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Determine easily the influence of an additive by direct accelerated stability testing

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Abstract

Cosmetics, personal and home care products are often formulated as dispersions. Separation stability is one of their important characteristics. Its determination in real-time is often contradictory to the market demands of a quick product release. Instrumental methods for the accelerated stability testing belong to the concepts of choice to provide quick information in R&D as well as in QC/QA. Physical acceleration at different temperatures in combination with a patented optical technology is presented here on the example of a nail polish without and with a stabilizing additive.

Keywords: nail polish, additive, separation stability, accelerated testing, ISO/TR13097, ISO/TR18811

Introduction

Cosmetics, personal and home care products are often formulated as suspensions, emulsions or suspoemulsions. They feature a complex composition with many different ingredients to ensure the required manifold product properties.

While the consumers demand a high product stability against e. g. phase separation or an easy redispersibility in case phase separation does occur, the marketing departments of the industry demand a quick product release in much shorter time than allowing for a complete final product testing under real storage conditions. Instrumental methods for accelerated stability testing are suggested by ISO/TR 13097:2013 and ISO/TR 18811:2018 to solve the challenge.

ISO/TR 18811:2018 (Cosmetics -Guidelines on the stability testing of cosmetic products) serves as a technical/scientific framework to identify the most suitable methods for the assessment of the stability of cosmetic products, but it does not aim to specify conditions, parameters of criteria of stability testing [1].

Earlier released ISO/TR 13097:2013 addresses the stability characterization of liquid dispersions (suspensions, emulsions, foams and mixtures thereof) for applications, such as new product design, optimization of existing products, quality control during processing and during usage of the product. The stability of a dispersion in the sense of ISO/TR 13097:2013 is defined in terms of the change in one or more physical properties over a given time period [2].

For nail polish different sources [3-5] report a so-called shelf life equal to one or two years, not revealing the necessary specification of the stability matrix and stability criteria, as described in chapter 3 of [2].

This paper highlights the advantages of direct accelerated stability testing for nail polish to understand its physical separation behaviour and the influence of an additive on it. In much shorter time than required for real-time storage, the additive influence can be investigated under different conditions. When applying the procedures for typically a larger variety of product formulation approaches, e.g., additive selection or optimization of additive concentration, most promising candidates can be proceeded and can later undergo real-time storage tests, while less satisfactory samples can easily be dismissed. Thus, saving time, storage place, raw material towards better sustainability and last but not least money.

Experimental

Nail polish

Two samples were received from a nail polish producer, one with a new additive and one without additive. Neither the chemical composition nor the age of the samples were disclosed to LUM.

Unpacking the samples, a thin sediment was observed in the sample without additive. Above that, the turbidity decreased towards the top.

In the case of the sample with additive, on the other hand, a clear phase could be seen in the uppermost layer, below which the sample was homogeneous.

Before the measurements, the samples were thoroughly homogenized in the container with a magnetic stirrer. After filling into the cells, the samples were each rehomogenized immediately (shaking horizontally 10 times by hand) before the measurement.

Accelerated stability testing in original concentration

Approximately 1.75 g of the samples were weighed into 10 mm sample cells made of

polyamide. The selection of 10 mm cells refers to the present case, for other nail polish samples 2 mm or even 1 mm cells could be appropriate.
Polyamide cells are obligatory for all nail polish samples known to LUM.

Determination of sedimentation velocity distributions for individual particles

For the determination of the separation velocity distribution and the particle size distribution for individual particles conditions apply to avoid hindered settling and multiple scattering [6].
To achieve an initial extinction E in the linear range of Lambert-Beer’s law 0<E<1 the samples were diluted 1/50 with butyl acetate, selected in agreement with the customer.

Measuring instrument and technology

The analytical centrifuge ‘Dispersion Analyser’ LUMiSizer$^{®}$ (Fig.1) allows to speed-up the separation of dispersions

- by application of higher gravity [relative centrifugal acceleration (RCA) of movement of particles and droplets compared to earth gravity]
- by raising the temperature (decreasing the viscosity and possibly acceleration of diffusion limited processes, the latter depending on RCA).

