Nanoparticles in chemistry and their industrial applications

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ABSTRACT

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Chemistry has anticipated for long the importance of decreasing the size in the search for new properties of materials, and of materials structured at the nanosize in a number of applications related to daily life.

Based on research initiated in the late 80s, industrial production of particles with controlled sizes at the nanometre scale is now possible.

Three main examples illustrating these achievements are presented : silicas for the reinforcement of mechanical properties of elastomers, cerium oxides as additives in the depollution of diesel engines, ceriul oxides as anti-UV in paints and coatings

1. INTRODUCTION

Micro- and nanotechnologies are at the centre of numerous investigations and huge investments, essentially in the areas of information technologies and health care. The technologies utilised mainly take advantage of microelectronics and/or more and more sophisticated "physical" techniques (laser ablation, PVD, ..).

On a different hand, chemical industry has anticipated for long the importance of decreasing the size in the search for new properties of materials, particularly when materials are structured at the nanosize. This has led to a number of applications related to daily life. For example magnetic recording media (chromium or iron oxides), photographic emulsions (silver halogenides), catalysis (precious metals) applications successfully developed by using dispersions of nanoparticles in various application media.

Today, based on research initiated in the late 80s, we at Rhodia are mastering industrially the synthesis of particles in a range of sizes from 5 to hundreds of nanometers and their functionalisation for adaptation to use in specific application media.

Three main examples illustrating these achievements are presented here-under :

- the use of precipitated silicas for the reinforcement of mechanical properties of elastomers,

- the use of cerium oxide dispersions as additives for the depollution of diesel engines,

- the properties of cerium oxide as an active element for the protection of coatings against degradation by UV radiations.

2. PRECIPITATED SILICAS FOR RUBBER REINFORCEMENT

Precipitated silicas are traditionally used as reinforcing fillers in rubber applications. For example, these white reinforcing fillers give an improved resistance to wear and tear to the soles of athletic footwear, without any constraint on the option of accessing to all possible colours through complementary addition of dyes or pigments in the formulation. On another hand, precipitated silicas are often used to increase tear resistance or to decrease self-heating in technical rubber parts.

In the tire industry, silicas have initially been used to improve the tear resistance of truck and heavy equipment tires, and also to enhance adhesion between the metallic reinforcement and the rubber of radial tires. Over the two last decades, the use of precipitated silica has been extended to passenger car tires. Owing to its excellent dispersion capacity, a new-generation of Rhodia's silica (HDS/Highly Dispersible Silica) has permitted to develop the « green tires », which have among other properties, low rolling resistance and improved wet grip, while maintaining longevity

This optimum combination of properties was impossible to obtain with the conventional precipitated silicas. Finely tuning the precipitation conditions has made it possible to synthesize at the industrial scale a very specific, highly dispersible, silica. Additionally, and owing to the control of the surface properties, silica – polymer interactions can be managed as well at a very intimate level.

Precipitated silicas are obtained in aqueous medium through neutralisation of sodium silicate by an acid solution. The most accurate control of this step is a key point, as the physical and chemical properties of the obtained silica, and particularly its dispersion behaviour, strongly depend on the first steps of the particles nucleation. Precipitation controls the obtention of aggregates of tens of nanometers.

Further washing, filtration, drying and shaping steps allow to obtain a ready-to-use silica in various forms adapted to the application forecasted : powder, micropearls, granules,… Aggregates agglomeration is controlled and reversible, and these can be restored in the application medium through shearing. The final properties in the application are completely mastered by the synthesis and shaping of the particles.

During the rubber mixing process, the agglomerates of silica are broken into the original aggregates. Such aggregates, really dispersed within the rubber, are nanometric reinforcing fillers. A key reinforcement parameter is the total filler contact area within the rubber. For dispersed aggregates, the contact area between polymer and filler is managed by the size of these elementary particles. Unbroken agglomerates are considered as defects which act notably in the negative way at high deformations. Thus monitoring the highest degree of silica dispersion is a key parameter for the reinforcement.

