Automatic Stability Analysis for Inkjet Inks

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Abstract

Stability is a key issue for the formulator developing new inkjet ink formulations using pigments. Sedimentation can take place in such systems due to the difference of density of the pigment particles compared to the continuous phase. This phenomenon cannot be eliminated *via* viscosity increase due to technical constraints in the cartridge. Aggregation can also arise leading to packing of the sediment. All these phenomena can be monitored and quantified using the Turbiscan® technology. Analyses are done on the real product, without dilution and can be accelerated through temperature increase and automated with an ageing station.

Introduction

More and more of the inkjet inks are becoming pigment based, as they give more environmentally friendly products that also have a better durability and compatibility with the packaging. However, the colloidal properties of pigments are much more complicated than dyes. These are soluble and therefore do not show common instability phenomena such as sedimentation and/or aggregation. Pigments, on the other hand, are solid particles that are not miscible in the continuous phase and tend to settle and aggregate. These destabilisations can have a great impact on the quality of the finished product (concentration gradients, blocking of the jet leading to inconsistency of the colour, *etc.*). Keeping the pigments in suspension in the cartridge is therefore the day-to-day challenge of the formulator. To do so he can play around with various additives in order to wet the particles, prevent them from agglomerating and avoid any sedimentation.

However, because of the opacity of inks and their high concentration of particles, the analytical tools available to help the formulator are not numerous. Common techniques such as visual observation are not only time consuming, subjective and tedious but they also give only partial information on the system, giving no insight into particle size variation. Particle size analysis, on the other hand, is not appropriate to such system, as the dilution taking place during the analysis can modify the colloidal properties (de-flocculation, *etc.*).

In this paper, we propose the use of the Turbiscan® technology as an analytical tool designed to monitor the stability of ink formulations and compare their stability. We discuss various types of ink such as yellow inks that are known for being one of the most difficult to formulate. We also go through the different behaviours encountered as observed with the Turbiscan®.

Experimentals

Principle of Measurement

The Turbiscan® is based on Multiple Light Scattering (MLS) theory, where photons are sent in the analysed dispersion where they are scattered by the particles. When the product is concentrated, the photons are scattered many times and eventually come backwards where they are detected by the backscattering detector. If the product is more diluted, the photons cross the sample without being much scattered and are detected by the transmission detector.

The heart of the optical scanning analyser, Turbiscan®, is a detection head, which moves up and down along a flat-bottom cylindrical glass cell (Figure 1). The detection head is composed of a pulsed near infrared light source (λ = 880 nm) and two synchronous detectors (transmission and backscattering detector). The detection head scans the entire height of the sample, acquiring transmission and backscattering data every 40 μm. The equipment can be thermo-regulated from 4 to 60°C and linked to a fully automated ageing station for long-term stability analyses.

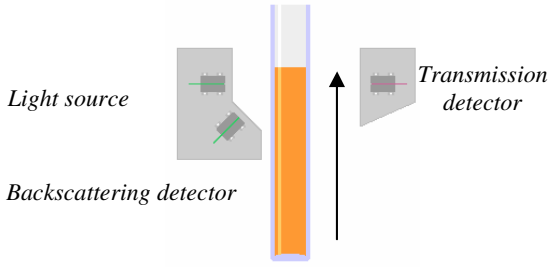

Figure 1. Principle of Turbiscan® measurement

The Turbiscan® makes scans at various pre-programmed times and overlays the profiles on one graph in order to show the destabilisation. A stable product has all the profiles overlaid on one curve, and an unstable formulation shows variations of the profiles over time (Figure 2).

Backscattering and/or transmission fluxes are shown in ordinate and the height of the cell in abscissa (Figure 2). The first profile is displayed in pink, the last one in red.

