

Part IV
Functional Materials

16

Organic Particles and Pigments

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16.1

Introduction

This chapter gives an overview of the synthesis and processing of organic particles and pigments using microfluidic devices. Materials with particle sizes between 1 and 100 nm exhibit remarkable and technologically attractive application properties. This new class of material is referred to in the literature as nanocrystalline, nanophase or nanostructured materials. This interest stems not only from the outstanding properties that can be obtained from such materials, but also from the realization that early skepticism about the ability to produce high-quality nanoscale powders at a competitive cost was unfounded. Today, dozens of methods are available for producing nanopowders from metals and ceramics, some of which have already been commercialized. Accordingly, the emphasis is shifting from powder synthesis to powder processing, that is., the challenge of making useful coatings or bulk structures from nanopowders. Nanostructured bulk materials and protective coatings present major opportunities for advances in materials properties and performance in a broad range of engineering applications. Over the past decade, research on the synthesis and refinement of nanoparticles has had an increasing impact on materials and surface science.

16.1.1

Definition of Microfluidics

For almost two centuries, researchers and chemists all over the world have been equipped with standardized equipment as a toolkit for the synthesis and preparation of innovative chemical substances. This consists predominately of glass round-bottomed flasks, columns, condenser or beakers, which have remained mostly unchanged since Wöhler's laboratory urea synthesis in 1828 [1]. Established traditional large-volume stirring vessels remain the standard production reactor of today. In the last decade, newly developing process technology has begun to change the

fundamental processes of chemistry. Starting with the first IMRET conference on microreaction technology, there has been an increasing number of microfluidic devices for different chemical applications (e.g. [2]). Recently, increasing attention has been paid to chemical reactions performed in so-called microfluidic devices [3]. Microfluidics handle, process and manipulate small amounts of fluids, small quantities of samples and reagents. Reactions are performed in these microfluidic devices having three-dimensional structures with inner dimensions which are smaller than 1 mm in size and more specifically between tens and several hundred micrometers [4]. On account of its small dimensions, a microfluidic device provides specific surface areas between 10 000 and 50 000 m² m⁻³, whereas those of traditional flasks and vessels are generally about 10–100 m² m⁻³. Therefore, microfluidic devices are suited to investigations of highly exothermic and fast reactions. Although microfluidic devices provide options for the optimization of many synthetic challenges, they have not yet received the attention they deserve.

16.1.1.1 Further Definitions

According to NIST [5], a particle distribution can be considered as monodisperse if at least 90% of the distribution lies within 5% of the median size.

A material can be termed a nanomaterial if one of its linear dimensions is less than 100 nm. The term microparticle is generally defined as substances having a particle size of more than 100 nm and less than 100 μm.

16.1.2

Historical Development of Pigments/Colorants

One of the most widely used classes of organic particles and powders are colorants. Certain wavelengths of the visible spectrum can be reflected and absorbed by colorants, the human eyes observing these physical processes as the appearance of color. Colorants are now an inevitable part of everyday life. Other organic particles are widely applied in such domains as optics, mechanics, medical diagnostics, catalysis, automotive, building and safety. The physical process itself differs from those such as fluorescence in which the material itself can emit light [6].

Colorants are classified as either pigments or dyes. Unlike pigments, dyes are dissolved in the application processes. Pigments are inorganic or organic, colored, black or white substances which are practically insoluble in the media in which they are incorporated. The chemical structures of dyes and pigments are in most cases similar. The main difference between them is the insolubility through incorporation of additional functional groups or formation of insoluble metal salts by laking. Most inorganic pigments exhibit some excellent application attributes such as extreme heat stability for ceramics applications or weatherfast and hiding power. However, they also frequently exhibit application challenges and have limitations in coloristic variety such as hues, tinctorial strength and brilliance.

