Prediction of Emulsion Stability: Facts and Myth

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Introduction

The achievement of long time stability of cosmetic products (3 years shelf life) is a difficult and costly step in the development of new formulations.

Stability is also one of the first conditions that has to be respected when one wishes to develop new ingredients (after toxicity and cosmetic elegance). However, it remains a very tedious procedure to determine stability because many formulations are first prepared, then stored at various temperature and analysed during storage.

The aim of this work is to show that it is possible to reduce the amount of formulations stored and storage time - and therefore reduce costs and time - by analysing potential instabilities at a very early stage, namely, 24 hours after the formulation has been prepared.

Besides, in the search for new basis formulation it can be helpful to test only a part of the formulation (not all the components together, only a few chosen ones) and see how the system behaves without having to store a complete sample.

However since many factors can lead to instabilities[1] and these factors are not always easy to identify, several analytical methods are necessary in order to represent an unambiguous diagnostic tool.

These methods are not always available to every formulator, therefore it is useful for a supplier to achieve an in-depth understanding of raw materials in regard of the formulation stabilities.

The idea is, of course not, to formulate as broadly as our customers but to work on a basis that can be used for further improvements of the raw materials.

One aim of this work was to gain a better understanding of the role of pigments in the stability of emulsion and to learn if there is a possibility of being able to predict the related stability in a reliable manner.

Samples

Sample preparation - formulation of "real" emulsions

We chose only oil in water emulsions all containing zinc oxide or titanium dioxide at a concentration of 4%. In all cases the pigment was given to the oil phase and dispersed.

The base of the emulsion was the following:

Table 1	
8	dibutyl adipate
8	C12-C15 alkyl benzoate
12	cocoglycerides
1	sodium cetearyl sulfate
4	lauryl glucoside polyglyceryl-2 dipolhydroxystearate, glycerin
2	cetearyl alkohol
3	ethylhexyl triazone
4	zinc oxide, dimethicone or titanium dioxide, trimethoxycaprylysilane
3	glycerin
0.3	xanthan gum
1.5	magnesium aluminium silicate
0.2	allantoin
0.05	disodium EDTA
ad 100	water

The samples are the following:

1435: stable over one year, emulsion containing zinc oxide

1575: same preparation without pigments (comparison sample)

1533: showed signs of phase separation under the microscope after 24 hours, containing zinc oxide but based on a different oil phase than in the classical emulsion

1435 (contained silicone oils as the oil phase and propylenglycol 50P, thickener: xantham gum and acrylamide sodium acryloyldimethyltaurate copolymer).

1519: unstable after 3 months, containing TiO2

1518: unstable, signs of phase separation after 6 weeks, containing a mixture of both pigments in the oil phase

Model emulsions

These emulsions were only used for the analysis with the ultra centrifuge in order to gain a deeper understanding of emulsion stability. The aim is to understand the data obtained with such easy systems and to transfer it to real systems with 20 to 25 components.

The model emulsion chosen to show the capability of the method is the following

- 73.9 % wt water,
- 21.1 % wt paraffin oil
- 5 or 2.5wt % of a mixture of Cremophor® A6 and A25 (in a weight ratio 7 to 3)

During emulsification (at 80°C under stirring) the water phase was poured into the oily one (containing the surfactant mixture), during this procedure inversion of coexisting phases occurred (W/O ⟶ O/W).

Microscopy for the observation of emulsion structure

Optical microscopy observation of fresh samples

Traditionally the emulsions are observed under the microscope 24 hours after the preparation. It is the ideal tool for the observation of the pigment dispersion as well as for early signs of instabilities. Indeed sample 1533 was already showing such signs (**Figure 1**) and would not be stored under normal conditions. The difference with the stable sample (1435) is very clearly seen as well as with the third sample (1519) that turned unstable after 3 months only.