Fig.1 Dispersion Analyser LUMiSizer$^{®}$.

The LUMiSizer$^{®}$ employs the optical STEP-Technology$^{®}$, which allows measuring the intensity of the transmitted light as function of time and position over the full sample length simultaneously. (Measurement principle see Fig.2).

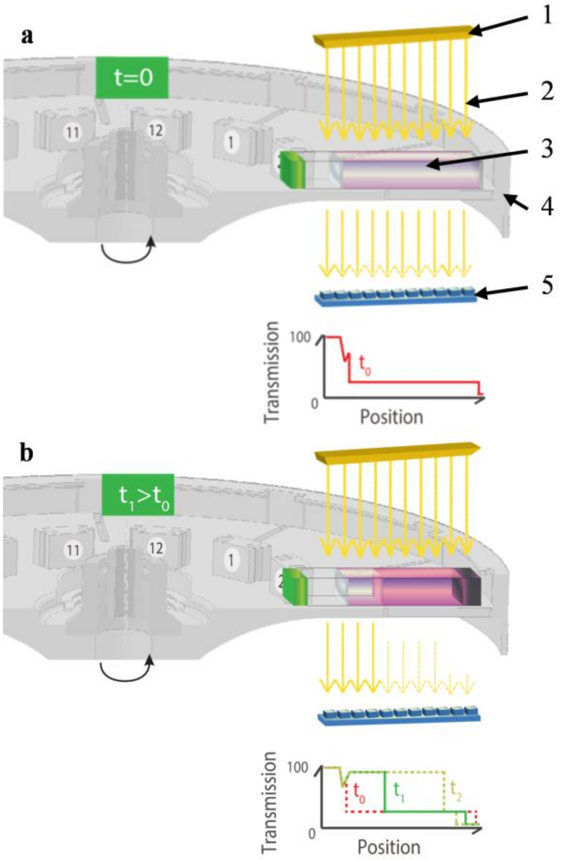


Fig.2 Principle of measuring space- and time-resolved extinction profiles (displayed as transmission profiles) implemented in an analytical photo centrifuge (© by LUM GmbH, Berlin). a) Transmission profile of an unseparated sample at t0. b) Transmission profile (green line) at t1. Dotted lines indicate the situation at t0 and t2 for comparison. (1) light source(s); (2) parallel NIR or VIS light; (3) sample cell; (4) multi-sample rotor with indicated channel numbers 11, 12, 1 and 2; (5) line detector [11].

The data are displayed as function of the position inside the sample, as distance from the centre of the rotation. At the same time up to 12 different samples can be analysed.
For a given type of sample cell the position corresponds to a defined sample volume, this allows to directly determine separated phase volumes and to calculate packing densities.
The progression of the transmission profiles contains the information on stability and on the kinetics of the separation processes. By means of the available analysis modes Instability index [7] and Front Tracking [8, 9] the separation behaviour, i.e., the different destabilizing processes, can be analysed in detail.

The LUMiSizer® also enables the determination of the particle size distribution.
The separation velocity distribution of the particles can already be determined from the concentration-dependent change in transmission as a function of time and position, without material parameters having to be known [10]. The velocity distribution contains the qualitative information about the polydispersity and multimodality of the samples. It is suitable for showing changes in the distribution of the samples as a function of process parameters or aging or as a result of fluctuations in product quality.
When the necessary material data are known, the software enables an extinction-weighted determination of the particle size distribution as well as a volume-weighted determination of the particle size distribution according to ISO 13318-2.
For the comprehensive explanation of STEP-Technology® see [11].

