APPLICATION NOTE - PAINT PRODUCTS
ACCELERATED STABILITY AND QUALITY TESTING

Scope

To assure continued consumer satisfaction the following stability issues of paint products have to be minimized or avoided:

- Syneresis – separation of the liquid dispersion media
- Pigment segregation – change of colour composition inside a container
- Particle segregation – change of particle size distribution inside a container.

These stability issues have to be addressed not only during development of new paint products but also for quality assurance during production on a regular basis.
This application note demonstrates that multisample analytical centrifugation can be used as an efficient tool for the accelerated evaluation of separation stability of paint products.
In addition this technique provides for high resolution data of particle size distributions of pigments or emulsions.

How does multi-sample analytical centrifugation work

The LUMiFuge® / LUMiSizer® instruments employ the STEP-Technology®, which allows measuring the intensity of the transmitted light as function of time and position over the full sample length simultaneously. The data is displayed as function of the radial position, as distance from the centre of the rotation.
Up to 12 different samples can be measured in one test run providing high volume data output.
By means of the available analysis modes "Integral Transmission" (clarification speed) and "Front Tracking" (separation velocity) the separation behaviour of the individual samples can be compared and analysed in detail.

Samples vulnerable to syneresis and pigment segregation

Figure 1 displays the transmission profiles of a colorant formulation exhibiting syneresis and pigment segregation analysed at 4000 rpm (2300 g) (inserted photo shows the sample after centrifugation). As documented in Fig. 1 (upper part) visual observation of the sample after centrifugation reveals syneresis (clear liquid on top of the sample) and pigment segregation (deeper red of the lower half of the sediment). Movement and final position of the interface colorant dispersion – particle free supernatant can be directly traced by the optical detection system. Pigment segregation is also visible by optical inspection after centrifugation.

The detection wavelength (near infrared) is selected purposely as it is not sensitive to colours. This way the movement of particles can be traced even in solutions of dark colour.

The sharp increase in the transmission profiles at about 107.5 mm corresponds to the filling height of the sample. The position of the cell bottom is at about 130 mm.
The transmission profiles are representative for the variation of particle concentration inside the sample (low transmission means high particle concentration, high transmission means low particle concentration).