Since prehistoric times, humans have beautified their environment through painting by using naturally occurring colorants. Stone age tribes used colorants derived from animal and vegetable sources or from iron oxide to paint their bodies



Figure 16.1 Paintings of bison in the Altamira Caves, Spain. Courtesy of Elsevier Science [8].

during hunting rituals and other ceremonies. Naturally occurring black carbon, iron oxide and ochre were the primary pigments used in the well-preserved painting of Paleolithic fauna at Lascaux, France, 17 000 years ago [7]. Recently, archaeologists in Zambia have uncovered evidence that early humans used paint for aesthetic purposes far earlier than previously thought, Figure 16.1 shows bison painted on a cave wall in Altamira, Spain. The oldest known prehistoric paintings date from 35 000 years ago [8].

Before the Industrial Revolution, the range of color available for art and decorative uses was technically limited. Most of the pigments in use were earth and mineral pigments or pigments of biological origin. Pigments from unusual sources such as botanical materials, animal waste, insects and mollusks were harvested and traded over long distances.

By the middle of nineteenth century, the Industrial Revolutions brought a huge expansion in the range of synthetic pigments, pigments that are manufactured or refined from naturally occurring materials, available for both manufacturing and artistic expression (Figure 16.2).

16.1.3

Conventional Production Methods/Conventional Continuous Processes

For the syntheses of particles, two main strategies are known: the breakdown method and the buildup method. Generally, milling methods [9] (Figure 16.3), especially high-energy ball milling, constitute a mechanical breakdown technique which is mainly used for the production of nanoparticles of various materials; in this first



Figure 16.2 Red lead manufacture in the nineteenth century. Courtesy of Elsevier [8].

option, macroscale particles are ground in a ball mill, a planetary ball mill or other size-reducing mechanism to obtain desired organic nanoparticles.

The build-up technique is illustrated by a conventional synthesis through precipitation from a precursor salt solution. In these batch precipitation processes, crystallization is started by adding a second reactant to the full concentrated reaction solution. The precipitation starts immediately, but unfortunately in an uncontrolled way at the contact point. As a result, one has particle formation with a very wide range of particle size distribution. Due to the classical scale-up phenomenon of parameter adaptations, scale-up processes from the laboratory to production scale are often time

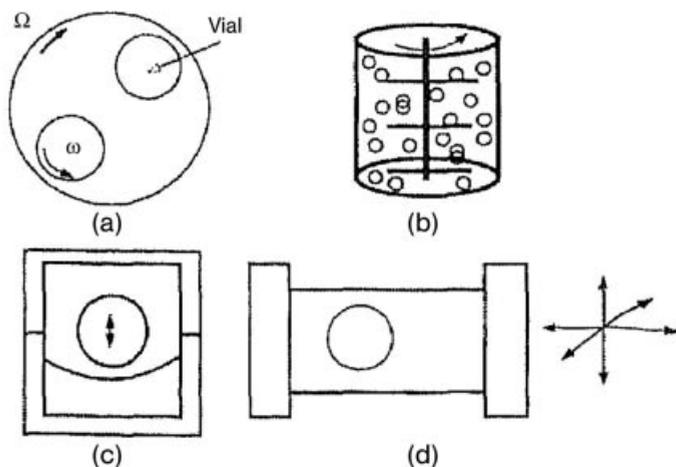
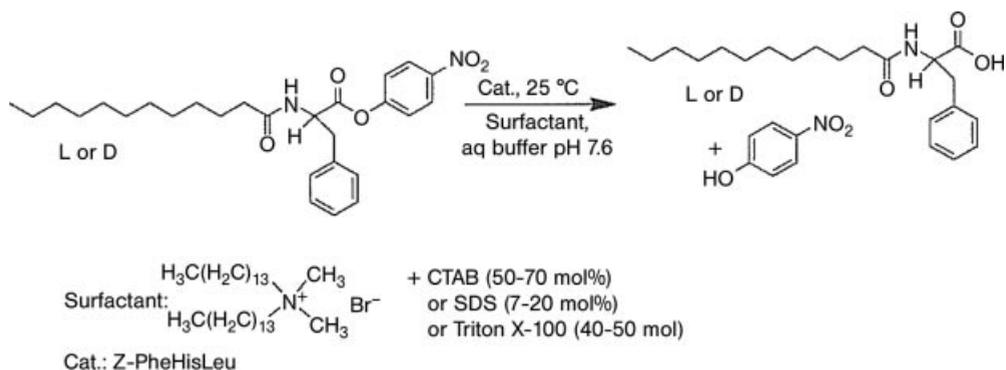


Figure 16.3 Various types of mills. Courtesy of American Scientific Publishers [9].