The accelerated analysis was performed in a LUMiSizer® 611 (near infrared (NIR) light source at 870 nm) at different constant temperatures. The RCA of 327 (refers to cell bottom position at 130 mm; 1500 rpm rotor speed) was applied. RCA is equal to centrifugal acceleration *a* divided by earth acceleration *g* [11]. The transmission profiles were recorded every 26 s. The total measuring time was 110 min. The applicable necessary time for analysis, i.e., resulting obligatory measuring time for subsequent tests is discussed below.
For the separation velocity distribution, the following parameters were applied: 7°C, RCA ramp from 13 to 2300 (rotor speed ramp from 300 to 4000 rpm) within 5 min and then kept constant for another 10 min, with ramping of the measuring interval from 10s to 45 s.

Detailed results and discussion

Visual inspection after 110 min at RCA 327, 20 °C

Fig.3 Nail polish without additive.

Fig.4 Nail polish with additive.

After accelerated separation the sample without additive (Fig.3) shows a small sediment and a turbid supernatant. The sample with additive (Fig.4) has a clear supernatant and an increasing turbidity towards the cell bottom.

Evolution of NIR transmission profiles

The transmission profiles represent concentration profiles of the particles (low transmission-high concentration, high transmission-low concentration).

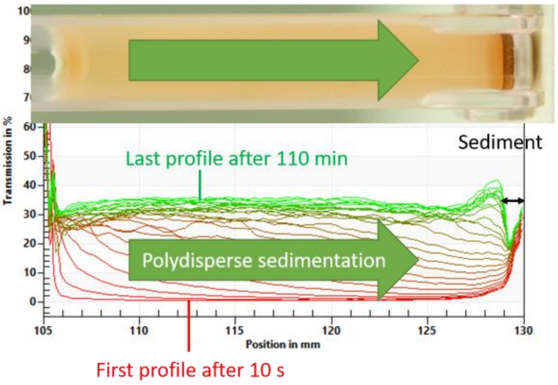


Fig.5 Evolution of transmission profiles, recorded by SEPView® software, for nail polish without additive, RCA 327, 110 min, 20°C. Every 10th profile displayed.

The course of the transmission profiles in Fig.5 indicates a highly polydisperse sedimentation for the sample without additive, the particles sediment at different velocities. Accordingly, a segregation of the different particle sizes is to be expected during storage [12]. A high residual cloudiness remains in the supernatant. This can be caused by very fine or very light particles.

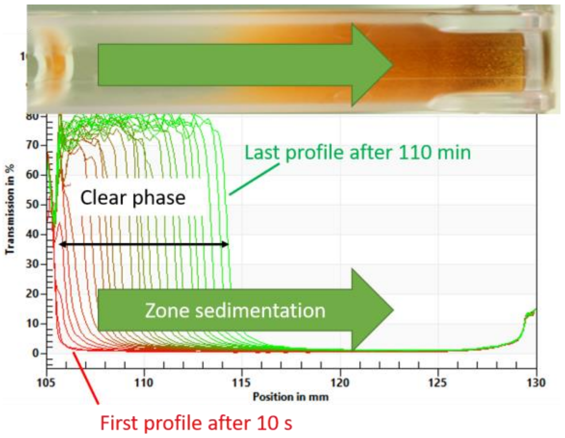


Fig.6 Evolution of transmission profiles for nail polish with additive, RCA 327, 110 min, 20°C. Every 10th profile displayed.

The separation behaviour of the sample with additive is shown in Figure 6. In this case, a sharp front migrates towards the bottom of the cell (zone sedimentation). Syneresis (separation of the continuous phase on the surface) is to be expected during storage [12], as was also observed before the measurement. In addition to the sharp sedimentation front, a gradual increase in transmission can be seen in the cleared area. In addition to the particles that settle together, a widely distributed fine or light fraction is separated.
For the detailed sediment analysis and its concentration profiling, either in real-time or in combination with the accelerated separation, which did not form part of the presented investigation, the additional LUMiReader X-Ray® is recommended, see [13-15]. When using near infrared wavelength for sediment analysis of nail polish the 2 mm or even 1 mm cells are recommended.

The last NIR transmission profiles of the two samples and the information by naked eye after removal of the cells from the instrument are in agreement with each other.

