STABILITY OF PIGMENT INKJET INKS

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®. Analyses are done on the real product, without dilution and can be accelerated through temperature increase and automated with the ageing station (Turbiscan ags).

Keywords: inkjet, pigment, suspension, stability, Turbiscan®.

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. The main problem with dyes remains the solubility parameter and, in some cases, the crystallisation than can appear over time and changes in the external conditions (temperature, *etc.*). 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 the most difficult to formulate. We also go through the different behaviours encountered as observed with the Turbiscan®.

Experimental procedure

1. Principle of the measurement

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)[1-2]. The detection head is composed of a pulsed near infrared light source (λ = 880 nm) and two synchronous detectors. The transmission detector (at 180°) receives the light, which goes through the sample, while the backscattering detector (at 45°) receives the light scattered backward by the sample. The detection head scans the entire height of the sample, acquiring transmission and backscattering data every 40 µm. The Turbiscan LAB can be thermo-regulated from 4 to 60°C and linked to a fully automated ageing station (Turbiscan ags) for long-term stability analyses. Increasing temperature is the ideal parameter to accelerate destabilisation processes, while maintaining realistic testing conditions.

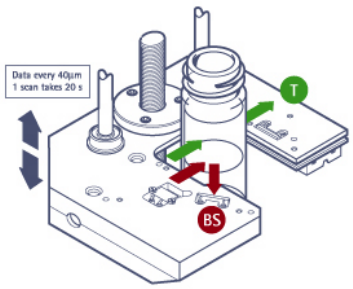

Figure 1. Principle of Turbiscan® measurement

The Turbiscan® makes scans at various pre-programmed times and overlays the profiles on one graph in order to show the destabilisation. Graphs are usually displayed in reference mode, whereby the first profile is subtracted to all other profiles, in order to enhance variations. A stable product has all the profiles overlaid on one curve (Figure 2), as an unstable formulation shows variations of the profiles (Figure 3). Backscattering and/or transmission fluxes are shown in ordinate and the height of the cell in abscissa (Figure 2 and 3). The first profile is displayed in pink, the last one in red.

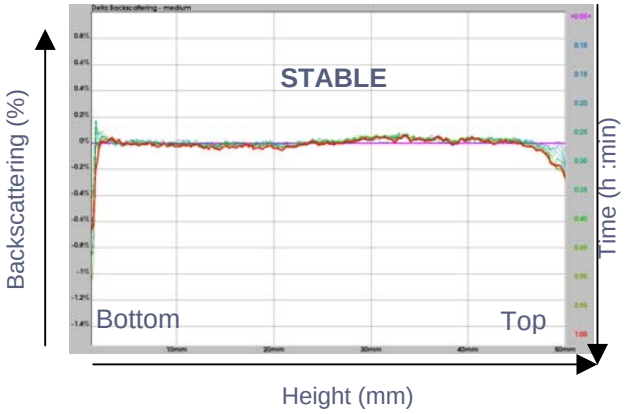

Figure 2. Superposition of scans with time for a stable sample

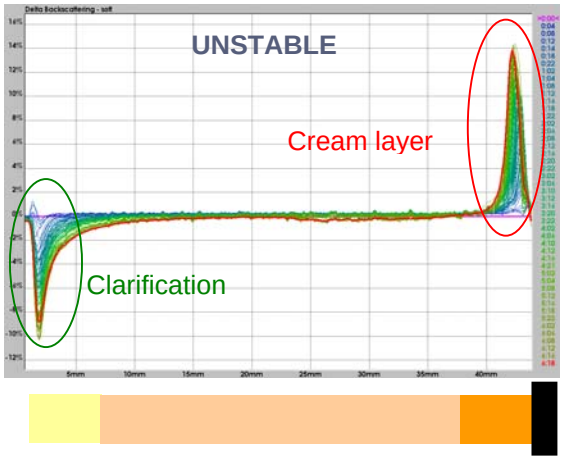

Figure 3. Superposition of scans with time for an unstable sample (creaming)

2. Instability detection

The measurement principle of the Turbiscan® range is based on multiple light scattering (MLS), where the photons are scattered many times by the particles / droplets of the dispersions before being detected by the backscattering detector. The intensity of the light backscattered by the sample depends on three parameters: the diameter of the particles, their volume fraction and the relative refractive index between the dispersed and continuous phases. Therefore, any change due to a variation of the particle size (flocculation, coalescence) or a local variation of the volume fraction (migration phenomena: creaming, sedimentation) is detected by the optical device.

a. Particle size variation

Figure 4, the variation of the backscattering level is shown as a function of the particle diameter for a fixed volume fraction of latex particles.