Silanols are the main components of surface chemistry of precipitated silica, and the main source of interactions between precipitated silica and elastomer formulation. But these interactions are not strong enough to avoid decohesion under strain between polymers and silicas. In order to modify the silica-rubber interface, several interfacial agents can be used from the silane family, either coupling agents (TESPT - MPTES) or covering agents (alkylsilanes). They react on one end with the silanols of the silica surface and on the other end with the rubber by the way of specific chemical functions.

The interface between silica and rubber has proved to be a key parameter to describe the Payne effect (behaviour at low deformations) but it is also an important parameter to obtain a reinforcement at large deformations. The higher the permanent interactions (coupling) between rubber/silica, the lower is the Payne effect and the higher the reinforcement at large deformations. Such parameters as the specific surface of the filler, the amount of filler which controls the total interface area, the nature of interface agent, and the optimum dispersion of the silica, which can be readily obtained with the new Z1165 MP, allow to obtain the best properties and have been of considerable impact in the development of new, high performance, "green tires".

More recently, and owing to the knowledge developed in the surface modification of silicas, we have been able to synthesize a new gamut of silica (Sil*O*a$^{TM)}$. The physico-chemical characteristics of this silica are a very low surface density of silanols and high degree of openness of aggregates, which make it well adapted to applications in silicones (EVC) and transparent rubbers. This represents a break in the utilisation of precipitated silicas in silicones and rubbers.

3. NANO-CEO2 DISPERSIONS AS DIESEL FUEL ADDITIVES FOR FUEL-BORNE CATALYSTS SYSTEMS

Since the early 80s, catalytic systems for the depollution of automobiles have allowed to decrease emissions of CO, NOx, and unburnt hydrocarbons at the level of tens of ppm. They consist in the dispersion at the nanoscale of particles of precious metals on a support made of Alumina and Cerium-Zirconium mixed oxides, eventually doped. The development of these systems was only possible owing to the ability to prepare oxide powders textured at the nanometric scale, which allows saving high specific surface areas at elevated temperatures, resulting in good and constant reactivity of the catalyst along the lifetime of the muffler.

The problem of diesel exhaust control was a different case to solve, and the set up of Fuel-Borne Catalyst (FBC) for Deep Particulates Filters (DPF) regeneration has been one of the means to get cleaners diesel cars. It also represents a very good illustration of the positive role of nanoparticles, in this case to allow control of car emissions.

As a matter of fact, particulate filters have been developed for diesel cars, in order to capture the soots generated by diesel oil combustion. But along with the life of the car, a problem arises, due to the filling of the filter, which may induce the total stop of the engine. Filters are thus useful only if their regular regeneration is possible. To this goal, Rhodia proposed to utilise a Cerium based catalyst that can be continuously introduced in the diesel oil before the combustion chamber. We could stabilise dispersions of Cerium oxide nanoparticles, pure or doped, that allow the feeding of the catalyst in the combustion chamber through a perfect dispersion in the diesel oil, and the formation of an intimate mixture with the soots in the combustion chamber. These "composite" soots are collected in the filter and the combustion is operated every 500 to 1000 km when the back pressure on the filter becomes too high. Owing to the strong oxidation power of cerium and the intimate contact between the nanoparticles of the catalyst and the soot in the filter, the combustion temperature of the soots can be decreased to temperatures as low as 400 -450°C.

This catalyst is so effective that such a low dosage as 10 ppm of the diesel oil allows the complete combustion of soots in some minutes. Today only two litres of EOLYS^{TM} suspension allow an effective depollution of a diesel engine for as long as 180 000 kilometres. New generation of additives, on the way to their development, will allow an even more effective functioning, up to 240 000 kilometres.