Quick sample comparison by instability index in few minutes

The instability index, as explained in [6], is the analysis module of choice for the easy and reliable sample comparison, as occurring in quality control/quality assurance (QC/QA) applications. The higher the index value, the more separated the sample. The instability index was calculated for the analysis range 2 mm below the individual filling height at 300 s with a reference transmission of 90 %.

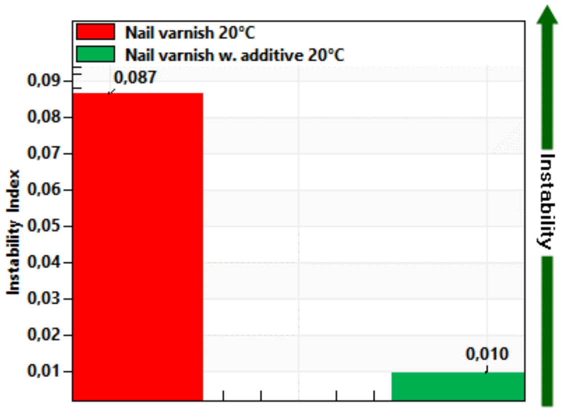


Fig.7 Instability index at 300 s, mean RCA=268 for the applied analysis range.

The stabilizing effect of the additive (green sample in Fig. 7) is confirmed by significantly reducing the separation of the nail polish. Such quick comparison, e. g., when varying the concentration or type of additive or performing a batch-to-batch comparison requires just 5 min under the given conditions.

Sedimentation kinetics at 20°C and at 25°C

A detailed analysis of the kinetics of the separation for the two samples is possible using the analysis mode Front Tracking of SEPView® software (Fig.8). The shift in the phase boundary between the continuous phase and the dispersion was analysed at a transmission value of 10 %.

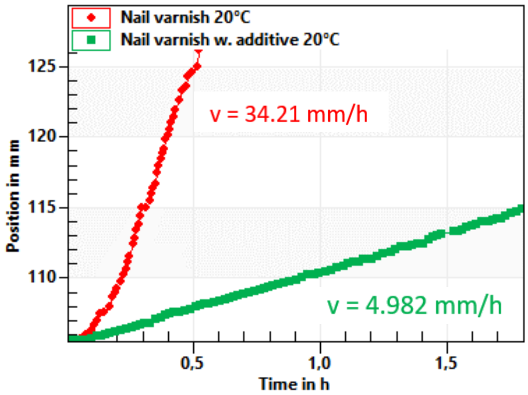


Fig.8 Sedimentation kinetics at 20°C.

The significantly faster sedimentation of the sample without additive (red dots in Fig.8) is reflected in the higher slope of the curve (sedimentation velocity v = 34.21 mm/h). With this sample, the sedimentation of the coarse fraction is recorded, which is separated off much more quickly than the finest fraction.

The final sedimentation state of the sample with the additive (green dots in Fig.8, dark green column in Fig.9) is far from being reached. The slopes obtained by linear regression in Fig. 8 are compared to the data from a second measurement at 25°C and identical RCA=327 in Fig.9 and Table 1.

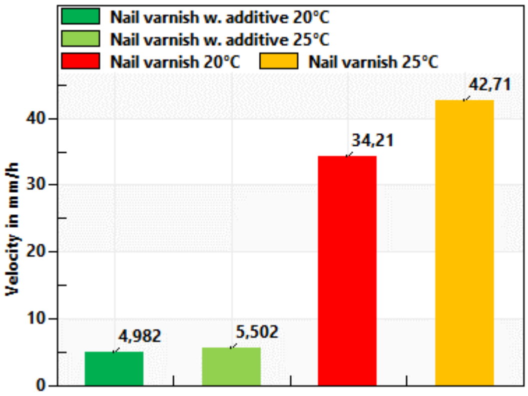


Fig.9 Sedimentation velocities for 20°C and 25°C

Tab.1 Sedimentation velocity with the standard deviation, mean RCA for the range of analysis and correlation coefficient for linear regression.

