

# Adaptive speckle imaging interferometry (ASII): New technology for advanced drying analysis of coatings

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## Keywords

Film formation, drying, optical analysis, instrumentation

## Summary

**Adaptive speckle imaging interferometry (ASII): New technology for advanced drying analysis of coatings**

In this work a new optical technology, ASII, is presented, for the study of film formation from all kinds of dispersed systems, such as latexes, emulsions or solvent-borne suspensions. Various film-forming products have been investigated, including water-borne coatings, on various types of substrates. A wide range of information can be extracted such as objective drying times (dust-free, dry-hard times, etc) or mechanism taking place, thereby offering new possibilities to analyse film formation from complex colloidal systems.

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## Introduction

Recent EU environmental legislation on the emission of volatile organic compounds (VOCs) has forced coatings manufacturers to re-formulate their products to decrease the VOC content more and more. Manufacturers tend to develop more water-borne coatings and re-formulate their solvent-borne products in water. New formulations meet the European requirements (low VOC content) but undergo different drying processes. Water-borne coatings have different drying times, poorer gloss, and are more prone to defects such as sagging, blisters and orange peel. The control and understanding of the film-formation process therefore remains of great importance.

Coatings manufacturers use different techniques to evaluate drying times or to test the drying or curing properties of coatings. The BK recorder test is one of these techniques. The length of a line, left by a needle drawn through the drying film at a known rate, gives the drying time. However, this technique suffers from subjective interpretation of the results and poor reproducibility. Standard methods such as the solvent scrub test, the paper test, the cotton fibre test etc, are other alternatives but remain labour-intensive, tedious to carry out, or show user variability. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA) and thermal mechanical analysis (TMA) offer more quantitative results. However, they are not capable of measuring the build-up of properties in-situ in drying films under realistic conditions of solvent evaporation and on the appropriate substrate.

The work presented in this paper is of a new optical technology, namely ASII (adaptive speckle imaging interferometry), to study film formation from all kinds of dispersed systems such as latexes, emulsions, or solvent-borne suspensions. The authors will present the measurement principle and special features of ASII technology and will show results obtained on various film-forming products, including water-borne coatings.

## Measurement principle

The technology, developed by Formulation, is based on the technique called diffusing wave spectroscopy (DWS), an extension of the classical dynamic light scattering (DLS), to concentrated and opaque media. More precisely, it deals with 'multispeckle' DWS which has

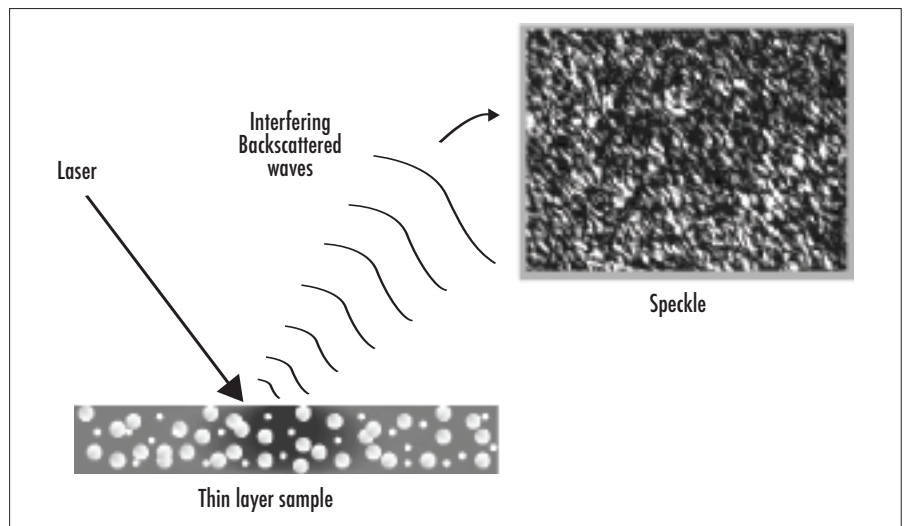


Figure 1: Measurement principle

been studied by several groups around the world.<sup>1-3</sup>

The experimental set-up is presented in Figure 1.

