Nanoparticles for coatings. Why is reality so much less than the promise?

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We're a typical coating company. We need to respond to the challenges of new products for our customers and one way forward is to use nanoparticles to create extra functionality. Lots of other coating companies are doing the same.

In our case the products are hardcoats for high-end applications. Each hardcoat must combine multiple (sometimes conflicting) functionalities – toughness, hardness, clarity, flexibility, anti-microbial, anti-static, anti-smudge. If a typical product is 1m m^2 per year and a typical coating is 5µm thick with 20% nanoparticle, then that's 1 gsm of nanoparticles in the coating which works out as 1000kg (2000lb) of nanoparticles per year. That's not a vast quantity, but it has the prospect of being a mutually beneficial business for nanoparticle suppliers and for us.

For other companies the details will be different, but the general shape of the opportunity is similar.

The good news

The good news is that there is no shortage of companies out there ready to offer nanoparticles. And there are lots of different ways to prepare them:

- Flames
- Plasmas
- Precipitates
- Sol gel
- Microemulsions
- Etc.

There's more good news. There are particles out there that deliver the functionalities we need:

- Hardness
- Scratch resistance,
- Anti-static
- Anti-microbial,
- Anti-smudge
- UV absorbing
- High refractive index
- Etc.

But there's plenty of bad news to follow.

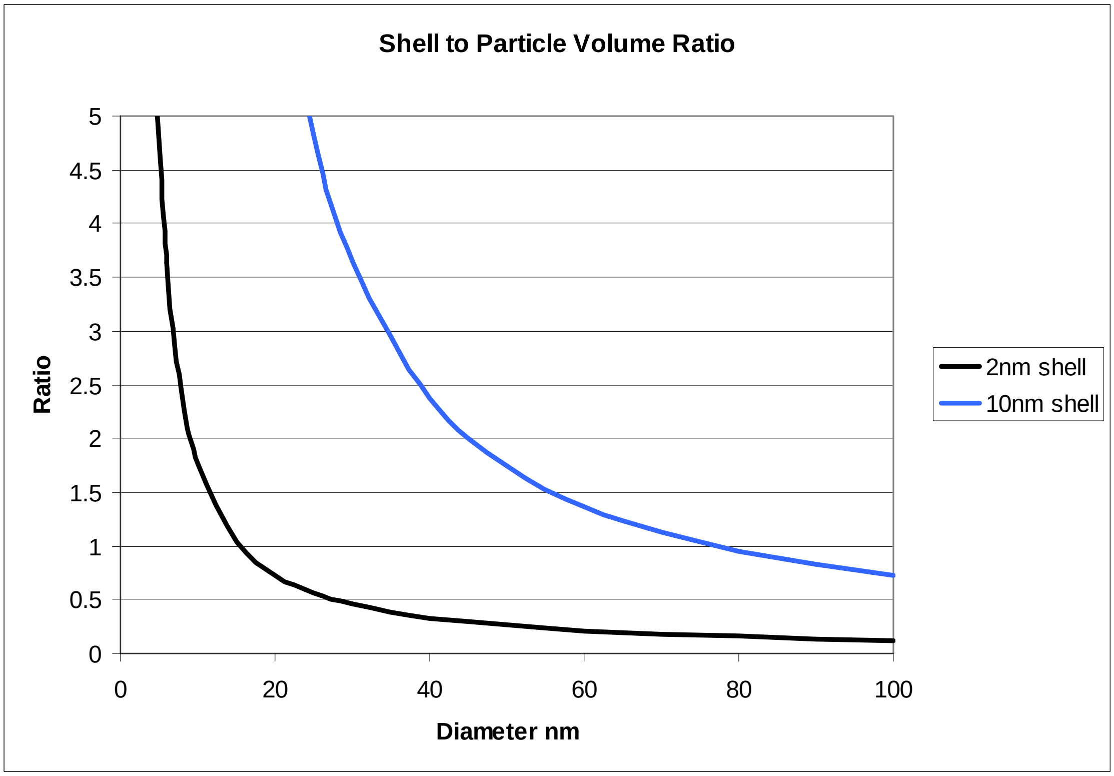
Problem #1 – Nanoparticle safety
I don’t want to handle nanoparticle powders. This is mostly because I’ve promised my workforce that we won’t bring in any new nanoparticle powders since none of us know the health risks from such powders. Instead we are following the advice of the UK’s Royal Society and assuming that (within reason) nanoparticles dispersed into a liquid media are OK to handle. This is a simplistic position to adopt, but despite much effort and many promises, the amount of solid SHE advice on nanoparticles that we can apply to our businesses is minimal. In turn this is due to the fact that the problem is a tough one for regulatory committees to get their heads around.