Sample	Velocity in mm/h	StdDev in mm/h	Mean RCA in g	Corr. coeff.
With additive 20°C	4.982	0.083	277.5	0.9994
With additive 25°C	5.502	0.3787	278.9	0.9982
20°C	34.21	2.888	291.5	0.9868
25°C	42.71	11.47	289.7	0.9305

The stabilizing effect of the additive (green columns in Fig.9) is again confirmed by significantly reducing the sedimentation velocity of the nail polish. As expected, sedimentation rates are higher at 25°C than at 20°C, a possible reason being the reduced viscosity of the continuous phase. Since the chemical composition was not disclosed, an exemplary calculation was carried out using the viscosity values for water at 20°C and 25°C. For pure water as a continuous phase, one has to conclude that not only does the decreasing viscosity lead to faster sedimentation, but there are also additional influences.

Sedimentation behaviour of stabilized nail polish at different temperatures

When the measuring temperature is increased to 45°C, the behaviour of the sample with the additive, changes fundamentally (Fig.10). Very obvious is the decrease of the sediment thickness and a zone sedimentation changing to polydisperse sedimentation.

Degradation of the existing structure obviously occurs at temperatures ≥40°C, there is no stabilization seen. At the beginning of the separation there is an accelerated polydisperse sedimentation, probably of flocculated particles. At the end of the separation, on the other hand, a particle sediment has developed which exhibits consolidation (increase of sediment packing) with time. In addition to this process, a gradual separation of a widely distributed fine or light fraction takes place (gradual increase in transmission in the supernatant).

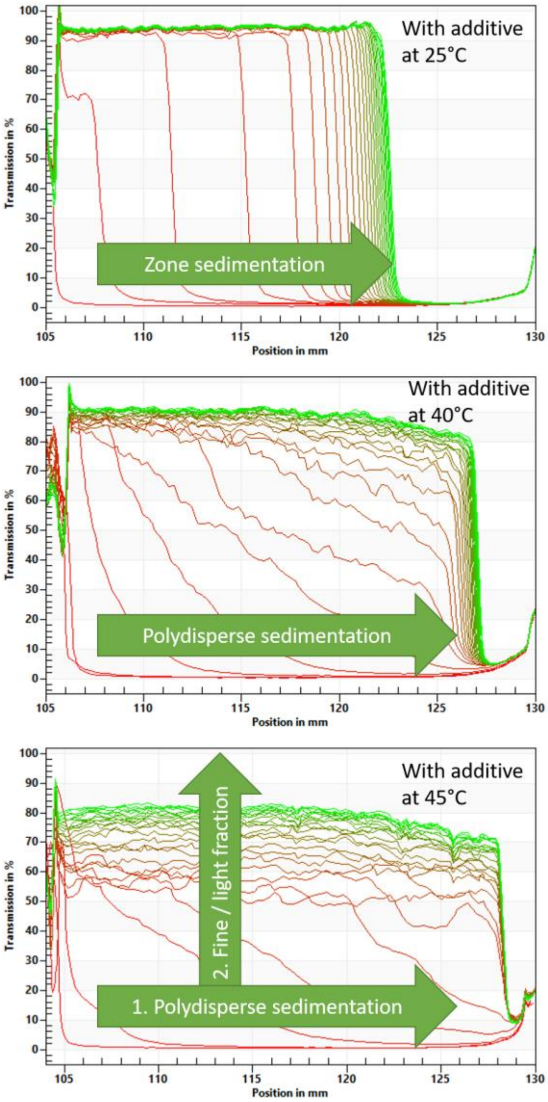


Fig.10 Nail polish with additive, RCA 327, every 10th profile displayed.

The sample with additive is significantly destabilized at higher temperatures.

The nail polish without additive separates faster at higher temperatures but does not change the separation characteristics, its transmission profiles look qualitatively similar to those at 20°C (Fig.5).

Separation velocity distribution

The sedimentation velocity distributions were calculated from the change in transmission over time at positions 125 and 127 mm and averaged. Fig. 11 and Table 2 show the determined extinction-weighted distributions and statistics for the samples.