Scheme 16.1 Stereoselective hydrolysis of phenylalanine esters in aggregates of mixed surfactants. Z = benzylloxycarbonyl. Courtesy of Wiley-VCH Verlag [10].

consuming and cost intensive. The most common and widely used liquid-phase chemistry process is the sol-gel method. Other wet chemistry processing methods include hydrothermal processing and the use of micellar and microemulsion phases [10] (Scheme 16.1).

These methods are suitable for the manufacture of multicomponent oxide powders and nanocomposites [11]. Starting from a high-purity metal rod, such as Al or Fe, the second common method involves the evaporation of this elemental material, subsequent convective transport and either oxidation in the gas phase or thermally controlled deposition/decomposition under reduced pressure conditions, followed by condensation from the vapor phase. There are several specific means to vaporize the precursor species, such as conventional furnaces, laser ablation, microwave plasma and spray pyrolysis [12]. In pyrolysis, an organic precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting ash is air classified to recover oxide nanopowder. A thermal plasma can also deliver the energy necessary to cause evaporation of small micron-size particles. The thermal plasma temperatures are in the order of 10 000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region [13]. Oxide nanoparticles are produced commercially on a large scale in a flame reactor [14]. The vaporized precursor is fed into a reactor in the presence of oxygen and ignited. Other gaseous atmospheres, for example inert gas, hydrogen or methane, for the burning step are also possible. This method is used commercially for the production of silica from silicon tetrachloride.

For the batchwise or continuous preparation of emulsions or dispersions, the market offers a huge range of static and dynamic mixers. Conventional static mixers with integrated mixing inner fittings, which have to be adapted depending on the viscosity of educts and product recipe, are very common as a mixing tool. Most of the batch processes for the production of emulsions or dispersions are based on homogenization through turbulent mixing caused by a mechanical stirrer or others types of rotor-stator systems or porous membrane contactors. High energetic mixing

systems such as high-pressure homogenizers and ultrasonic homogenizers require an additional step of batchwise preparation of a pre-emulsion or pre-dispersion.

Recently, application examples for the preparation of emulsions and dispersions using microfluidics have been published.

16.2

Suitability of Microfluidic Devices for the Preparation of Organic Particles and Pigments

Recently, microstructured devices have become of great interest for chemical, pharmaceutical and biotechnical applications. Microreaction technology is normally restricted to gas or liquid reactions due to the channel dimensions in the submillimeter range. Investigations on reactions carried out in microreactors involving or forming solid substances are uncommon. There are difficulties accompanying the handling of heterogeneous systems in microreactors, such as adhesion and transport behavior, which often lead to fouling or blocking of microchannels. Until a few years ago, no efforts to run those reactions using microreactors had been reported in the literature. Although there is a strong bias that solids or particles may block microchannels, many scientists meet this obstacle with pragmatic approaches. They may prepare emulsions or suspensions using microfluidic devices and use these local isolated/entrapped disperse phase as “micellar microreactors”, in which solid-forming reactions can be performed. The continuous phase prevents direct contact of the disperse phase with the inner channel wall and thus fouling effects or even blockage of the channels through solid particles. Investigations into the formation of inorganic and organic fine particles have followed this approach. For example, workers at the Institut für Mikrotechnik Mainz (IMM) reported the generation of micro- and nanoscale solid particles in IMM’s interdigital micromixer, such as the precipitation of copper oxalate.

16.2.1

Mixing and Nucleation

Mixing is the most essential key factor in the control of nucleation formation and particle growth.

In recent years, pigment-based inks have become more and more attractive for office and wide-format inkjet applications. This non-impact printing technology poses special requirements, not only for pigment preparations, but also for the pigments themselves. In addition to the exploration of new dispersants and the optimization of the dispersant system, tailoring the properties of the pigments, such as particle size distribution, surface charge and polarity, morphology and especially purity, is key. As a result, the desired features of preparation and inks such as transparency, hue, viscosity and storage stability (no flocculation or sedimentation) can be improved, in addition to the elimination of abrasion in the print head. New test methods for inkjet applications and new concepts for production processes such as microreactor technology and finish treatment can significantly improve the

suitability of specific organic pigments for inkjet printing and the performance of the resulting inks.

