Application note

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VASCO^{TM} Particle size Analyzer

Ink pigment size characterization by Dynamic Light Scattering with the VASCO^{TM} analyzer

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Key Words: paint, ink, pigments, nano-particle sizing, dynamic light scattering (DLS), colloidal suspensions, concentrated, opaque, VASCO^{TM}.

Abstract

Printing inks made of nano sized pigments dispersed in liquids are more than ever used in the industry because of their unique properties (color, thinness, visual aspect, durability, conductivity, etc). Characterizing the size of the dispersed pigments at initial concentration in such inks is often mandatory in order to guaranty stability and adequate physical/chemical properties. Unfortunately, such characterization remains an inaccessible challenge to most conventional optical measurement techniques like Dynamic Light Scattering (DLS) systems because of high concentrations effects. But such limitations are note a fate; thus in this note, we demonstrate through some illustrative examples how the VASCO^{TM} analyzer, thanks to its unique innovative patented optical cell design, can overcome these limitations for the characterizations of dark/colored and concentrated colloidal suspensions. A concrete example of industrial application is presented with the measurement of concentrated pigmented jet printer inks.

INTRODUCTION

Since recent years, ink industry is putting a lot of efforts to improve the quality and/or create new properties of ink products. These manufacturers are producing ink and paint incorporating smaller and smaller pigments particles, some not exceeding few hundred nanometers. Indeed, the size of these pigments is one of the major parameters controlling properties of inks or paints. The pigment size affects the aspect of the final product (light absorption, visual aspect, printing resolution, depth of color…) as well as the quality of deposits on a substrate (homogeneity, texture, thinness…). Moreover, pigment size also plays an important role in the stability and usability of colored materials [1]. For example, the size of pigment particles/aggregates in inkjet printers has to be smaller than the printer microscopic nozzle aperture in order to guaranty good printing quality and prevent nozzle fouling. Consequently, an accurate control of the dispersed pigments size is critical to manufacturers who want to guaranty final product properties, production yield and quality.

Printing INK with nano pigment

Among existing techniques used for nano-particle size measurement in liquids, Dynamic Light Scattering (DLS) is the preferred one in many applications because of its relative simplicity of use, its measurement range from one manometer up to few microns and its ability to give information about particle/aggregates size distribution. Based on the analysis of scattered light fluctuations caused by the Brownian motion of particles, DLS is a powerful optical technique to characterize dilute and transparent dispersions of particles. Nevertheless, as shown in [2], conventional DLS techniques which measure the scattered light at 90° from incident light usually fail when analysing dark and concentrated dispersions because of light absorption, sample heating and multiple scattering artefacts. Thus, the analysis of concentrated ink or paint Suspensions (with typical concentration between 0.1% up to few %) by conventional DLS instruments is not achievable unless the sample is drastically diluted by several decades. Dilution requires tedious sample preparation and is time consuming for routine measurements. Moreover dilution can strongly impact sample chemical properties (Ph, colloidal stability, conductivity, etc) giving poor representative measurements. In this application note, we first illustrate the limitation in measuring dark and concentrated colloids comparing conventional DLS to the VASCO^{TM} system. Then in a concrete example of industrial application, we show how the use of the VASCO^{TM} particle analyser enables particle size measurements of pigments in a concentrated printing ink.

MEASURING CONCENTRATED AND OPAQUE SAMPLES: CONVENTIONAL DLS VS VASCO

In conventional DLS system, scattered light is detected at 90° the from the incident laser light (see figure 1). With this optical configuration, light absorption and multiple scattering can be important and can induce significant measurement artefacts. That's the reason why most conventional DLS systems are usually ineffective for measuring opaque/concentrated media. In order to compare the impact of these two effects between a conventional DLS and VASCO for concentrated pigmented ink measurements, we have prepared test solutions with commercial standards polystyrene latex[1] of known particle size and concentration. The latex sphere size and concentration were selected to be in the range of typical pigment size and concentration in non diluted industrial ink samples.