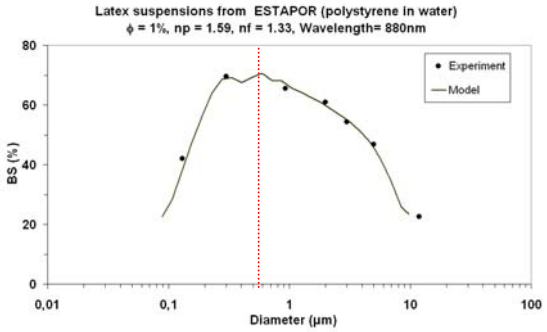

Figure 4. Backscattering level versus diameter for latex particles at 1%

The curve obtained is a bell shaped curve, where the top is linked to the wavelength of the incident light (880 nm). For particles smaller than the incident light (left part of the curve), an increase of particle size is showed by an increase in backscattering. For particles bigger than the incident light (right part of the curve), an increase in size leads to a decrease in backscattering.
On the Turbiscan® profiles, the particle size variations are displayed by a variation of the backscattering level over the total height of the sample (Figure 5).

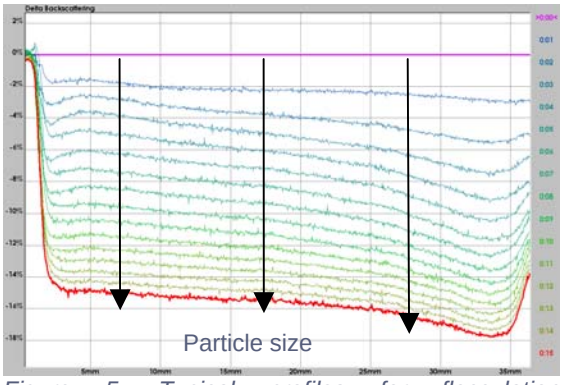

Figure 5. Typical profiles for flocculation phenomenon (initial size = 1µm)

b. Migration phenomena

Migration phenomena (sedimentation or creaming) lead to local variation of the concentration of particles in the sample.
Figure 6, the variation of transmission and backscattering levels are shown as a function of the volume fraction for a fixed diameter of latex particles.
If the concentration of particles is smaller than the critical concentration ϕ_c, the product can be considered as diluted and the transmission level decreases with an increase in concentration.

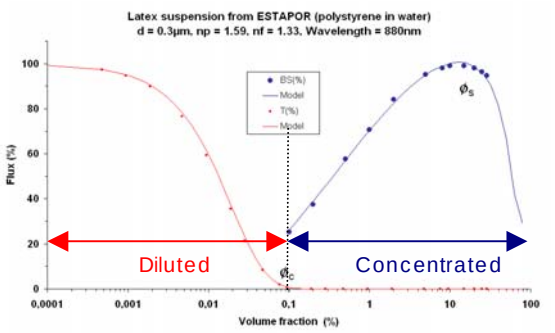

Figure 6. Transmission (red) and backscattering (blue) levels versus volume fraction for latex particles of 0.3 µm

When the concentration is sufficient ($\phi > \phi_c$), there is no transmission signal (opaque product) and the backscattering level increases with an increase of the volume fraction.
When the concentration of particles becomes too high ($\phi > \phi_s$), the backscattering level starts to decrease as the distance between particles is smaller than the wavelength of incident light. This phenomenon is called dependent diffusion and is mostly observed for small particles (< 1µm).
On the Turbiscan® profiles migration phenomena are displayed by local variations of the backscattering. Figure 7, the backscattering level decreases at the top (right part of the graph), due to a decrease of the concentration of particles, hence a clarification, while it increases at the bottom due to the increase of particle concentration consecutive to the sediment formation. It is interesting to note that there is no variation in the middle of the sample, indicating no particle size variation.

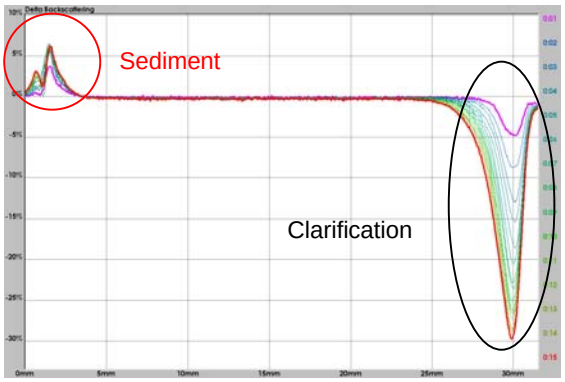

Figure 7. Typical backscattering profiles for a sedimentation phenomenon.