The intrinsic advantage of microfluidic reaction systems is that temperature and concentration can be changed rapidly and reproducibly on the scale of micrometers and milliseconds, as desired for nanocrystal synthesis. Microfluidic approaches have been applied to run a variety of chemical reactions, including organic syntheses [15], biochemical reactions and heterogeneous catalysis.

To overcome the drawbacks, it is essential to improve the mixing process of the reactants involved to achieve fast and homogeneous mixing properties.

16.3 Laboratory-Scale Preparation

16.3.1 Pigments, Colorants

The synthesis of azo pigments is a typical batch process. The azo coupling is only one of a three-step pigment synthesis (diazotization, azo coupling and pigmentation). Wille *et al.* [16] described the first successful production of pigments in microfluidic devices.

Two industrially relevant azo coupling processes are carried out. The two azo coupling steps are successfully carried out in a laboratory-scale microreactor at flow rates of up to 80 mL min^{-1} . Whereas in the first example a diazonium salt solution is applied, the second diazonium salt is fed as suspended starting material into the microchannels. The microfluidic-derived pigments show improvements in application properties such as color strength compared with batch-derived standards. One reason for the improvements of color properties is the significant reduction in mean particle size from 600 to 90 nm. (Figure 16.4).

The estimated output of the laboratory-scale microreactor for pigment synthesis is about 1 t year^{-1} . To increase the output to 10 t year^{-1} and to demonstrate a simple scaling up without redesign of the process, a pilot plant based on the numbering-up concept is realized (Figure 16.5).

Maeta *et al.* [17] proposed a new synthesis method for the production of fine organic pigment particles by shifting the pH value or acidic precipitation. The pigment having dissociative protons is able to form a homogeneous pigment solution by adding alkali with a polar organic solvent. According to this scheme, 5 wt% of Pigment Yellow 128 in DMSO was obtained with an appropriate dispersing agent. A three-step mechanism for the particle formation is proposed. After bringing the pigment solution into contact with water, where the pigment clusters are generated with decreasing pH value, the second step is dominated by the competition process between the primary particle growth and the growth limitation by the adsorption of dispersant on the particle. Finally, the last step delivers dispersant-stabilized pigment nanoparticles with a particle size of about 20 nm. The corresponding pilot plant is shown in Figure 16.6.

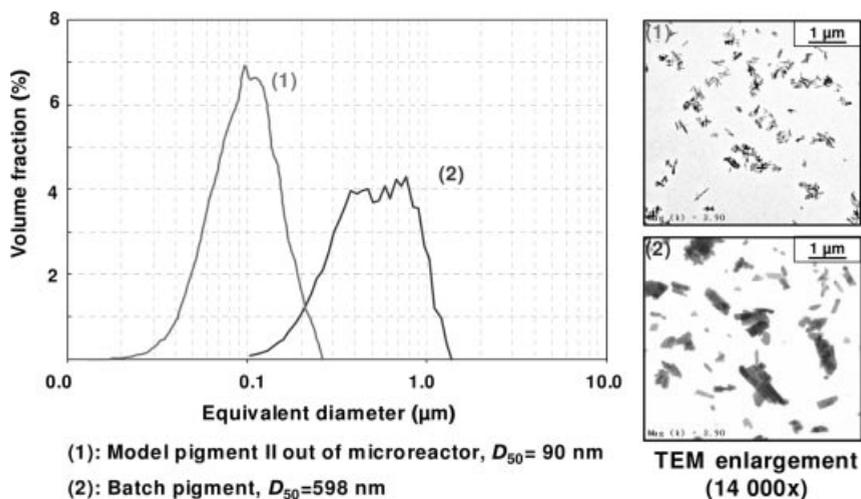


Figure 16.4 Comparison of model pigment yielded in the pilot plant microreactor and batch standard pigment. Courtesy of C. Wille, Clariant GmbH [16].