[1] *standard latex from DUKE and Merck*

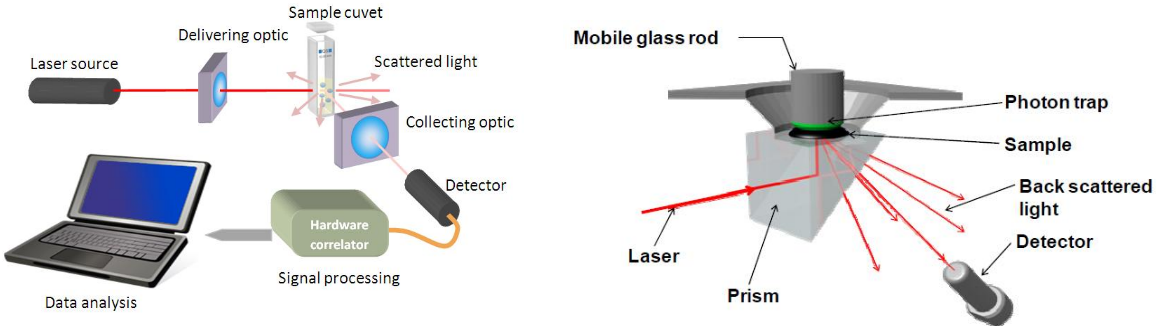

Figure 1: example of commercial DLS measurement configuration; left: conventional DLS ; right: VASCO with its DTC and solvent proof cell.

a) Absorption /heating artefacts

The first major impairment one could expect from pigmented ink measurement is laser light absorption and local heating of the sample; In order to illustrate this effect we have prepared a test solution made of commercial standard 30 nm diameter latex particle (Thermo Fischer® 3030A, 33+/-1.5 nm hydrodynamic Radius) dispersed in water and stabilized by ionic surfactants. For the purpose of the demonstration and sake of interpretation, this sample was first diluted to 0.001wt% to avoid concentration effects (particle interaction and multiple scattering). The effect of light absorption on particle size measurement is shown in Figure 2. In order to have statistical information on size dispersion of the sample, the NanoQ™ software of VASCO was operated in the multi-acquisition mode with each correlogram acquisition processed by the Pade-Laplace inversion algorithm [3]

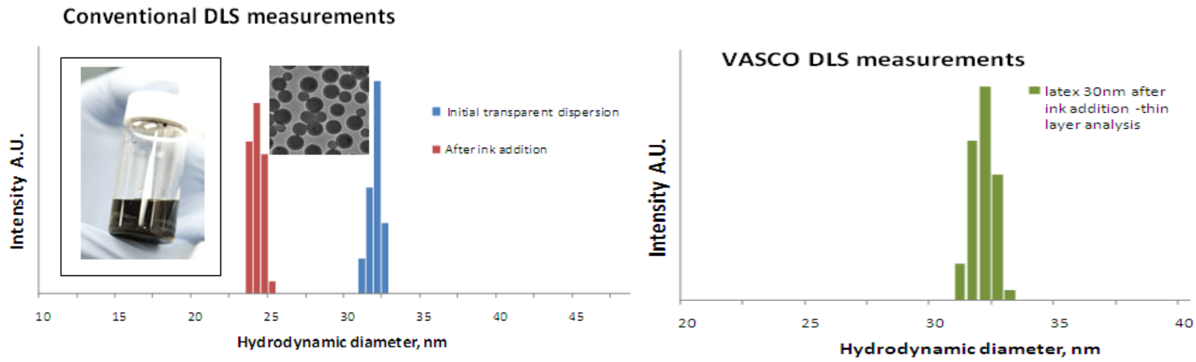

Figure 2: left : Conventional DLS analysis of a 30 nm latex test solution before (blue) and after (red) addition of absorbing ink. The normalized amplitude of scattered intensity is plotted as a function of the hydrodynamic diameter. right: VASCO DLS analysis;

A direct DLS analysis of this transparent dispersion indicates that the average hydrodynamic diameter is 32 nm (see fig 2, blue bars on the graph), in good agreement with TEM measurement (fig2, right picture). After adding 10wt% of black and soluble organic ink to the sample to simulated the case of an absorbing pigmented ink, we measure a diameter of 24 nm (fig 2, red bars on the graph); This corresponds to a decreased of 25% of the measured size value compared to the nominal value. This apparent decrease is due to local heating of the sample due to absorption of the laser probe. Comparatively, the VASCO system with an appropriate adjustment of its The Dual Thickness Controller system (DTC™) gives very consistent results for the same dark latex sample (fig 2- right).

