer.

Genotoxicity
Three in vitro genotoxicity studies (OECD 471, 476 & 487) were performed on the same modified silica product showing that the substance has no genotoxic potential.

Environmental toxicity
Studies with colloidal silica, both untreated, 12 nm diameter and aluminate treated, 50-70 nm diameter, indicated that the acute aquatic toxicity of these particles is low (algae 72-h EC50, growth rate > 100 mg/L; Daphnia 48-h EC50 > 100 mg/L, Fish 96-h LC50 >1000 mg/L). There are also clear evidences that these particles adhere strongly to organic matter in suspension, which would lead to rapid clearance in wastewater treatment installations. Taken together, this supports our earlier position that modern colloidal silica can be considered environmentally safe.

Regulatory status

In a recent (2021) communication to all registrants of synthetic amorphous silica, ECHA has indicated that the substance evaluation process of synthetic amorphous silica is completed and that the information available in the REACh dossier is sufficient to address the hazard- based concerns indicated in the Community Rolling Action Plan (CORAP) in 2012. The conclusions of the CORAP can be found on the ECHA website.

Questions & Answers: Amorphous silica behavior

The following paragraphs summarize the behavior of silica in different applications and the likelihood of human exposure to nanoparticles.

Paper applications

1. Do any nanosized particles remain on the sheet after paper has been dried? How complete is the agglomeration? Is there a residual amount that does not agglomerate?

When silica nanoparticles are dried almost all the nanoparticles agglomerate irreversibly to big aggregates and agglomerates. When the nanoparticles come into close contact during the drying process strong siloxane bonds are formed between the particles due to the relatively high solubility of silica (in contrast to many other nanoparticles).

2. How stable are the dried agglomerates found in a sheet of paper? Can nanosized particles be reformed from the dried agglomeration during any downstream paper converting operations, such as folding, cutting, gluing, printing, wetting or heating?

When trying to de-agglomerate the dried particles with various techniques it could easily be shown based on particle size measurements (light scattering) that the original size could not be recreated.

3. If there are nanosized particles in a sheet (either residual from incomplete agglomeration or formed due to instability of the agglomerates), can they be released from the sheet during downstream operations such as folding, cutting, gluing, printing, wetting, or heating?

As mentioned previously, almost no nanoparticles remain and it is impossible to reform them.

Other applications such as coatings (e.g. wood, mineral, plastic or metal surfaces) and binder uses (e.g. catalysts, precision casting molds or ceramics).

1. How complete is the agglomeration of amorphous silica (SiO_2) particles, when colloidal silica is dried as supplied after being spilled or as part of a coating formulation together with organic polymers?

When silica nanoparticles are dried almost all the nanoparticles agglomerate irreversibly to large aggregates and agglomerates. When the nanoparticles come into close contact during the drying process, strong siloxane bonds are formed between the particles due to the relative high solubility of silica (in contrast to many other nanoparticles).

2. How stable are the dried agglomerates found on different substrates? Can nanosized particles be reformed from the dried agglomeration during any mechanical operations of a coated surface, such as wiping, folding, cutting, gluing, printing, wetting, or heating?

When trying to de-agglomerate the dried particles with various techniques it can easily be shown based on particle size measurements (light scattering) that the original size could not be recreated.

3. Does sanding dust from paints, lacquer and filler containing nanoparticles pose a risk?

A publication of the National Research Centre for the Working Environment in Denmark shows

that the addition of colloidal silica particles does not increase the adverse effects of sanding dust from paint, lacquer and fillers. As a matter of fact, “the results indicate that the matrix itself (paint, lacquer or filler) has a greater impact on the adverse effects than the addition of nanoparticles”.

4. If there are nanosized particles in a coating or any other form of dried layer (either residual from incomplete agglomeration or formed due to instability of the agglomerates), can they be released from the sheet during downstream operations, such as folding, cutting, gluing, printing, wetting or heating?

As mentioned previously, almost no nanoparticles remain and it is impossible to reform them.

Household applications; hard surface cleaning agents

1. Are silica nanoparticles present in sprayable versions of cleaning products? Is there a risk of inhalation of silica particles and if so, will these nanoparticles penetrate deep into the body?

Silica nanoparticles are present in formulations for hard surface cleaning. These formulations are applied on the surface using spray nozzles that release droplets of > 100 microns. These droplets can contain non-agglomerated silica particles; however, considering the size of the droplets they will not reach the lungs. They will be deposited in the upper respiratory tract, then ingested and finally cleared via the gut. As mentioned previously a recent 90 days inhalation study on silica establishes a NOAEC at 1mg/m^3 whereas the concentration of respirable particles in air will always be significantly lower than 1mg/m^3.

2. What happens when the product is applied on a hard surface?

When the product is applied on the surface it will form a film and dry out. When silica nanoparticles are dried almost all the nanoparticles agglomerate irreversibly to large aggregates and agglomerates. When the nanoparticles come into close contact during the drying process strong siloxane bonds are formed between the particles due to the relatively high solubility of silica (in contrast to many other nanoparticles).

Product Safety and Regulatory Affairs
on behalf of Nouryon Pulp and Performance Chemicals AB

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