Cryo-replica-TEM (freeze-fracture-TEM):

A small emulsion droplet is shock frozen in liquid ethane at -183°C and freeze-fractured in an evaporation chamber. Freeze-etching of the fracture surface - by ice sublimation at elevated temperature (-120°C) - results in the topographical presentation of the oil phase and solid particles at the surface. This topography is replicated by oblique evaporation of a thin Pt/C layer that now contains the morphological information of the phase and particle distribution of the emulsion droplet. At room temperature the replica

is cleaned from adhering emulsion material in a chromic-sulfuric acid mixture and imaged in a transmission electron microscope.
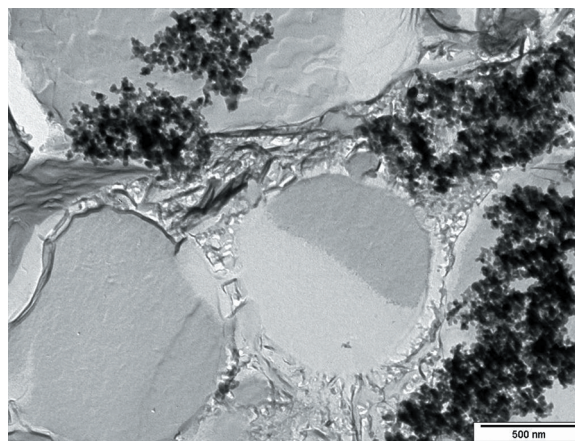
This method is not used routinely because the

Figure 2: Cryo-TEM of the O/W emulsion with 4% titanium dioxide (stable 3 months, 1519). The black particles are titanium dioxide, the big droplets the oil phase.
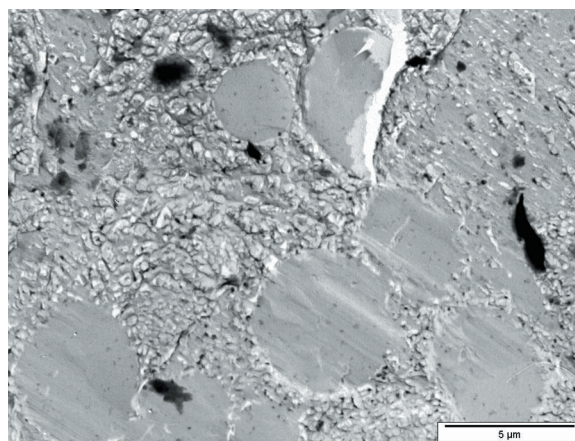

Figure 3: Cryo-TEM of the O/W emulsion with 4% zinc oxide, very unstable (sample 1533). In that case the droplets represent the oil and the black aggregates the pigments. The other crystalline structures represent probably our surfactant system (investigations are under way).

Figure 1: Optical microscopy on freshly prepared emulsions: left, stable one year (1435), middle stable 3 months (1519), right unstable (1533)

sample preparation can be very tedious, however it helps to understand where the pigment is located as well as its behaviour (aggregation, migration from one phase to the other). In sample 1533 we could see that the oil droplets were large (almost 5μm) and that the system would necessarily coalesce.

It is also possible with this method to identify new or different structures in an emulsion depending on the formulation. The interpretation of the results requires a lot of additional work in order to obtain a better insight in structure-properties relationship: for example the influence of the crystallinity of the emulsifiers and of the oil phase on macroscopic properties. These data will be part of a broader study in the future. In the centrifuge data (last part of this paper), the cryo-replica data helped identifying structures that are not seen usually - like for example the existence of a bimodal droplet distribution.

Dynamic mechanical analysis (DMA)

In a dynamic mechanical analysis experiment the sample is exposed to a sinusoidally varying shear deformation with fixed amplitude and frequency. The complex dynamic shear modulus $G^* = G' + i\ G''$ is determined from the amplitude and phase shift of the resulting mechanical stress.

Its real part, the storage modulus G' characterizes the elastic properties of the material, i.e. its ability to store energy reversibly. The loss modulus G'' describes the viscous properties of the fluid, i.e. how energy is dissipated.

Due to the small strain amplitude, which is typically applied, the modulus corresponds to the structure of the fluid at rest. Generally, it is not possible to correlate the modulus uniquely to a certain microstructure. Nevertheless, it is a very sensitive tool to detect even slight morphological or structural changes in complex fluids like suspensions or emulsions and related formulations[2a,b].

Experiments presented here have been done with a controlled strain ARES Dynamic Mechanical Analyzer (Rheometrics Scientific, USA) equipped with a transducer 2KFRTN1 (torque range 2.10^{-6} Nm - 0.2 Nm) and a parallel plate geometry (diameter d = 25 mm, gap height h = 1 mm).