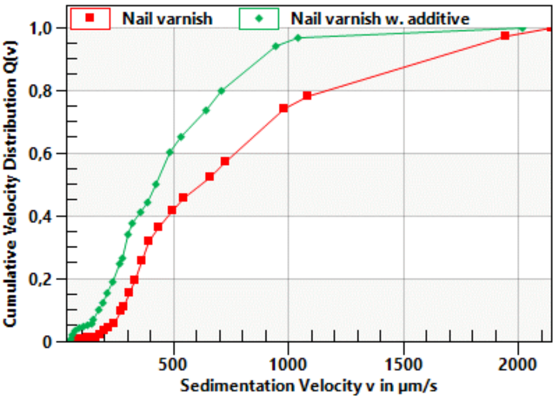
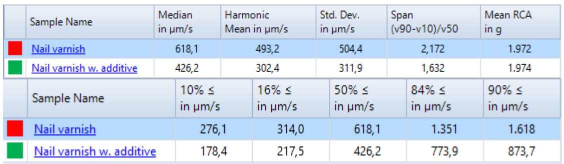


Fig.11 Cumulative extinction weighted sedimentation velocity distribution

Tab.2 Statistics for distributions



	Sample Name	Median in µm/s	Harmonic Mean in µm/s	Std. Dev. in µm/s	Span (v90-v10)/v50	Mean RCA in g
🟥	Nail varnish	618,1	493,2	504,4	2,172	1.972
🟩	Nail varnish w. additive	426,2	302,4	311,9	1,632	1.974

	Sample Name	10% ≤ in µm/s	16% ≤ in µm/s	50% ≤ in µm/s	84% ≤ in µm/s	90% ≤ in µm/s
🟥	Nail varnish	276,1	314,0	618,1	1.351	1.618
🟩	Nail varnish w. additive	178,4	217,5	426,2	773,9	873,7

Both samples have a relatively broad distribution, which can be caused by a broad size distribution as well as a broad density distribution. Both have a small, widely distributed fine or light fraction as a sub-fraction. The distribution of the sample with additive is clearly shifted to slower velocities.
By e. g. comparing the x_{50}=426 µm/s (with additive) with x_{50}=618 µm/s (without additive), the sample with additive can be regarded more stable against sedimentation. This is also in agreement with the stability ranking from the tests of the samples in original concentration. The sub-fraction of very light or fine particles is increased in this sample.

Conclusion and Outlook

Direct accelerated stability testing at higher gravity and constant, different temperatures was performed for a nail polish with and without an additive. The experiments were performed in accordance with ISO/TR13097 and ISO/TR18811. The nail polish with additive features a significantly higher stability against physical separation at 20°C and 25°C, which represent typical temperatures of storage in the beauty shop, drugstore and supermarket.

Tests at 40°C and 45°C qualitatively and quantitatively reveal change the separation pattern of the stabilized nail polish, as obvious from the NIR transmission fingerprints. One might want to conclude that the stabilized nail polish must not be left in the sun, nor be stored or transported at such elevated temperatures.
The fast stability ranking of the original samples is in agreement with the sedimentation velocity distribution ranking of the dilute samples, e. g. using their x_{50}-values.

By applying direct accelerated stability testing using analytical centrifugation and STEP-Technology®, nail polish with a specified shelf life of one to two years can be investigated in few minutes and few hours instead of waiting for such years. Early formulation development and product improvement procedures are significantly accelerated and only the remaining most promising candidates undergo a subsequent real-time storage test.
By applying the concept of comparative analysis for the prediction of the shelf life of a dispersion [2], the presented method is applicable in QC/QA departments.
The predictive shelf-life analysis [2] would require the repetition of the tests at the same temperature but at different RCA.
Examples on comparative and predictive analysis for cosmetics, home and personal care products are given in the literature [16-20].

In addition to particle and dispersion characterization of nail polish, a second analytical centrifugation method – Centrifugal Adhesion Testing (CAT)-Technology® has been tested. A general proof-of-application for tensile testing of cured nail polish layers has been performed by using an Adhesion Analyser LUMiFrac® [21-22].

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