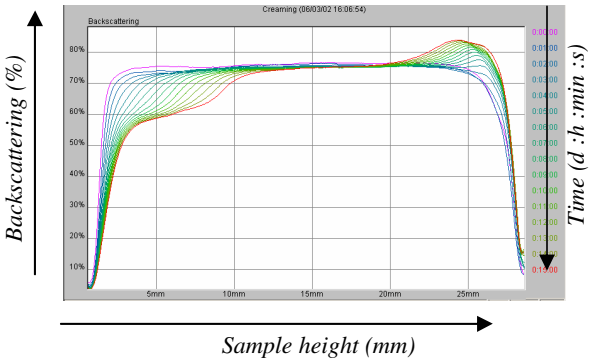

Figure 2. Superposition of scans with time for an unstable sample

Influence of Particle Volume Fraction

Figure 3 shows the experimental and theoretical (transport models based on the photon diffusion approximation) variations of the backscattering BS and the transmittance T versus particle volume fraction ϕ for a latex beads aqueous suspension (d = 0.3 µm).

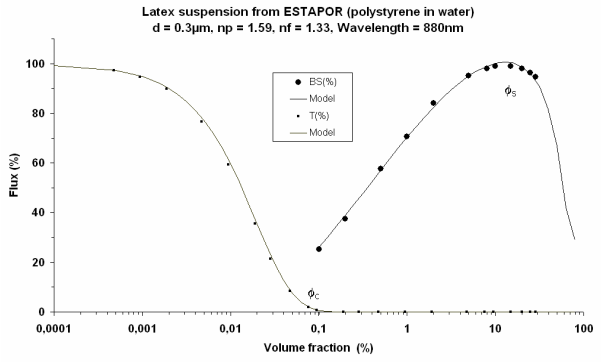

Figure 3. Variation of the transmittance and the backscattering versus particle volume fraction

In the diluted regime ($\phi < \phi_c$), the transmittance T decreases exponentially with particle volume fraction in good agreement with its analytical expression.

In the concentrated regime ($\phi > \phi_c$), both the transport model and the experiments show a zero transmission level and an increase of the backscattering with particle volume fraction before reaching a maximum.

Influence of Particle Mean Diameter

Figure 4 shows the particle diameter dependence of the backscattering for aqueous suspensions of latex beads (ϕ = 1%).

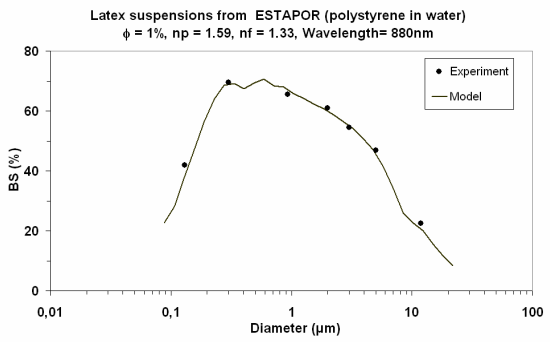

Figure 4 . Backscattering versus particle mean diameter.

For small Rayleigh – Debye scatterers (d < dc ≈ Λ), the backscattering BS increases with particle diameter in good correlation with the transport model and the numerical simulations. On the other hand, it decreases with particle diameter for large anisotropic scatterers (d > dc ≈Λ).

Materials

Various inks coming from different suppliers and with pigments of different colors and sizes have been tested. The effect of temperature has also been investigated, working at ambient, 40 and 50°C.

Results and Discussion

Stability of Yellow Ink

A sample of highly unstable yellow ink is analysed during 22 hours in the Turbiscan®. Figure 5 shows the backscattering profiles over time in reference mode (first profile subtracted from all other profiles), enabling migration phenomenon to be more easily seen.

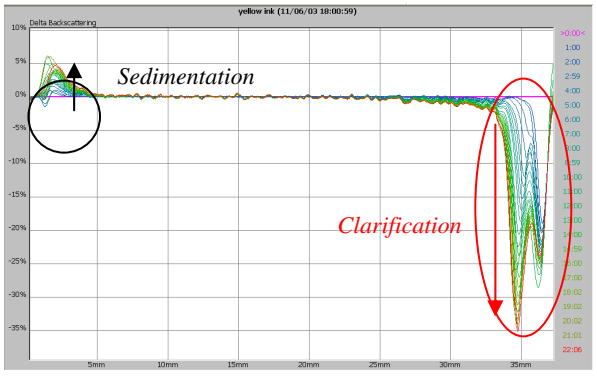

Figure 5. Backscattering profile of yellow ink (reference mode).