According to a procedure proposed by Brummer et al.[3] the samples are exposed to several temperature cycles (heating/cooling rate = 3 K/min) while measuring the modulus G^* at fixed frequency (f = 1 Hz) and strain amplitude ($\gamma^0 = 0.05$). The applied shear deformation is so small that in general it does not alter the sample structure.

Two types of information are gained from such experiments:

Firstly, the variation of the moduli G' and G'' with temperature is obtained and may be correlated to application properties, like flow or rub resistance.

Secondly and most important here, a change of the moduli from cycle to cycle indicates structural or morphological changes induced by the applied thermal stresses. Accordingly, this test can serve as a quick tool to predict the stability of emulsions like, e.g. cosmetic formulations.

Various sunscreen formulations have been characterized using DMA. All samples were measured 24 h after formulation. In **Figure 4** the loss modulus G'' is plotted in the T-range from -10°C to 50°C. The data show that G'' can vary by more than two orders of magnitude in this temperature range. The strong decrease in G'' between 30°C and 40°C for samples A-D can be attributed to a change of solubility of the thickener used in these formulations.

In **Figures 5a** and **5b** the variation of G' and G'' during three subsequent temperature cycles is shown for two different samples. For sample A (=1435) the moduli at a given temperature T are almost constant throughout the temperature cycles at least in the temperature range below 20°C, at elevated temperatures a slight increase of G' and G'' from T-cycle to T-cycle is detected. This sample is supposed to be stable although some trouble might be expected during high temperature storage. In contrast, the moduli for sample B (=1533) increase from cycle to cycle both in the low and high temperature range thus predicting instability and especially strong sensitivity to temperature changes

This instability is not detectable by visual inspection after such a short time and it is clearly due to the
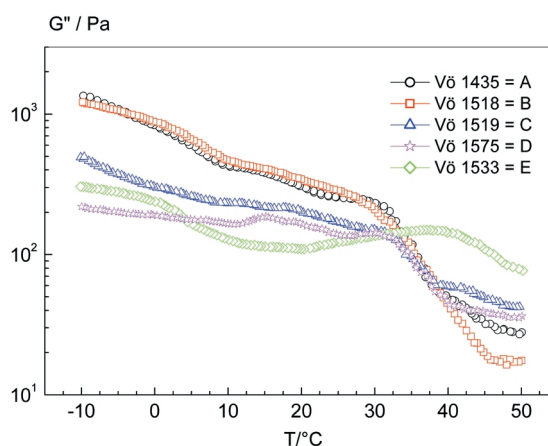

Figure. 4: Variation of loss modulus G'' with temperature for various model formulations
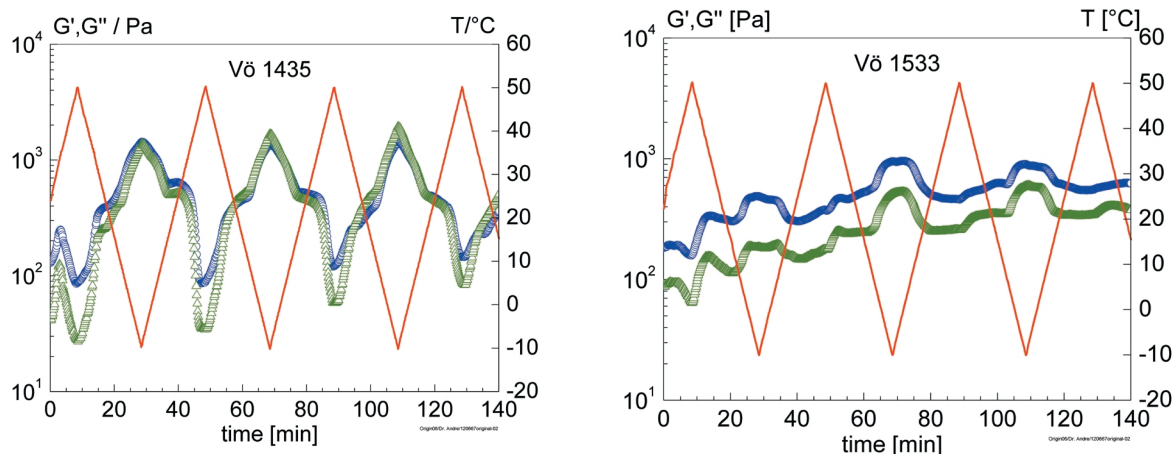
*Figure 5a and 5b : Shear moduli G' and G'' versus time during subsequent heating
and cooling cycles for sample 1435 (a) and 1533 (b).
Symbols: G' (blue line), G'' (green line), measured 24 h after sample preparation Red line: temperature*

thermal stress induced by the temperature change. Another measurement after three additional days of storage at room temperature yields essentially the same results (**Figure 5b**). The modulus vs. time curves start at the same values as in the first experiment and show a similar change in subsequent T-cycles.