3. Materials

Various inks coming from different suppliers and with pigments of different colours and sizes have been tested. The effect of temperature has also been investigated, working at ambient, 40 and 50°C. For each experiment, the sample was shaken before use and 7 or 20 mL (for the Turbiscan Classic and LA*b* respectively) was sampled in a borosilicate glass cell. The cell is then closed with a stopper and placed in the Turbiscan®.

Results and discussion

1. Stability of yellow ink

A sample of highly unstable yellow ink is analysed during 13 hours in the Turbiscan®. Figure 8 shows the backscattering profiles over time. In Figure 9, we see the same graph in reference mode (first profile subtracted from all other profiles), enabling migration phenomenon to be seen more easily.

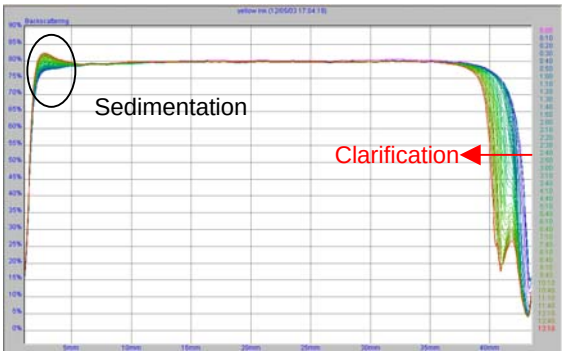

Figure 8. Backscattering profile of yellow ink (raw data).

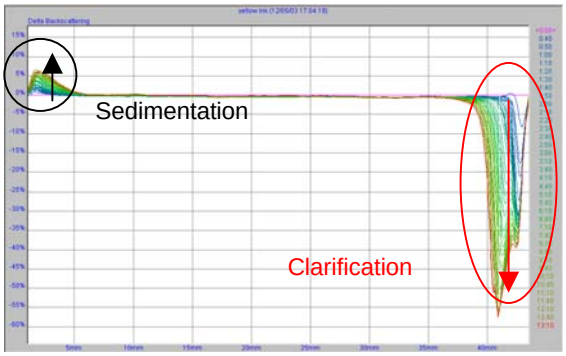

Figure 9. Backscattering profile of yellow ink (reference mode).

We see from these two graphs that the backscattering level is increasing at the bottom due to an increase of the concentration 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 10), where a peak appears after a while at the top of the cell.

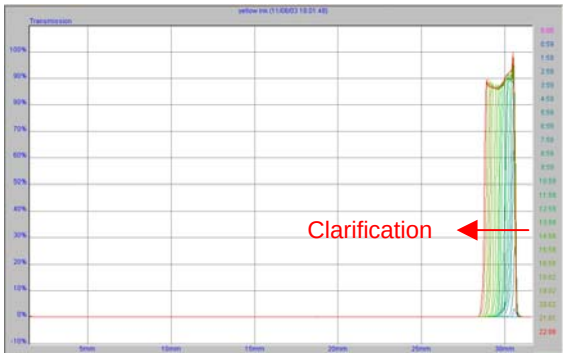

Figure 10. Transmission profile of yellow ink (raw data).

Given the graph in backscattering, it is possible to compute the migration velocity from the clarification front *via* the Turbisoft®. The value obtained is 2.51µm/min. It can be used to compute hydrodynamic parameters using the migration law of Stokes-Einstein extended to concentrated systems, also *via* the Turbisoft®.
Finally, peak thickness kinetics of the sediment can be monitored (Figure 11) 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.

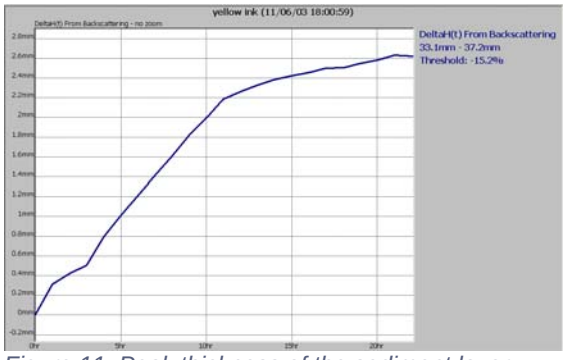

Figure 11. Peak thickness of the sediment layer.