We see from this graph that the backscattering level is increasing at the bottom due to an increase of the concentration of particles in this part of the cell, hence a sedimentation phenomenon. This increase is visible through

the scans in the first minutes of the analysis, although the sample remains completely homogeneous to the eye.

When looking to the right part of the graph (top of the cell), we observe a decrease of the backscattering, which is due to the clarification in this part of the sample. We also see that the negative peak at the top is actually composed of two peaks. This highlights the existence of two populations of pigment particles in the ink. This result is correlated by the knowledge in the field, as it is well known that yellow pigments are found as two populations of particles. The reasons why this is and the solutions to prevent it are highly debated in the scientific world and different theories oppose. It is not the purpose of this document to debate on this issue, and we only propose a technical tool to monitor it.

If the experiment is performed long enough, it becomes possible to observe the clarification via the graph in transmission (Figure 6), where a peak appears after a while at the top of the cell.

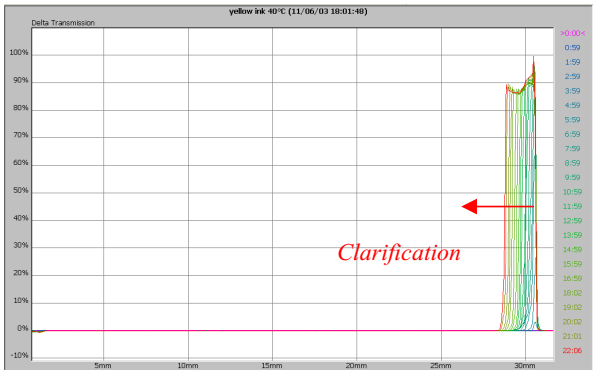

Figure 6. Transmission profile of yellow ink (raw data).

Given the graph in backscattering, it is possible to compute the migration velocity from the clarification front. The value obtained in this example is 2.51µm/min. It can be used to compute hydrodynamic parameters using the migration law of Stokes-Einstein extended to concentrated systems.

Finally, peak thickness kinetics of the sediment can be monitored (Figure 7) in order to follow the thickness (in mm) of the sediment layer as a function of time (in h). In this example, after 12 hours, the sediment is 3.7mm thick. This curve is a direct measurement of what would be measured by the eye, should the sediment layer be visible.

Aggregation of Pigment Particles

A sample of pink ink is analyzed at room temperature during 17 days using the Turbiscan®. The results obtained (Figure 8), show that in addition to the previous sedimentation phenomenon (increase of the backscattering at the bottom and decrease at the top), there is a decrease of the backscattering on the whole height of the cell. This decrease is characteristic of a particle size increase, hence a flocculation of the particles.

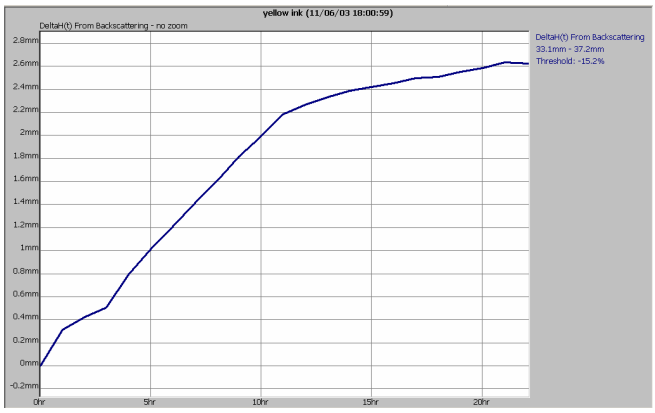

Figure 7. Peak thickness of the sediment layer.