Problem #2 Dispersion
I also don’t want to handle nanopowders because I am not an expert at dispersions. Sure, I can disperse most normal pigments/powders. But there’s no way I can acquire the specialist knowledge and equipment to disperse the huge variety of nanoparticles that are on offer to me.

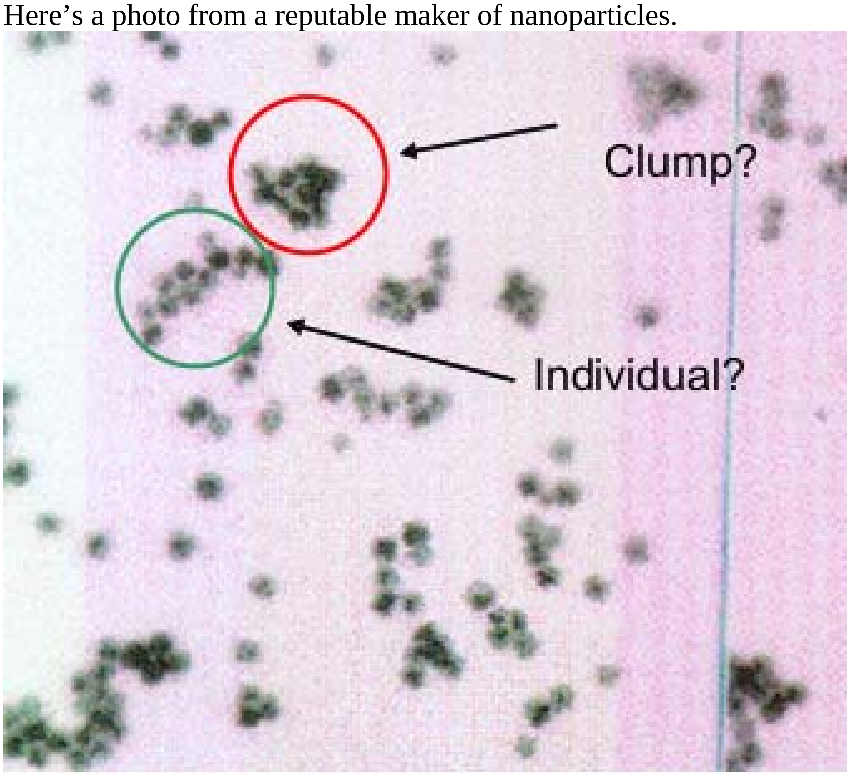
And I can speak from experience on this. We have an excellent supplier of nanosilica. With their help we created a hardcoat formulation that worked very well in pilot trials. Then, without warning, our nanodispersions started to go solid. Our supplier confirmed that it was a problem with their dispersion and it took a year of hard work before they could offer us a stable reformulation. This is not because they were stupid or lazy; they’re a great company. It’s simply because fine silica in acrylates loves to start cross-linking them. Finally, once we’d confirmed we had a stable formulation, we scaled up onto our big machine. The coating run failed before it started – the formulation went solid instantly inside our filter cartridges. It was some months later when our filter supplier made a casual comment about trace contaminants in their type of filter that we found the root cause of this disaster. Life at the bleeding edge is tough!

Problem #3 The case of the absent nanoparticle
If I buy, say, 1 kg of nanoparticle I might naively think that I’m buying 1kg of nanoparticle. But there’s a good chance that I’m buying quite a large amount of organic gunk instead. This isn’t because the nanoparticle supplier is trying to cheat me. It’s because the supplier is trying to keep my nanoparticles from clumping.