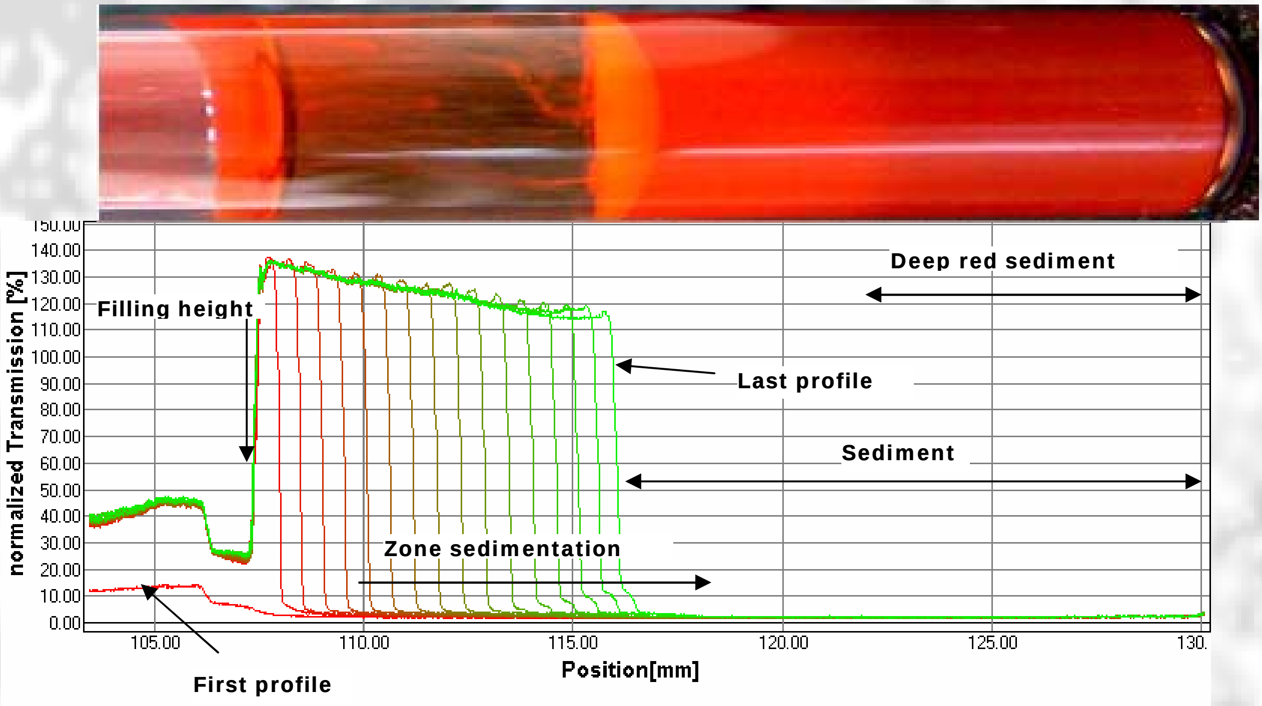

Fig. 1 Evolution of transmission profiles with time – first recorded profile after 30 seconds lowest (red), last profile after 2 hours uppermost (green), centrifugation of a colorant formulation (exhibiting zone sedimentation and pigment segregation) at 2300 *x*g, 20 °C, above the sample after centrifugation.

As can be observed from the time line of the transmission profiles, the separation process is characterized by a sharp front moving towards the cell bottom, i.e. all particles are moving together (zone sedimentation). As particles are moving as a particle collective no particle segregation (particle sorting according to size) is taking place.

Samples vulnerable to particle segregation

Below is a set of transmission profiles obtained from a latex based paint (Fig. 2). A very polydisperse sedimentation (no sharp front) can be observed as particles move with different speeds. The marked increase in transmission at about 106 mm corresponds to the filling height of the sample.
Polydisperse sedimentation is characteristic for colloidal stable dispersions (this does not mean physical stability against sedimentation, but stability against aggregation). Further the diffuse front also characterizes a broad particle size distribution. Based on the polydisperse sedimentation one has to expect particle segregation as the main demixing process for this latex paint.

How to compare the quality of different samples/batches

As strict quality criteria one may specify that no variation in transmission and no pigment segregation should be observed after a long duration of centrifugation at high acceleration. In addition the software of the multisample analytical centrifuge allows for a direct comparison of the kinetics of the separation processes (polydisperse or zone separation) for different samples measured under exactly the same conditions (Fig. 3). This allows specifying a target behaviour, i.e. kinetics of separation should be at least as slow as for a standard product of a proven quality.