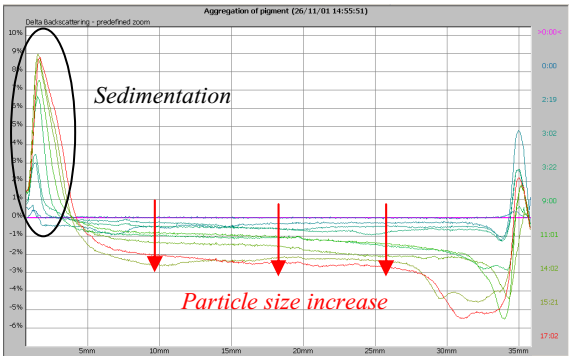

Figure 8. Delta backscattering profile of pink ink.

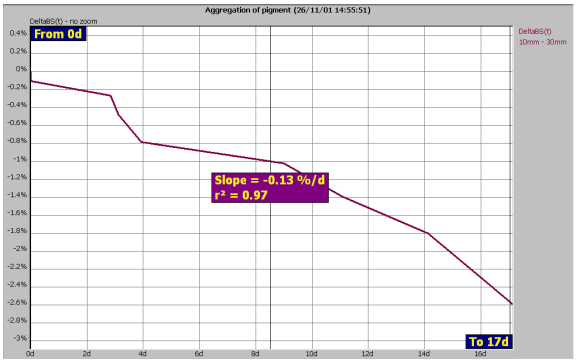

Figure 9. Variation of the backscattering (in %) versus time.

It is possible to monitor of the particle size increase through the variation of the backscattering flux over time. The slope of the curve giving the rate of flocculation (Figure 9). In this example, the flocculation rate is 0.13%/day.

Packing of the Sediment

Packing of the sediment is one of the major issues for the formulation of cartridge or industrial ink. If the pigments

are forming a cake at the bottom of the tank there can be important loss in the quality of the colour.

The following graph is obtained after 15 hours of analysis with the Turbiscan®.

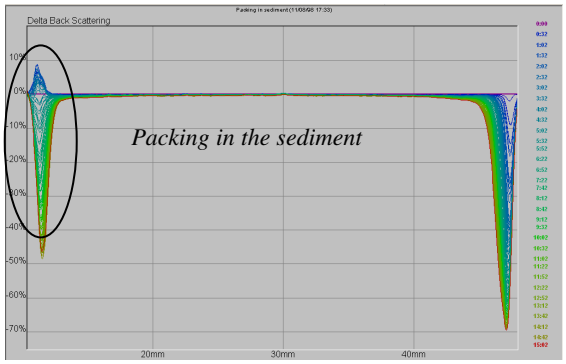

Figure 10. Backscattering profile in reference mode.

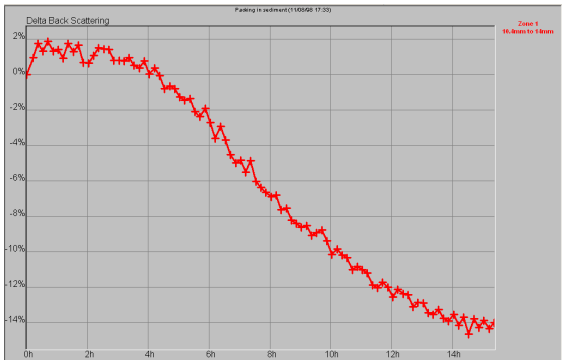

Figure 11. Variation of the backscattering profile in the sediment layer.

If we focus on the sediment layer and we compute the variation of backscattering in this part, we get the graph Figure 11.

We can note that the backscattering is increasing during the first minutes of the sedimentation, which is the normal behaviour observed for sedimentation. However, after a few minutes the backscattering starts to decrease in the sediment. This phenomenon is characteristic of a packing of the sediment. Indeed, we know that when aggregation takes place, the level of backscattering decreases with time (Figure 4). Therefore, we can conclude that the particles are aggregating in the sediment, hence the packing issue.

