Organic Pigments
Well-established Nano Materials

The economic importance of the organic pigment industry

Several hundred companies globally produce organic pigments in synthetic processes. Around 90% of these businesses are small and mid-sized enterprises. With roughly more than 100,000 staff they achieve sales of 10 billion Euros. Both the EU and the US are major production locations and additionally the head offices and centres of technology expertise of major organic pigment manufacturers are located there. US and Europe represent more than 50% of the global demand for organic pigments.

What does “nano” mean?

The term or prefix “nano” is used often without any clear understanding of what is meant by it. Nano materials are generally considered as materials of a size of the order of 100 nm or less, and currently international organisations are trying to agree definitions. Chemical, physical and biological substance properties of particles and structures, which do not materialize in macroscopic objects of the same composition, may be brought about in the nanometer range.

Nano materials are considered new and technologically advanced and expected to offer benefits to society both in high tech area such as Life Sciences, electronics and optics as well as to more traditional areas such as engineering, household appliances and cosmetics. Along with the benefits there is as well the concern that the very small particle size may also give rise to properties which may be hazardous both to humans and the environment.

ISO has been charged with defining nanomaterials and draft ISO TS 1291 proposes the following:

Nanopowder: Solid particulate substance containing nano objects or agglomerates or aggregates of nano objects

Nanoobject: Material with one, two or three external dimensions in the nano scale

Nanoscale: Range from approximately 1 nm to 100nm

What are organic pigments and where are they used?

Organic pigments are substances which consist of solid particles and are insoluble in the application medium, as described in the definitions of standard DIN EN 55943. Thus they are differentiated from dyestuffs which also consist of solid particles but are soluble in the end application medium

Standard DIN 55944 lists pigments according to colouristic and chemical aspects. Organic pigments are used for colouring purposes in a wide variety of end application media e.g. coatings, both decorative and protective paints for buildings and machinery; plastics, printing inks, candles, paper products, pharmaceuticals, rubber materials, abrasives, soaps, decorative cosmetics, toys, road signs, safety technology equipment and road markings. Many more examples can be provided. Pigment applications demand properties such as e.g. dispersibility, colour strength, light and weather fastness, migration resistance, colour shade and hiding power. These properties depend both on the chemical composition of pigments and on the size and morphology of their particles. In the beginning it was observed experimentally that for example colour strength was strongly influenced by particle size and in the sixties the effect of particle size on optics of pigmented systems was put on a sound theoretical basis using Mie theory.

This showed that for colouristically strong organic pigments there was a very marked dependence of optical properties on particle size; the maximum colour strength was given when the particles in the final application media were approx one twentieth of the wave length of light. This size also gave very transparent systems which for example in the printing industry is desirable.

From this time onward much of the research and development work concentrated on producing very small particles referred to then as sub-micron particles – which we now call “nanoparticles” – while at the same time ensuring that other properties were not too adversely effected.

Pigments are optimized for specific application conditions, often by way of mechanical and chemical surface treatment. The thickness of such layers on pigment surfaces is determined exclusively by the sought technical properties.

Organic pigment production

Organic pigments are generally manufactured by a “bottom-up” process though there are a few “top-down” processes in use. In a typical “bottom-up” process the raw materials are brought together and reacted to give the colour producing molecules, which nucleate and then as the reaction continues new nuclei are formed while those already formed grow to give the so-called primary particles with a high surface energy. As the manufacturing process continues, the primary (individual) particles assemble together to build larger clusters referred to as aggregates or agglomerates depending on their structure. This building of larger particles is from process considerations absolutely necessary or else it would not be possible to separate the particles from the reaction media. Additionally at the end of reaction the slurry may be heated up to around 100°C, this would be expected to anneal the surface reducing the surface energy and at the same time “Ostwald ripening” occurs; the very small particles dissolving and the larger particles growing. The particles are filtered off and the resultant press-cake dried, during drying further aggregation takes place. Thus in the organic pigment powder placed on the market there is a wide distribution of particle sizes, from primary nano-size particles whose size maybe as small as 20 nm to clusters of primary particles in the 1 to 5 micron range. Studies over the last few decades have shown that organic pigment powders as they are placed on the market do contain a greater or smaller amount of nanosize particles, the quantity of which is strongly influenced by the production process.