Analytical centrifuge (LUMiFuge™)

In some cases the instability of an emulsion is detected because of creaming, i.e. the appearance of an oil phase at the surface of the system or by the sedimentation of components having a higher density. It is thus obvious to use centrifugation methods in order to speed up the potential destabilization process. In this and the following chapter two centrifugation methods are described that have been used for our studies.

LUMiFuge™ 114 is a microprocessor controlled analytical centrifuge that detects a large variety of demixing phenomena of disperse systems during centrifugation over the whole sample height[4]. Whether sedimentation, flotation or clarification, the LUMiFuge directly measures the stability/demixing of concentrated suspensions and emulsions. Like to a time-lapse motion picture the LUMiFuge analysis the demixing processes up to 2500 times faster compared to tests under gravity by naked eyes. It processes up to 8 samples simultaneously.

The centrifugation at 12g - 1200g results in an accelerated migration of the particles/droplets. Local alterations of particles concentration are detected due to changes in light transmission. The graphic representation of transmission as a function of the local position reveals the corresponding transmission profile. Zones of well mixed dispersions scatter and absorb the light, so transmission is low. In contrast, any clarification allows more light to reach the CCD-line: transmission raises.

The samples are analyzed in user-defined intervals between 10 s to 600s up to 24 hours. The corresponding sequence of the profiles is shown in red to green color codes. The evolution of the transmission profiles during the centrifugation allows the quantification of dispersion/emulsion stability and - in favorable cases and if additional information is available about the ingredients of the sample - the understanding of the demixing phenomena or destabilization causes.
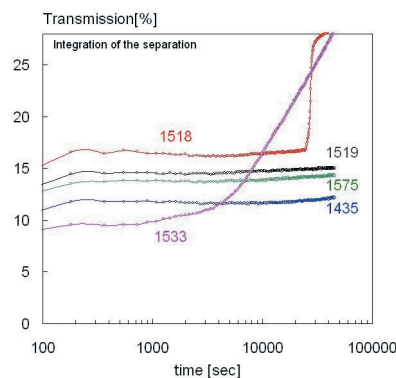

*Figure 6: Centrifugation measurements of
the five samples at 23°C. The two unstable samples(1=
1518 and 5 =1533) are identified as such by a rapid
increase in the light
transmission along the cuvette.*

Figure 6 provides a typical result of a centrifugation run; the set of transmission curves - measured along the cuvette - shows how a clear (oil) phase appears during the measurement. The data of a run can be reduced to a single curve by a suitable integration of each of the transmission profiles. The data were recorded at room temperature (**Figure 6**) and at 40°C (**Figure 7**), respectively and are interpreted as follows. A horizontal segment of the curve indicates that the emulsion under consideration does not change with respect to its transmission profile along the cuvette in the time interval considered. An upturn of the curve is traced to sedimentation/creaming, i.e. to the appearance of a clear phase in the present case. Comparing the samples one notices that samples 1575, 1435 and 1519 show only minor changes with respect to the centrifugation stability, though sample 1435 exhibits a slightly reduced long-term stability at 40°C. Sample 1518 provides an example of a sudden phase separation after about 7 hours, when measured at room temperature. Performing the measurements at 40°C provokes a slowly progressing phase separation starting already after 10 minutes. Sample 1533 exhibits continuously increasing phase separation both at room temperature and at 40°C. As will be discussed below the present data compare favorably with shelf stability data.

Ultracentrifugation technique for the study of oil-in-water model emulsions

Ultra-centrifugation (UC) is well known as a method for the determination of the coalescence pressure of emulsions[5-7].