b) Concentration/multiple scattering artefacts

The second major impairment one could expect from concentrated pigmented ink measurement is multiple scattering artefacts. Indeed, when measuring a concentrated colloidal suspension with conventional DLS, the photons can be scattered several time as light propagates through the medium before reaching the detector. Multiple scattering quickly occurs with increasing concentration, and can be observed as soon as the sample becomes turbid. It induces an under-estimation of the hydrodynamic radius of the particle. To illustrate this phenomenon, a second test solution has been prepared with a commercial standard latex (Merck Estapor® K010 microsphere, having a diameter of 98 nm by TEM analysis) at two concentrations differing by two decades: 0.001wt% and 0.1wt%. For sake of interpretation, no absorbent was added to these solutions. Figure 3 below clearly shows that a conventional DLS measurement give coherent results for the low concentration sample (blue bars on the graph). But it significantly underestimates the latex particle size for the high concentration sample (red bars on the graph) with a measured effective diameter of 84 nm. Comparatively (fig 3 right), measurements on the concentrated sample thanks to the VASCO™ system with its DTC set in concentrated sample measurement position [2] give very coherent results with an average hydrodynamic diameter of 115 nm, consistently with Merck latex data.

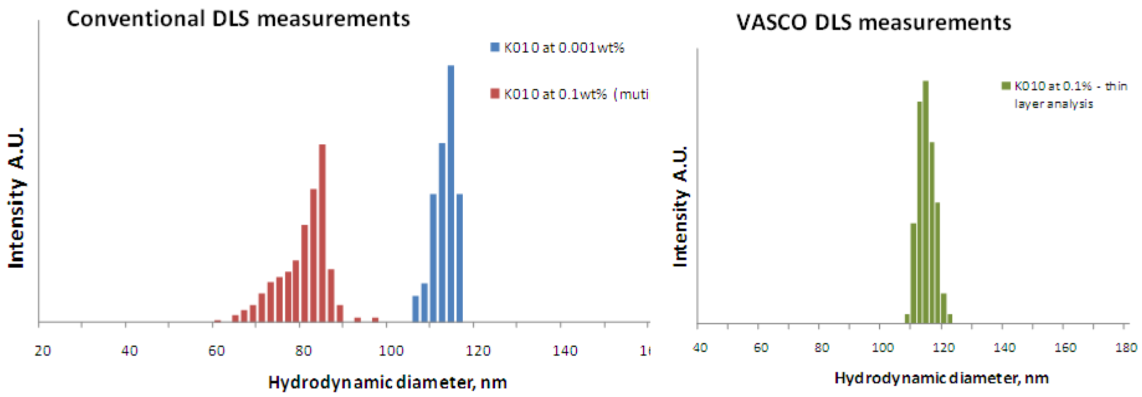

Figure 3: Left: Conventional DLS analysis of the K010 latex before dilution, i.e. at 0.1wt% (red) and after dilution at 0.001wt% (blue). The normalized amplitude of scattered intensity is plotted as a function of the hydrodynamic diameter; right: same measurement on the 0.1%wt sample with VASCO™

APPLICATION TO INDUSTRIAL PIGMENTED INK CHARACTERIZATION

In the previous section we have shown that, thanks to the innovative design of its sample cell and its DTC system, the VASCO™ Particles size analyzer is a perfect tool to characterize nano-particles directly in concentrated or colored/opaque media. Let us show now how to exploit these capabilities in a concrete example of measurement of a concentrated pigmented ink manufactured in industrial conditions. The tested product is a magenta printing ink manufactured by the French company Encres Dubuit[2]. It is a UV ink which polymerizes on the substrate under UV light insulation. The composition of such kind of inks is complex but usually consist mainly in pigments dispersed in a liquid phase of acrylate polymers and monomers. Here, the weight concentration of the studied ink is closed to 5% in pigment. This specific formulation makes the material very viscous (about 25mPa.s at 25°c) and very opaque as shown on figure 4.