This development was only possible through the combination of several complementary expertises :

- new developments in wet inorganic synthesis, and the capacity to control particle size at the level of 5 nanometers, on well defined crystalline particles, with a high degree of monodispersity.

- the definitive contribution of the physical chemistry of complex fluids, which allowed the selection of the most adapted additives to the formulation in order to stabilize cerium oxide nanoparticles in any kind of dispersed medium, either acidic or basic, and finally organic owing to the possibility of phase transfer. Most of all this has been possible at elevated concentrations, up to 400 g/l, when conventional synthesis methods for the stabilization of small particles suspensions work generally only at very high dilutions. Stabilisation of nanoparticles in organic media allows to obtain colloidal suspensions with high stability and perfectly compatible with the various kinds of diesel oils found on the market, without any demixing problem

- the capacity to extrapolate this synthesis at the industrial level, making it possible to prepare the necessary quantities for such a development. Control of the size and degree of agglomeration of the nanoparticles have make it possible to stabilize a catalyst composed of nanoparticles of 3 to 5 nm in size, completely individualized.

The use of a Fuel Borne Catalyst for diesel particulate filter regeneration combined with engine management is now a proven technology with now more than 1,5 million diesel passenger cars equipped in Europe without any recall nor failure since its introduction in 2000.

4. APPLICATIONS OF CERIUM OXIDE NANOPARTICLES IN UV-PROTECTIVE FORMULATIONS

The utilization of Rhodia's experience in the stabilization of cerium oxides nanoparticles can also be taken advantage of for UV-protective coatings, particularly when transparency is required in addition to the protection to UV rays.

Stable sols of cerium oxide nanoparticles with diameters of 10 nm, appear as a clear liquid suspension, owing to the small size of the particles with respect to visible light wavelength.

With a charge transfer band located between 3.0 and 3.2 eV, Cerium oxide shows a cut-off threshold at around 370nm, well adapted to UV absorption, and does not show photocatalysis, as the charge carriers recombination is very fast, before they migrate to the surface to cause the creation of free radicals.

As cerium oxide has no other absorption in the visible band (between 400 and 800nm), transparent UV protection can thus be obtained in materials, provided incorporation can be managed in the formulation.

To this goal, we have developed a set of proprietary treatments which can be used to obtain alkaline aqueous cerium oxide sols (from 100 up to 300g/l solids content), as well as organic sols with the same high concentrations.

Standard aqueous and organic wood stain formulations (respectively acrylic-polyurethane and alkyd formulations) have been prepared using nano cerium oxide dispersion as an additive.

Ageing standard Xenotest tests of the formulations have been performed (874 hours accelerated test) and showed the very good effect of cerium oxide based formulations protect. These were further confirmed by natural exposure tests.

In addition to the long lasting UV protection, secondary benefits have been evidenced : hardness and abrasion resistance tests, tensile properties performed on the coatings show that the surface mechanical properties (hardness and scratch resistance) are clearly improved by cerium oxide nanoparticles. Lower water sensitivity has also been shown.

The combination of the performances obtained allows to position this technology as an additive for long lasting UV protection with protections in the 10 years range at least.

5. CONCLUSIONS AND PERSPECTIVES

Mastering the synthesis and formulation of nanoparticles at the industrial scale has made it possible to develop applications both in the dispersed state and in the area of nanostructured materials.

Coupling the skills in mineral synthesis, organic synthesis, physical-chemistry of complex media, and physics of materials, is a necessary element to the success of these developments. These are finally made possible by the capacity to develop at the industrial scale the processes adapted to the synthesis and stabilisation of nanoparticles.

Other developments are underway, for example in the area of thermoplastics where reinforcement and gas-barrier effects can eventually be obtained owing to the use of lamellar zirconium phosphates (alpha form). Further identification of nanoparticles potentiality through the better knowledge of their application properties, and the correlating these to the unmet needs expressed by the application markets will with no doubt open new areas for the development of nanostructured materials.