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Immersion liquid techniques in solid particle characterization: A review

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ABSTRACT

Chemical, physical and optical properties of small solid particles are widely utilized in our everyday merchandises. For example, tailored particles embedded in paper or cosmetics improve the visual appearance of the products substantially. As a consequence of the small size of particles, one particle characterization tool is a microscope. It may provide e.g. the particle size, shape and the refractive index. The determination of the refractive index, using the microscope, typically exploited the so-called immersion liquid method. In this review, we provide an overview of non-imaging immersion matching techniques including immersion liquid set, the temperature, the wavelength, the double variation and the liquid evaporation methods. The basic features, benefits and limitations of each technique have been described followed by examples of potential applications in a quality monitoring of particle suspensions and colloids in industry.

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1. Introduction

Nano- and micron-sized solid particles such as pigments and minerals are widely used as an ingredient in various products. Indeed, the total size of the world market for dyes, pigments and intermediaries is estimated to be US$ 23 billion per year [1]. The purpose of their use is to enhance the function, usability or visual image of products. Pigments commonly protect the substrate against corrosion, increase durability, hardness, dimensional stability and retard flammability [2]. For example, calcium carbonate and clay are commonly used in paper mills, since these pigments strongly affect optical properties of the paper such as brightness, gloss, smoothness, whiteness, opacity and generate better surface for printing [3]. Pigments are an essential component of cosmetics in order to create striking effects on the skin surface [4]. Sometimes the motivation for the use of small particles can be economic, for example, wood fibers are partly replaced by pigments in paper products due to lower cost [5]. Typical applications for pigments include food, paper products, fireproof applications, metallurgy, grinding pastes, catalyst, ceramics, plastics, paints, inks, building materials and drugs.

Industrial pigments are carefully controlled by qualitative and quantitative chemical analysis. In addition to chemical nature of the particle, many of its physical and optical properties play an important role in the end product. Such properties include particle size, shape, surface properties, mechanical properties, microstructure, color, opacity, charge properties and the refractive index [6]. In industry, there are several reasons to monitor those parameters: to control the product quality, to deepen the knowledge of products and ingredients, and understand better manufacturing processes.

We have recently developed immersion liquid measurement procedures, data-analysis and associated instrumentation towards off-laboratory applications [7–9]. Motivation has originated from fact that the information about the refractive index and related parameters of a particle in a suspension or colloid is important in physics, interdisciplinary fields such as life sciences and medicine and in industry (e.g. cosmetics, drugs, food). This article provides an overview of various immersion techniques, typical instrumentation and potential applications concerning small particles in industry.

1.1. Particle characterization tools

Particle size affects to material packing density, porosity, viscosity, flowability, visual appearance, stability and reactivity. Over the years various particle sizing techniques have been developed. Light scattering methods include laser diffraction [10], dynamic light scattering (DLS) [11], electrophoretic light scattering (ELS) [12] and dielectrophoretic dynamic light-scattering (DDLS) [13]. Imaging apparatuses provide size information even below 100 nanometers [14]. Scanning electron micrographs (SEM) and atomic force microscopy (AFM) are two most common microscopic methods [15,16]. Recently, three-dimensional images generated by super-resolution optical microscopy techniques expose the complex biomolecules structure or nanoparticles in atomic resolution. These new super-resolution technologies include photo-activated localization microscopy (PALM) [17], stimulated emission depletion microscopy (STED) [18], structured illumination microscopy (SIM) [19], stochastic optical reconstruction microscopy (STORM) [20], scanning near-field optical microscopy (SNOM) [21], saturated excitation microscopy (SAX) [22], and electron-beam excitation assisted microscopy πEXA) [23]. Novel super-resolution microscopy techniques achieve nanometer resolution of fluorescently labeled molecules with the exception of EXA [24]. Sedigraphic technique combines the information of particle mass obtained by X-ray absorption and the falling rate of particles under gravity to the particle size (equivalent spherical diameter). These apparatuses operate typically from 0.1 to 100 μm size range [25].

There are products that should be white in color. For example, when dealing with paper product the lignin should be removed efficiently, carry out bleaching and furthermore the “whiteness” can be enhanced by suitable fillers or pigments and the use of optical clearing agents. Whiteness, lightness or brightness can be determined by standardized reflectance measurement to characterize the sample quantitatively e.g. by ISO brightness [26]. Thus the color is one important quality parameter of pigments [27].

Substance purity is often a desired property – for example highly pure materials are needed in electronics where the function of semiconductor materials like Si and Ge is affected even by small traces of impurities and substances used in wet chemistry, the pharmaceutical manufacturing and food industry must fulfill purity criteria described in relevant standards. Analytical chemistry offers both qualitative and quantitative methods for demanding material analysis. In the characterization of advanced and high purity materials, techniques and devices like atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray photoelectron spectroscopy (XPS) have been exploited [28]. A sophisticated purity investigation method uses chromatography (e.g. HPLC) [29]. It is a method to separate, clean and identify chemical compounds, especially have been used with complicated substances like food additives and medicines. The method can detect chemicals even if they are in low concentrations. Pure materials have individual melting points and in the phase transition from solid to liquid the temperature remains constant [30]. A differential scanning calorimeter (DSC) measures the difference in heat flows into a sample and a reference as a function of time and temperature. DSC has several applications e.g. in the pharmaceutical industry where it has been used for testing the purity of drug samples [31,32]. Purity can also be estimated by the mass loss due to burning.

The refractive index is a fundamental property of a material and useful in many areas of science and engineering. Thus it has been widely used in quality inspection of liquids and solids and in material science to characterize minerals. Information on the refractive index of particles is often associated to visual appearance of material. In addition, it is a key parameter in the designing of optical systems. The refractive index is exploited in the detection of liquid concentration, purity, chemical identification, density, and even temperature [33,34]. Therefore, the refractive index data for various (pure) materials have been determined and exist in the common physics and chemistry handbooks. The refractive index of liquids and solids is typically determined by detecting the critical angle of an internal reflection at the wavelength of 589 nm (D1-line of Sodium) by using an Abbe refractometer. Unfortunately, its refractive index reading is disputable in the case that the sample (liquid or solid) absorbs light at the probe wavelength [35]. Ellipsometry is an optical technique for determining the complex