A laser light points at the coating sample. Part of the incident coherent light is absorbed into the sample and the other part is scattered out, detected by a camera. At the single condition that the sample is a diffuser, the camera monitor shows a peculiar image of a granular appearance called a 'speckle'.<sup>4,5</sup>

The geometrical structure of this granularity bears no obvious relationship to the macroscopic and microscopic properties of the illuminated sample; it is only related to the size and shape of the laser spot and the distance between the sample and the camera. However, when the sample undergoes time-dependent activity such as particle movements, refractive index changes etc, this activity causes temporal fluctuations in the scattered light and then random changes of light intensity on the speckle image. During paint film formation, the sample structure changes because of solvent evaporation, levelling and the diffusion of particles (latex particles, pigments, emulsion droplets etc). When fast changes occur inside the sample structure, fast changes of light intensity are observed on the speckle image, the visual appearance of the speckle pattern being similar to that of a boiling liquid. The speed of light fluctuations, 'the speckle rate', is directly related to the motion speed of the scatterers inside the sample. When no changes occur anymore (ie when the film is completely formed), the average speckle rate remains constant. The rate of speckle image fluctuations ('speckle rate') during the drying process can therefore be measured and used to monitor structur-

al changes in the film-forming coating sample.

## Analysis depth

The light injected in to the medium penetrates to a depth of a few  $l^*$ ,  $l^*$  being the transport length of the light in the medium (see Figure 2).  $l^*$  can be seen also by the photon path after which the photon direction is totally randomised. (Turbiscan Lab<sup>6-8</sup> can be used to measure  $l^*$ .) Practically, the depth of analysis for paints (ie the penetration depth of the light), goes from 100 $\mu\text{m}$  to 500 $\mu\text{m}$  depending upon the nature of the sample.

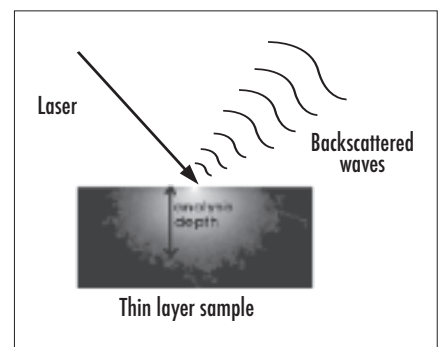


Figure 2: The light propagates in random directions inside the product. The depth of penetration is around ten times the so-called  $l^*$  or transport length

## Adaptive data processing

Formulation has developed its own original multispeckle DWS technique using a simple and direct processing of the backscattered light. Indeed, our signal processing was developed specifically for film-formation analysis. As mentioned before, a video camera is used as the detector of the backscattered waves. To display the kinetics of film formation, speckle images are acquired during an adapted time length, and these images

are processed to plot the speckle rate at time  $t$ . The unique and patented data processing extracts the decorrelation time  $t$  of the speckle images. In order to have decreasing kinetics, the speckle rate is plotted as the inverse of the decorrelation time  $t$  with respect to time. For maximum accuracy, the time length (duration) of acquisition is always adapted by setting it proportional to the decorrelation time  $t$  of the speckle pattern. The approximated value of  $t$  is obtained from the previous value of the decorrelation time calculated after the last acquisition. The very first approximated  $t$  is based on pure assumption. This algorithm can be considered as a feedback loop; if the first assumption is not correct, the algorithm converges towards the correct one. As the decorrelation time  $t$  of speckle images evolves along the drying process, the algorithm adapts for itself the time length of speckle image acquisition to the correct one, the acquisition duration being systematically minimised to get the best responsiveness. Consequently, in the case of a high speckle rate, speckle images are acquired at a high frame rate (short acquisition time), and inversely, at low speckle rate, images are acquired at a low frame rate (long acquisition time). This algorithm is consequently called ASII (adaptive speckle imaging interferometry). The benefits of adaptivity are numerous: responsiveness and accuracy, high dynamics and real-time displayed kinetics. Figure 3 presents an experiment that illustrates the responsiveness of ASII processing; the acceleration and the sharp deceleration of a pen mark drying are precisely monitored in a few seconds.