It is only during the incorporation (dispersion) step that the clusters are broken down into smaller moieties (ideally to the primary particles).

Occupational Health and Safety in the Pigment Industry

The production of organic pigments takes place in industrial-scale plants, where all aspects of occupational health and safety and environmental protection are reliably met. Dust extraction equipment as well as personal protection equipment is standard. Solvents are collected for recycling and any aqueous waste goes into special treatment plants before discharge into public systems. Rigorous controls and limits are set here by local authorities to ensure that the plants operate to minimise any adverse environmental risk. The systems currently in use can considered to be satisfactory.

In downstream uses – e.g. in the production of paints, of inks or master batches the individual constituents are mostly added automatically. In the final product the colorant is surrounded by a polymeric or resinous matrix. Thus it is only in the decanting stage that, emissions of finely divided substances may occur where, however, they are collected by filters. Such emissions need to be controlled to minimize human exposure and environmental release.

Consumer protection

In consumer use, pigments are present in printed matter, painted articles or coloured plastic or as a liquid preparation e.g. a DIY paint.
At that stage, pigments are fixed in solid respectively liquid system and should not be considered as nano powders.

Toxicology of Organic Pigments

As has been mentioned above research and development of organic pigments over the past four decades has been targeted at producing products that when incorporated into the final medium have a particle size of some 10 – 20 nm.

When new products have been developed and are ready to be marketed their toxicological and ecotoxicological properties have been studied, This is especially true for new substances where a significant package of data has to be prepared for authorities (In the EU following directive 92/32/EEC and there are similar regulations for other countries with chemical legislation in place). Also in order to communicate any potential hazards on any marketed product to downstream users data has to be obtained in order that the MSDS may be prepared. Testing is carried out on the powder *as is*. This contains aggregates and agglomerates as well as a larger or smaller nanosize proportion. No adverse effects have been observed that can be directly attributed to the nanosize material; though from a consideration of a weight size distribution this nanosize tail may not be so significant.

Organic Pigments have also been subject to evaluation under Council Regulation (EEC) No 793/93 on the evaluation and control of risks of existing substances. The evaluation was carried out on commercial products which contained nanosize particles and for those HPVC substances IUCLID data sheets have been prepared. Generally there was an absence of reported toxic and ecotoxic effects. In some cases where inhalation exposure has to be considered additional studies on inhalation toxicity and environmental monitoring have been undertaken.

Conclusions

Organic pigments are not new. They have been on the market now for several decades – and as what we now call nanosize particles. The experience over this time has given no indication of any adverse effects that can be attributed solely to their very small size and it would appear that the current regulatory regimes are capable of handling these substances and that the handling measures currently in place are adequate.

However in line with its commitment to Responsible Care and its code of ethics ETAD members acknowledge that good sound information on the hazards of nanosize materials needs to be available. The situation needs to be constantly monitored and exposure scenarios considered especially those where humans may come into prolonged and continuous contact with systems containing nano organic pigments. The effect of such particles on the eco systems additionally needs monitoring.

Programs are already in place both in Canada and in the USA. Environment Canada has commenced a program to gather basic information on nanomaterials that are in or soon to enter commerce, so that the government can assess potential risks and address them adequately. Organic pigments are excluded from this data gathering exercise.

Similarly the EPA has developed a draft concept paper for the Nanoscale Materials Stewardship Program under TSCA. Again this is aimed at assembling data and information of existing nanoscale materials to provide a firmer scientific foundation for future work and regulatory/policy decisions. Here too dyes and organic pigments are excluded from inclusion in the program.

ETAD would support similar programs in the EU and further would suggest working with the authorities to look more closely at exposure scenarios and potential toxic effects in cases where organic pigments are involved and there is a valid potential for concern.

This position paper is based on the VdMi position paper from 26 March 2009 where organic and inorganic pigments as well as fillers were considered. ETAD acknowledges their debt to this association and would like to record their thanks for allowing it to be used as the basis for this paper.

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