In this study we indicate that furthermore this technique is applicable to investigate a whole family of colloidal phenomena occurring in emulsions and during the demulsification process described below.
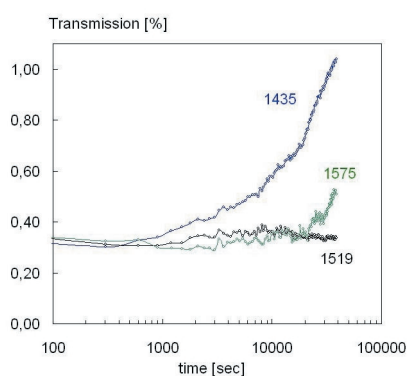
Oil-in-water (O/W) emulsions prepared with water, non-ionic surfactants, and paraffin oil as described above were investigated.

Samples were exposed to gravitational fields as high as 120,000 g in a Beckman XL-I Ultracentrifuge and demulsification was followed by online-detection.

After centrifugation the different phases obtained in the samples can be further used for investigations.

Emulsions react to high gravitational fields in several ways (**Figure 8**).

In the high gravitational field the UC provides the emulsion droplets in the emulsions are separated according to their size and density, and hence several layers appear (**Figure 8**). The result from this measurement suggested that the sample exhibits a bimodal distribution of the droplets, i.e. two droplet sizes are present in the emulsion.

The existence of different oil drops populations is expected to be related to a spontaneous emulsification process[8]. This process may arise from the inversion of the coexisting liquid phases, the change of temperature during emulsification and the surfactant concentration.

The centrifugation studies revealed that as a second effect surfactant aggregates were present in the aqueous continuous phase. They sediment to form a layer at the bottom of the centrifugation vessel (**Figure 9**). This finding implies that depletion effects must be taken into account, which may lead to coalescence phenomena[9].

The interpretation was confirmed by additional laser scattering particle size distribution measurements (not shown here) showing the bimodality with main drop sizes of ~6 μm and ~0.6 μm and TEM pictures (**Figure 10**).

The ultra centrifugation was found to be sensitive to spontaneous emulsification and excess surfactant. The differences in the particle size distribution observed in our emulsions led to different centrifugation profiles.

Interpretation of the results

In order to interpret the results correctly, one has to take in account the influence of the nature of the chosen samples. For example it is quite difficult to create artificially a stable or a non-stable sample. In our case we have chosen the samples using two criteria. First we wanted to verify that an instability taking place after a few weeks could have been detected within 24 hours.

In doing that we chose deliberately a system based on a new formulation that was different from our stable one (sample 1533 compared to the stable one 1345).
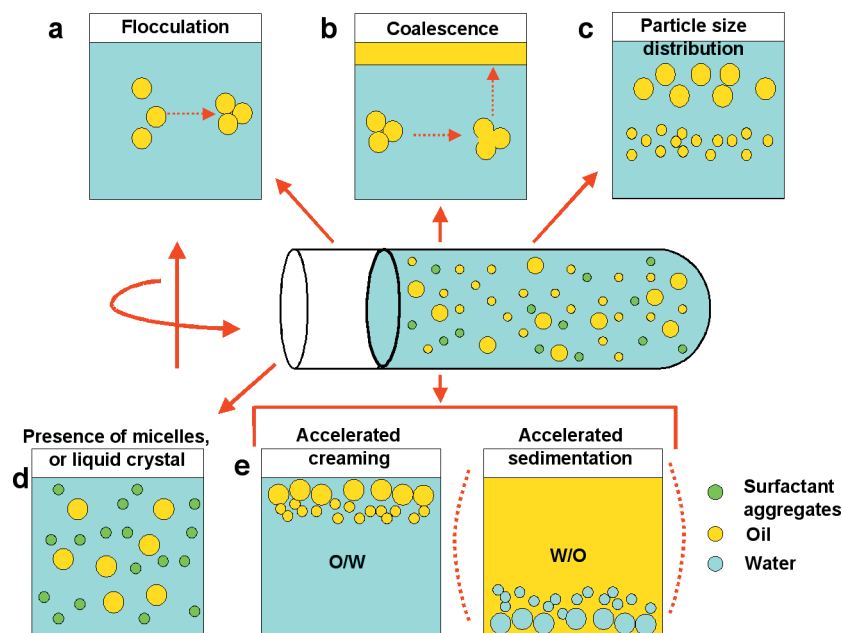