The reason is shown in the graph. The lower axis shows the diameter of the nanoparticle. The upper axis shows the ratio of the volume of the dispersing shell (typically some long-chain surfactant) to that of the nanoparticle. The upper curve is an extreme, but it makes the point. If I have a 10nm shell material sitting around a 25nm particle then the volume of the shell is $\pi(45^3-25^3)/6 = 39532$ and the volume of the nanoparticle itself is $\pi(25^3)/6 = 8181$, a ratio of almost 5:1. The 45nm comes from the fact that there’s 10nm of shell either side of the 25nm particle. I admit that this is an unlikely scenario. But even with a 2nm shell, 33% of the volume of your particle is dispersant! On a 10nm particle, the same 2nm shell is 1.7 times more volume than the particle itself.



Problem #4 – What size are my nanoparticles?
Here's a photo from a reputable maker of nanoparticles.



Now if you were the maker, would you say that that clump near the top is just a bunch of discrete nanoparticles, or would you say that it's a big non-dispersed lump? And if you are the purchaser, would you be confident that you were getting lots of small particles, or would you think you were getting some big lumps. As it happens, that "clump" is a statistical freak in the image and the particles really are well-dispersed. But it took my supplier a lot of work to prove it (and that's why I called them a reputable maker!).

It is *very* hard to measure nanoparticle sizes.

There's another trick that bad suppliers can play on you. If you measure your particles and report the *number* average, you will be able to claim, say, 99% < 10nm. But if you report the *weight* average of the same dispersion, you might only be able to claim 75%<10nm. This is because, for example, a single 1µm particle is equivalent (in weight terms) to 1 million 10nm particles.

Does it matter? Yes and no. For some applications, such as those requiring crystal clarity, just a few "big" particles can be a real problem. For other applications the same few "big" particles will not be noticed. You simply have to be aware of the number/weight average difference and make sure you know which you are getting and which is best suited for your application.

Problem #5 – Nanoclays or lumps of rock?

I think that nanoclays have a great future. In fact, for some applications they are already a storming success. Throw an average nanoclay into a nylon formulation and just about every desirable property improves. Yet for most of us they are a crashing disappointment. A nanoclay is only good if it's "exfoliated", i.e. split apart into individual nano layers. This is usually achieved by ion-exchange removal of the (sodium) ions holding the layers together and replacement with quaternary ammonium ions that are highly compatible with your formulation. Clays are great because they are cheap. But it's not cheap to do a 100% replacement of sodium ions and, at the same time, ensure there isn't some excess of dispersant which can mess things up for you. It's also not cheap to find out which is the perfect quaternary ammonium salt for compatibility with your coating. If you don't have the right compatibility you might as well throw lumps of rock into your formulation.

This is a tough problem. I've waded through acres of papers on nanoclay dispersions. It's hard to find the most compatible clay, it's hard to prove that you've got good exfoliation, it's hard to ensure that you get improved toughness, barrier properties or whatever it is you are seeking. And, above all, it's proving hard to make sense of the science behind it all, partly because modest levels of impurities in the (cheap) can have a dramatic effect on the scientific outcome.

Problem #6 – Carbon nanotubes or a tangled mat?

The same thing applies to carbon nanotubes. Sure, they will take over the world and are wonderful in every way. But just try getting them to prefer to be dispersed within your matrix rather than form a tangled mat amongst themselves. The science of doing this is slowly advancing, but for most of us we see more "slow" than "advance".

Problem #7 – None of us can solve the problems on our own

I would love to sit around waiting for the salesman to call with a tanker load of perfectly dispersed infinitesimally small nanoparticles, infinitely stable.

The disperser companies would love to sit by their phones ready to take orders for their dispersing equipment and chemicals

The nanoparticle makers would love to simply ship large bags of particles to happy customers.

Makers of AFMs, TEMs, SEMs and other expensive analytical equipment would love to take orders for their machines from all of the above.

But it’s not going to happen. We can’t go it alone.

The solution
For nanoparticles to take off it needs all of us to understand the problems, to understand that they are not going to be solved easily and to work across the boundaries to reach solutions. It needs a network of the nano community facing up to the issues and coming up with solutions.

Nanoparticles will be a big part of this industry. But to be a big, mutually profitable part will require a large cooperative effort from all of us.