This trend is also confirmed by the fact that when the concentration is increasing in the sediment, it is possible to have dependent diffusion in the sediment leading to a decrease of the backscattering. This is due to negative interferences between the scattered photons, because of the highly packed sediment. Both dependent diffusion and aggregation go in the same direction and prove the packing of the sediment layer.

Mixture of Pigments

It is common to mix different pigments in order to obtain special colours and effects. However, when doing so, the formulation gets even more complex, hence the stability behaviour. A sample composed of a mixture of two pigments, one green absorbing light and one white highly diffusive, was analysed at 40°C for 18 hours (Figure 12).

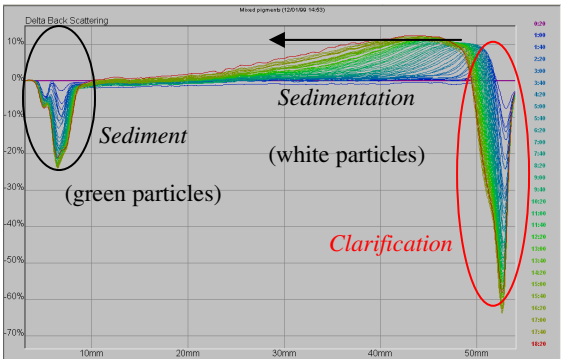

Figure 12. Backscattering profile in reference mode for mixed pigments.

We can observe a peculiar behaviour for this sample. We do see the clarification layer at the top (decrease of the backscattering on the right part of the graph). The sediment is shown on the left part of the graph and is negative due to absorption of light by the pigments in the sediment. However, in addition to these two negative peaks, we also see a positive peak in the top part of the sample.

We know the sample is composed of white and green pigments. The green pigments are the one falling faster and form a sediment that is absorbing light as the emitting source is in the near infrared. When these have fallen, the white pigments remain in suspension and they are known to be highly diffusive species. Therefore, we can attribute the positive peak to the white pigments that are slowly falling to the bottom, showed by the shift of the positive peak to the left.

Effect of Temperature

It is interesting to increase the temperature of the measurements in order to accelerate the destabilisation process.

One sample of yellow ink was analysed at 30 and 40°C for one day. The clarification layer is plotted for both temperatures (Figure 13).

We can see on the graph that increasing the temperature of measurement by 10°C accelerates significantly the migration; therefore results are available sooner.

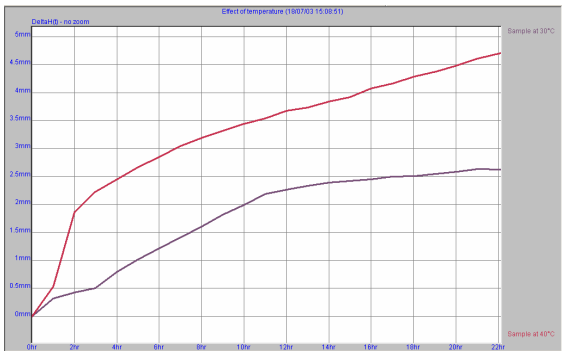

Figure 13. Clarification layer thickness at 30°C (purple) and 40°C (red) as a function of time.

Conclusion

The Turbiscan® is a complete technique that can be used during all the development of a product from the formulation in the lab through the stability study to the production and the control of the quality of the products. It enables to measure stability of inkjet ink samples in less than one day and to identify what sort of instability is taking place.

As the analysis is done on the real product, without any dilution, it is possible to detect aggregation of particles and packing of the sediment. This information is highly important for the formulator, as it will directly affect the quality of the printing.

Moreover, the analyses can be automated and accelerated through the temperature increase and the use of the ageing station.

Biography

Hélène Buron received her "diplôme d'ingénieur" in chemistry (MSc + 1 year) in 1997. She worked until 2001 in the research center of Unilever in Port Sunlight (UK) as a scientist in formulation for HPC products. Since 2002, she is application laboratory manager for Formulaction, company developing and commercializing the Turbiscan® range. The work of Formulaction focuses on the development of high technology equipments for scientists wanting to increase their knowledge on colloidal dispersions stability and characterization.