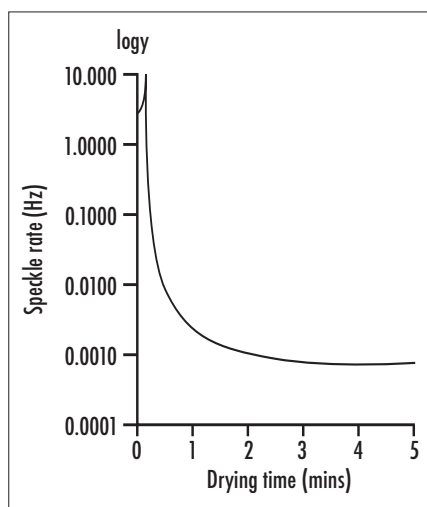


Figure 3: Drying kinetics of a pen mark on metal

## Examples of drying kinetics

Figure 4 presents an experiment performed on two different paints: a water-borne acrylic-styrene architectural paint, and a solvent-borne alkyd primer, applied on an opacity chart (60 microns). As the solvent-borne paint shows an exponential-like decay of the logarithm of the speckle rate, the water-borne paint shows complex kinetics composed of three different stages. The first noisy part shows a disturbed speckle activity; tensions created and released in the film generate accelerations and decelerations of the speckle rate. This first stage may correspond with the flocculation and coalescence of the acrylic latex.<sup>9</sup> The second stage is a smooth decay that might correspond with the autoadhesion stage of the film formation. In the third stage, the speckle rate reaches a plateau indicating that the paint is dried-hard.

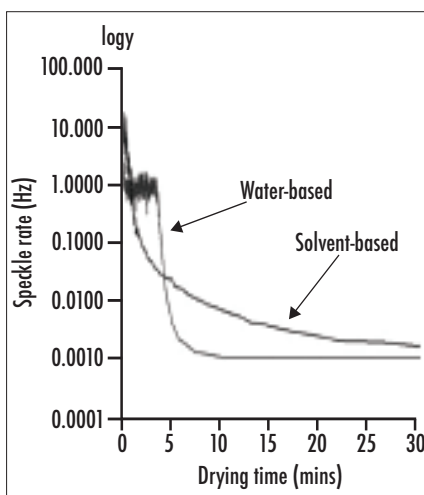


Figure 4: Drying kinetics of water-based (grey) and solvent-based (black) paints

Figure 5 and 6 show, respectively, the drying kinetics of an alkyd solvent-borne decorative paint and an acrylic water-borne decorative paint, applied at 40 microns on to glass. BK recorder experiments were performed in parallel, with the same sampling conditions; the dust-free time, the touch-dry time and the dry-hard time determined with the BK are reported on both graphs. A good correlation was observed between the BK times and changes in the slope of the kinetics. The very low speckle rate measured at the end of the experiment in Figure 5 demonstrates the high dynamics of ASII technology (ie 5 decades), the speckle rate being monitored from  $10^{-4}$  Hz.

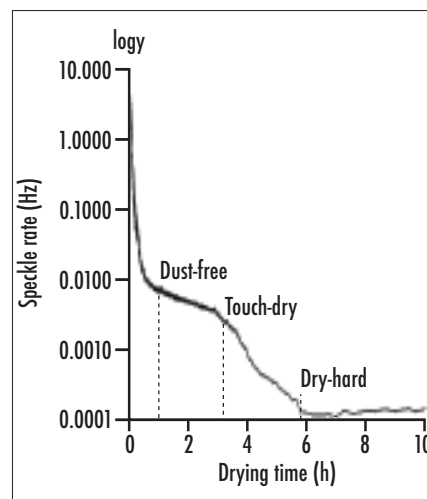


Figure 5: Drying kinetics of a solvent-based decorative paint and BK recorder experiment dust-free, touch-dry, and dry-hard times

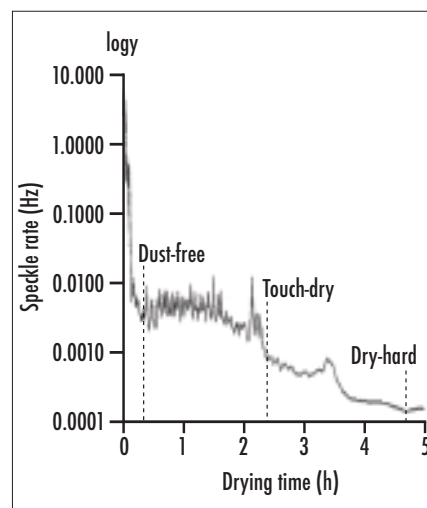


Figure 6: Drying kinetics of a water-borne decorative paint and BK recorder experiment dust-free, touch-dry, and dry-hard times

## Conclusion

A new technology to study the film formation of coatings has been presented. This technology is non-destructive and non-invasive. Measurements can be performed on different kinds of substrates. A specific software displays in real time the 'motion rate' inside the sample (in Hz) as a function of time. The experiments performed on different samples of paint show various drying kinetics. A wide range of information can be extracted such as objective drying times (dust-free, touch-dry, dry-hard times) or the mechanism taking place, thereby offering new possibilities to analyse film formation from complex colloidal systems.

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