Figure 7: As in Figure 6 but the measurements have been carried out at 40°C

Figure 8: Overview of the possible effects during emulsion centrifugation for O/W and W/O emulsions
(a); flocculation (b), coalescence (c), fractionation according to particle size distribution
(d), detection of the presence of a surfactant aggregate
(e) (promoting emulsion creaming by the depletion effect)
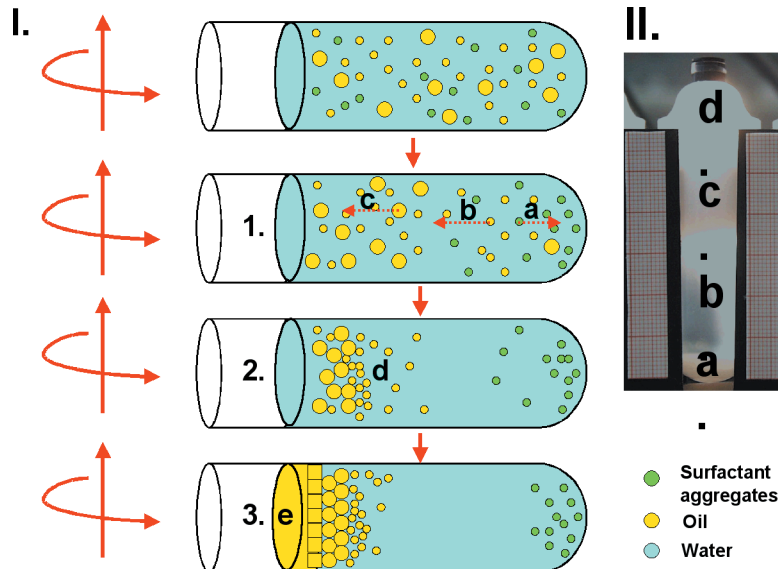

Figure 9: Schematic representation
(I.) of the time course of O/W emulsion centrifugation. (1) separation of surfactant aggregates (that sediment; (a))
and oil drops (according to their particle size; (b) and (c)).
Different layers (d) appear and a foam-like (e) emulsion layer is formed.
This layer may break (coalescence) and release oil.
Photograph (II.) of a centrifuged emulsion with surfactant sediment (a), aqueous layer (b),
emulsion layer (c), and close-packed oil droplets (d).

Figure 10: Cryo-TEM photograph of a O/W emulsion showing the bimodal droplet size distribution: 73.9 % wt water, 5 % wt Cremophor, mixture, 1.1 % wt paraffin oil.

We did observe the unstable behaviour with all three methods: rheology, microscopy and centrifugation. Such a sample does not need to be stored because all three observations go in the same direction.

In the case of our very stable sample, the beginning of instability or sensitivity to high temperature was detected with rheology and centrifugation at 40°C (not at 23°C). In that case it is wise to keep storing the formulation and keep working on improvements because there is a small chance that it does not reach the 3 years stability.

The three other samples were variations around the stable one and showed especially an unstable character with one of the methods.

For example sample 1518 simply contained a mixture of two pigments and became unstable after 6 weeks. Again the storage would have been useless because the centrifuge data showed a phase separation after 7 hours in the Lumifuge (what is not observable in 10 minutes of a classical centrifuge).

However the optical microscopy showed a fairly good picture of the pigment distribution (**Figure 1**). So our first goal was reached: we know how to save storage time on systems showing instabilities with at least one or two methods. In addition the ultra centrifuge helped us seeing new phenomena on model systems which should bring a better understanding of "real emulsions" in the future.

Sometimes it is claimed that the stability of emulsions cannot be predicted on the basis of physicochemical knowledge about the components and their interactions (the "myth" cited in the title of this article).

We know from extensive research activities on latices dispersions that it is indeed possible to explain and predict the application-related properties of such systems by knowing the respective structure-property relationships[10]. The key point for progress with respect to the description of the behaviour of emulsions - like stability - is therefore to gain a fundamental understanding about how structures are formed and evolve – and finally, of course, how these structures are related to the composition of the emulsion under consideration.

By the combination of modern techniques it is possible to provide the relevant insight (the "facts" cited in the title) that is necessary to "design" emulsions from a library of ingredients.

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