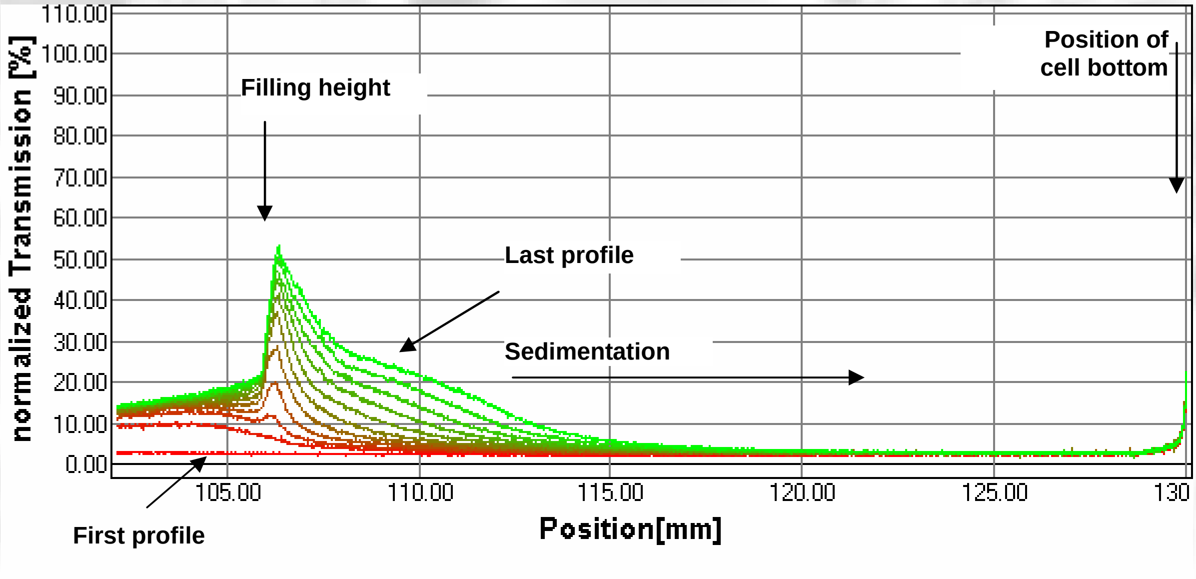

Fig. 2 Evolution of transmission profiles with time – first recorded profile after 10 seconds lowest (red), last profile after 15 hours uppermost (green), centrifugation of a latex based paint at 328 g, 20 °C, every 25th profile displayed.

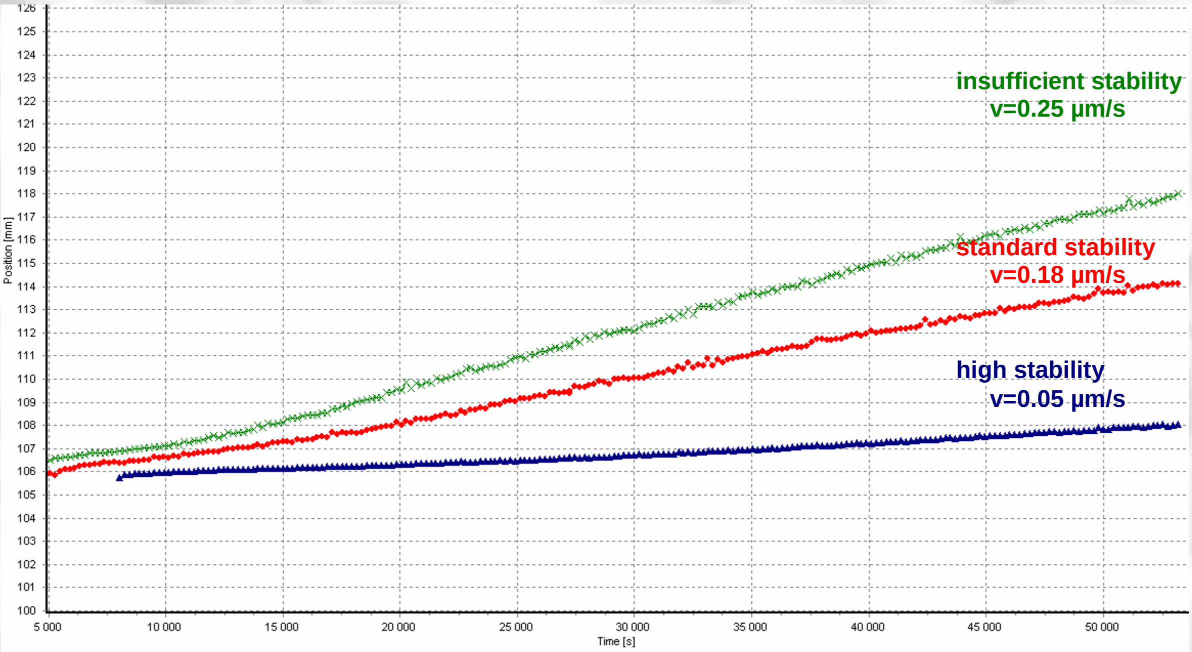

Fig. 3 Separation kinetics of three different batches of a latex paint during prolonged centrifugation at 328 g. Movement of the interface supernatant-dispersion. Comparison with a product of standard quality.