16.3.2

Monomeric Dyes

As it is known that the properties of azo dyes are primarily affected by the particle size as well as the size distribution, Pennemann *et al.* [18] investigated the synthesis of Pigment Yellow 12 using a micromixer apparatus (Figure 16.7). The micromixer

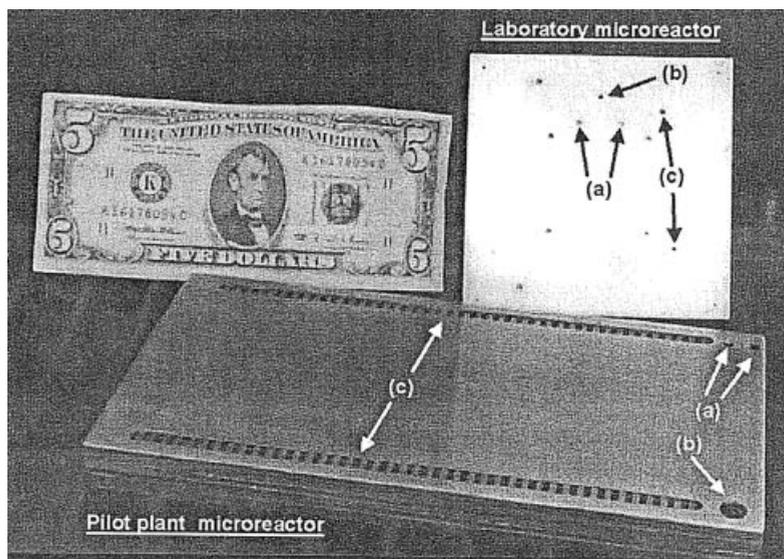


Figure 16.5 Laboratory and pilot-plant microreactor. Courtesy of C. Wille, Clariant GmbH [16].

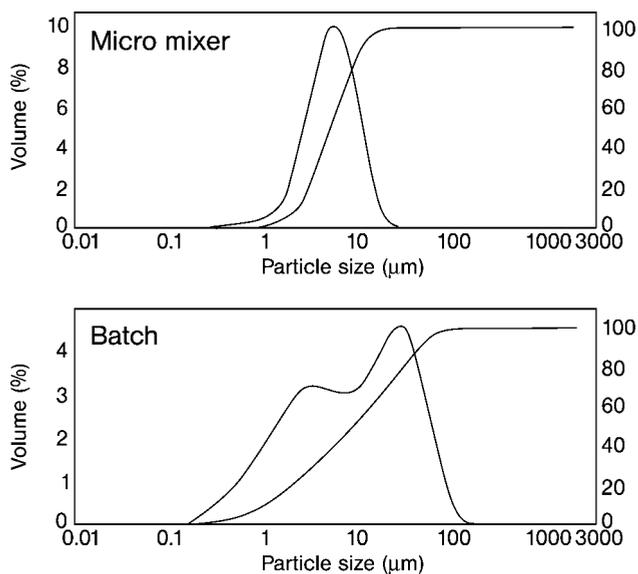


Figure 16.7 Pigment Yellow 12: particle size. Courtesy of the American Chemical Society [18].

16.4

Technical-scale Production of Organic Particles and Pigments

16.4.1

Pigments, Colorants

Wille *et al.* [20] reported on further application progress after realization of a pilot plant with a 10 t year^{-1} output. The authors confirmed how efficiently microdevices work both in the laboratory and on the pilot-plant scale. The absence of classical scaling-up effects can be confirmed by reproducing two pigment process

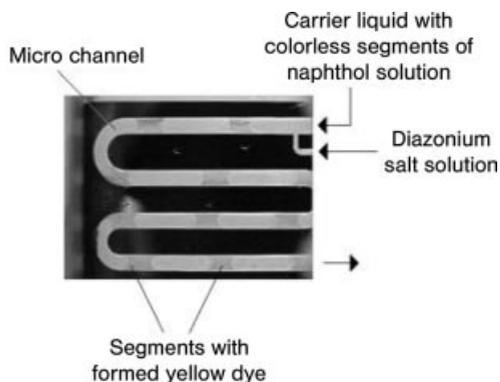


Figure 16.8 Formation of azo dyes in fluid segments inside the chip device. Courtesy of WILEY-VCH Verlag GmbH [19].

