Stabilized Dye–Pigment Formulations with Platy and Tubular Nanoclays

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Alumosilicate materials of different morphologies, such as platy and tubule nanoclays, may serve as an efficient, protective encasing for colored organic substances and nanoparticles. The adsorption of dyes onto the nanoclays increases their stability against thermal, oxidative, and acid–base-induced decomposition. Natural organic dyes form stable composites with clays, thus allowing for "green" technology in production of industrial nanopigments. In the presence of high-surface-area alumosilicate materials, semiconductor nanoparticles known as quantum dots are stabilized against agglomeration during their colloid synthesis, resulting in safe colors. The highly dispersed nanoclays such as tubule halloysite can be employed as biocompatible carriers of quantum dots for the dual labeling of living human cells—both for dark-field and fluorescence imaging. Therefore, complexation of dyes with nanoclays allows for new, stable, and inexpensive color formulations.

1. Introduction

Inorganic compounds have accounted for over 90% of the world pigments production. However, the heavy metal content of most inorganic pigments restricts their applications.[1] Natural colorants may substitute synthetic dyes or pigment products. Natural dyes are generally less toxic, biocompatible, more biodegradable, and their production is environmental friendly.[2] However, currently they have no major industrial applications because of low stability and fast decomposition. Natural organic dyes lose their properties under UV–vis radiation, at high temperatures, in presence of oxidants, and in wet basic or acidic environment. The other disadvantage of natural dyes is their limited color gamut.

Different alternatives have been sought after for the stabilization of natural dyes. For instance, biomordants from tannin extracts obtained from pomegranate peels were used to improve the natural dyes.[3] One of the most spectacular examples is the ancient Maya technique on the stabilization of indigo 2,2′-bis(2,3-dihydro-3-oxoindolyliden) in mixture with palygorskite clay, which preserved bright blue color for over 800 years (**Figure 1**). In this nanocomposite, the dye molecules were placed into 0.64 nm wide tunnels in the clay fibers.[4]

The most prominent approach for organic and especially natural dye protection is their intercalation into inorganic clays, thus having complete operations with "green" natural materials.[5] Abundant bulk clays have to be exfoliated for this purpose, converting to nanomaterials either of lamellar structure with alumo or magnesium/silicate sheets (like kaolin, montmorillonite, bentonite, and hydrotalcite) or tubule and fiber structures (halloysite, imogolite, sepiolite, and palygorskite) (**Figure 2**).

Organic dye/inorganic clay composites can be obtained at room temperature from aqueous solutions dispersions using a wide range of pH.[6] The polarity of the clay sheet or fibers (often with SiO_2 surface) also stabilized many incorporated dyes. Surface modifiers, such as surfactants or silane coupling agents, can be used to adjust the nanoclay polarity.[7] These modifiers can open lamellar structures and improve their exchange capacity. The benefits of the pH modification to modify the Al^{3+} site on the nanoclays were also reported.[8] The best synthetic or natural dyes—clay formulations which improved stability—needed maximal clay sheets exfoliation.[9] It takes a long time and essential energy for high stirring speed with smectite clays dispersion.[10] One has to avoid clay

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