Are results obtained under centrifugal acceleration reliable for evaluation of stability under normal earth gravity?

For paints with Newtonian behaviour the velocity of separation scales linearly with the acceleration applied. However, paint products usually exhibit complex non-Newtonian behaviour. Shear thinning and yield point are often desirable properties of paint formulations.
Therefore the question arises, how to deduce the behaviour at normal gravity from centrifugation results?
The simple answer is that centrifugal separation has to be evaluated as function of centrifugal acceleration, at least at a relatively low and at higher acceleration. This way it

can be established whether particle and pigment segregation is an issue at low acceleration (normal earth gravity) and whether separation velocity scales linearly with acceleration. The latter is an indication of the rheological behaviour of the formulation (shear thinning, shear thickening or Newtonian behaviour).
An example is given in Table 1, which compiles the results for colorant formulations of different trial batches. Measurements were conducted at 4000 rpm (2300 g, 2 hours) and at 1500 rpm (328 g, 14 hours). Note, the equal ratio between the accelerations 2300 g / 328 g and the duration of measurements 14 hours / 2 hours. In case of Newtonian behaviour one would expect the same ratio for the separation velocities too and the degree of phase separation (volume of supernatant / sample volume) should be equal for the two measurements.

Table 1 Evaluation of separation stability for different batches of a colorant formulation, centrifugation at 328 and 2300 g (14 and 2 hours, respectively), 20 °C.
(v328 and v2300 – separation velocity at 328 and 2300 g, v/v 2300/328 – ratio between separation velocity measured at 2300 and 328 g, which should be close to a value of 7 for Newtonian behaviour, < 7 indication of shear thickening behaviour and > 7 indication of shear thinning behaviour.

Sample	pigment segregation 328 xg	pigment segregation 2300 xg	phase ratio 2300 xg	phase ratio 328 xg	v2300 µm/s	v328 µm/s	v/v 2300/328
A	n.o.	+++	0.3	0	0.95	n.o.	> 7
B	+	+	0.37	0.39	1.01	0.14	7.2
C	+++	+++	0.14	0.17	0.30	0.056	5.4
D	+	++	0.15	0.16	0.33	0.054	6.1
E	+	+	0.05	0.12	0.13	0.045	2.9 !
F	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
G	+	+	0.17	0.35	0.56	0.15	3.7 !

n.o. =not observed; + ++ +++ - varying from minor to severe pigment segregation.

Sample A shows severe pigment segregation and phase separation at 2300 g. Nevertheless, this sample is highly stable as it has a yield point and no separation is traced at lower acceleration. Marked stability issues can be identified for sample B (intense syneresis), C (severe pigment segregation) and G (moderate syneresis traced, but sample exhibits shear thickening, i.e. even higher syneresis has to be expected at earth gravity).

Conclusion

- Multisample analytical centrifugation can be used as an efficient screening tool for the accelerated evaluation of separation stability of paint products.
- Stability issues like syneresis, pigment and particle segregation can be identified and quantified. The quality of different samples/batches can be directly compared in relatively short time.
- Measuring at a relatively low and at higher acceleration it is possible to obtain reliable information about stability at normal earth gravity. In addition, valuable information about the rheological behaviour of the paint formulation is obtained.

References

- Paint products - Optimization of deagglomeration of pigment particles, Application note L.U.M. GmbH
- Dispersion Stability and Particle Characterization by Sedimentation Kinetics in a Centrifugal Field, D. Lerche, J. Dispersion Sci. Technol. 23 (5), 699-709, 2002
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- Particle Size Distribution by Space or Time Dependent Extinction Profiles obtained by Analytical Centrifugation, T. Detloff, T. Sobisch, D. Lerche, Part. Part. Syst. Charact. 23 (2006), 184-187