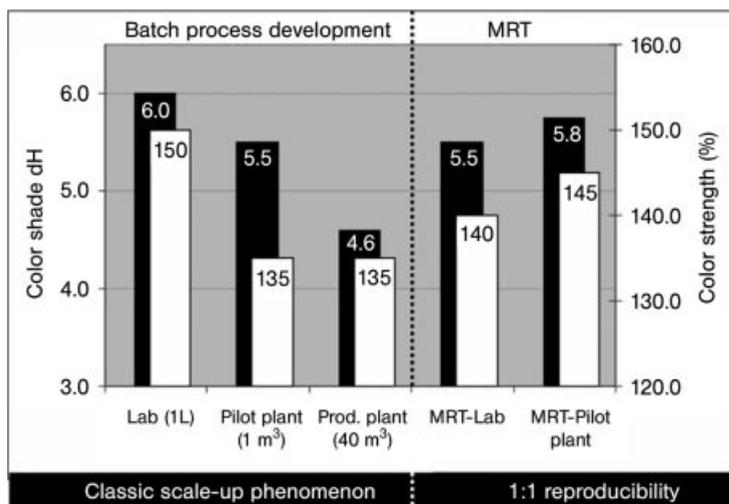


Figure 16.9 Pigment quality: scaling-up (batch synthesis) versus numbering-up of CPC microreactors for small-scale production of a yellow model pigment. Courtesy of Elsevier [20].

laboratory-scale parameters such as temperature and concentration in the realized pilot plant based on the numbering-up concept. The study demonstrates that there is no loss of product quality, as the numbering-up concept is successfully applied. This was demonstrated by the color properties such as color shade and color strength, which decrease strongly during classical scale-up, whereas a smaller increase in material functionality is observed during numbering-up (Figure 16.9).

16.5

Conclusion and Outlook

Over the past decade, research on nanoparticles has had an increasing impact on materials and surface science. The main advantage of these nanomaterials is their specific physical, chemical and biomedical properties. The extension of classical conventional synthesis and processing methods, which suffer from ineffective and inhomogeneous mixing and result in a broad particle size distribution, to new process technologies allows the manufacture of these new organic particles and pigments with defined morphology, desired particle size and, most importantly, particle size distribution [21]. In contrast to batch production technology, all microfluidic devices allow intensive and homogeneous mixing of the reactants. The development and application of new materials with new application properties has a significant effect on our health and our daily life.

These nanoscale materials are entering into new applications of existing areas, such as heterogeneous catalysis and electronic devices. As highlighted in this chapter, recent studies have demonstrated that microfluidic devices greatly outperform

macroscale systems concerning chemical processing of organic particles and pigments and also in product application properties. From an industrial point of view, microfluidic devices are advantageous because they avoid the need for scale-up adaptations of process parameters. There are a large number of published application examples on the laboratory scale, but application examples of microfluidic devices with technical output are still rare. It is less clear how microfluidics will ultimately impact the synthesis of organic particles and pigments on both the laboratory and technical scales. To increase the output of small-scale microfluidic devices there are still many challenges that have to be addressed. The published technical-scale examples are customized for a single process. The numbering-up and scale-out concept for increasing total output to tons per year is still at an early stage of development. Especially in the case of multiple reaction channels and layers in large quantities, the uniform supply of reactants and the distribution of fluid streams are challenging. For the reason of a preferred laminar flow regime in microchannels, the mixing of fluids with unequal viscosities is not always feasible. The fabrication of customized microfluidics, owing to their tailored design and custom-built fabrication approach, is time consuming and expensive. A mass production process for microfluidics is still in its infancy [22].

In the future, there will be an increasing need for organic particles with a defined particle size distribution such as for the construction of electronic devices with unique properties. As these attributes result from the particle size distribution and shape of the primary particles, alternative production processes for organic particles are required. The rising demands for nanomaterials and small entities can only be met by a multidisciplinary approach in hardware design, synthesis and characterization.

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