Figure 4: left: concentrated pigmented ink sample from Encres Dubuit Company; right: measurement of the ink sample with the VASCO analyzer

Few droplets of the pigmented ink to be characterized were directly dropped into the VASCO cell with a pipette. The Dual Thickness Controller system (DTC™) is set in the down position for concentrated sample measurements [2]. In order to have statistical information on size dispersion of the sample, the NanoQ™ software of VASCO was operated in the multi-acquisition mode. For comparison purpose a second set of measurement was performed on the initial solution diluted by a factor 100. The results are presented in figure 5 below.

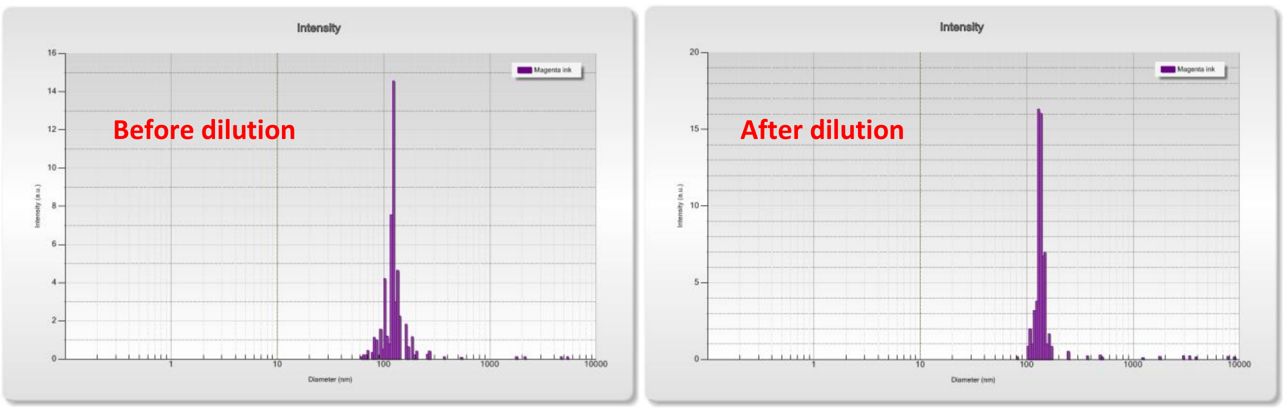

Figure 5: Dispersion size histogram analysis of concentrated printing ink sample using the VASCO™. The normalized amplitude of scattered intensity is plotted as a function of the hydrodynamic diameter. Left: initial concentration (ie, before dilution); Right: initial concentration ÷100 ((ie, after dilution)

[2] http://www.encresdubuit.com/

Figure 5 clearly shows that the measured pigmented ink presents only one main population of pigment size with a maximum of amplitude detected at a hydrodynamic diameter of about 125 nm. Moreover, the sample appears quite mono-disperse since a majority of particles are detected between 100 and 170nm. The comparison of the measurement results before (left) and after (right) dilution shows a very good coherence of the results proving the efficiency of the DTC system for concentrated ink measurement. Indeed, a dilution by a factor 100 gives quantitatively comparable results with the initial sample measurements. Moreover, these results are consistent with the TEM data provided by the ink supplier about their pigments.

CONCLUSION

We have shown that measuring concentrated and/or dark colloidal system like inkjet inks with conventional Dynamic Light Scattering (DLS) systems is not accurate. Nevertheless it is not a fate: the VASCO™ particle size analyser with its unique sample cell design and optics geometry combining backscattered light detection and an accurate sample thickness controller (DTC) allows to suppress the two major impairments with such sample measurements: concentration/ multiple scattering artefacts , light absorption/local heating effects. As demonstrated in this note, these innovations enable the VASCO™ to characterize accurately concentrated or opaque standard latex solution and even concentrated AND opaque suspension. This was successfully demonstrated on three concrete examples, in particular with a measurement on concentrated pigmented ink for industrial application. These results confirm that VASCO™ is an ideal characterization tool for a very board range of colloidal suspension, from diluted and transparent solutions to dark and concentrated colloids such as inks and paints.

Acknowledgment

We thank Encres Dubuit for providing technical information and printing ink samples used in these tests.

References:

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