2. Aggregation of pigment particles

A sample of pink ink is analysed at room temperature during 17 days using the Turbiscan®. The results obtained (Figure 12), 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.
The Turbisoft® allows a monitoring of the particle size increase through the variation of the backscattering flux over time. The slope of the curve gives the rate of flocculation (Figure 13). In this example, the flocculation rate is 0.14%/day.

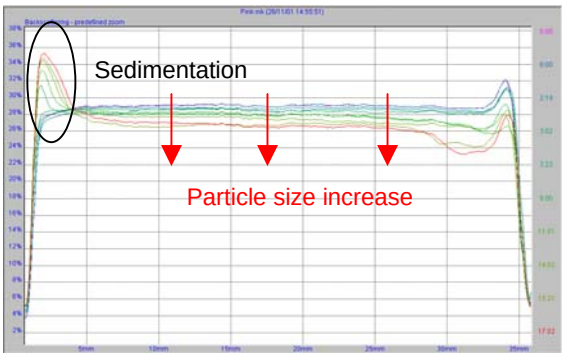

Figure 12. Backscattering profile of pink ink (raw data).

Figure 13. Variation of the backscattering (in %) as a function of time (in days).

3. 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 will be important loss in the quality of the colour.
The following graph is obtained after 15 hours of analysis with the Turbiscan®.

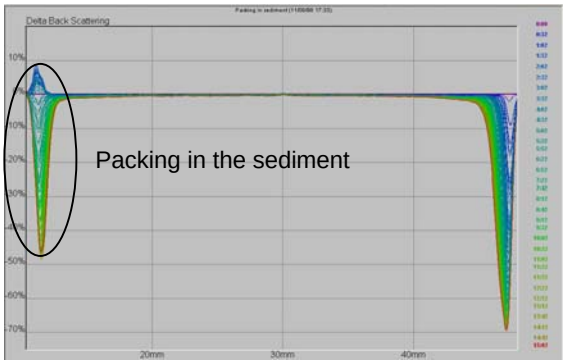

Figure 14. Backscattering profile in reference mode.

If we focus on the sediment layer and we compute the variation of backscattering in this part, we get the graph Figure 15.

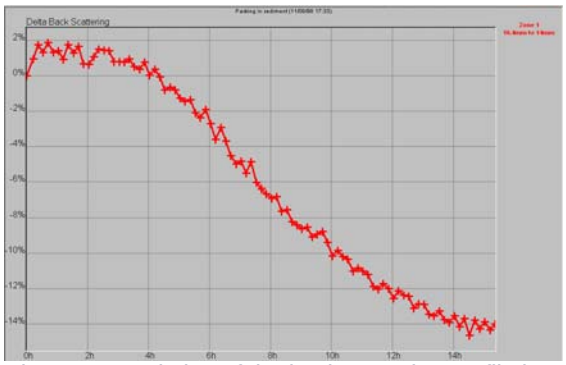

Figure 15. Variation of the backscattering profile in the sediment layer.

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 (see part 2.). 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.

4. 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 16).

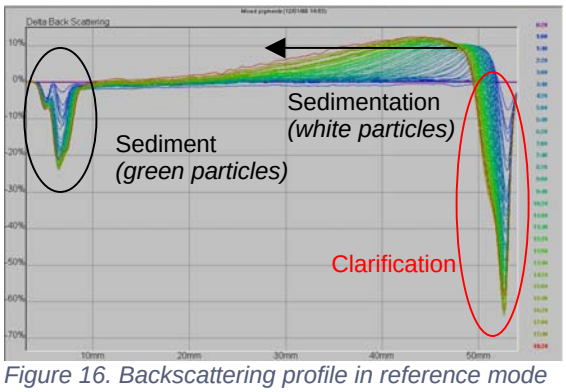

Figure 16. Backscattering profile in reference mode for mixed pigments.

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 infra-red. 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.

5. Effect of temperature

It is interesting to increase the temperature of the measurements in order to accelerate the destabilisation process. This can be done with the Turbiscan LA*b*^{Thermo}, Turbiscan LA*b*^{Expert} or the fully automated ageing station, Turbiscan ags.
One sample of yellow ink was analysed at 30 and 40°C for one day. The clarification layer is plotted for both temperatures (Figure 17).

Figure 17. Clarification layer thickness at 30°C (purple) and 40°C (red) as a function of time.

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

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 quality control. 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 directly affects the quality of the printing.
Moreover, the analyses can be automated and accelerated through the temperature increase and the use of the ageing station Turbiscan ags.