MICROTRAC

OPTIMIZE PARTICLE SUSPENSION STABILITY BY THE HANSEN APPROACH USING THE TURBISCAN TECHNOLOGY

Introduction

Formulating stable particle suspensions is of great interest for academic and industrials as it allows to enhance the properties and the lifetime of their products. Industrial fields which are interested in suspension stability are numerous and extensive ranging from cosmetics and pharmaceutics to agriculture and energy. Overall, the choice of the stabilization medium is the key factor to avoid particle agglomeration before adding additives (surfactants, polymers, …etc.) which are, most of the time, quite expensive. Methods have been already developed to predict this stabilization medium such as the Hansen Parameters (HP). The aim of this note is to demonstrate that accurate determination of the HP of particles, Titanium Dioxide (TiO_2) in this study, can be obtained using the TURBISCAN technology. Knowing the HP of particles, it is quite easy **to predict greener and cheaper solvents to optimize particles formulation** regarding the content of costly stabilizing additive or product regulatory requirements evolution.

Definition

The semi-empirical Hansen's approach, which has been historically developed to predict the solubility of molecules, can be adapted to describe the particles stability in various solvents. This approach is based on the decomposition of the Hildebrand parameter δ, linked to the binding energy between two particles, into three different parameters δ_D, δ_P and δ_H describing respectively non-polar, polar and hydrogen interactions between the particle surface and the dispersion media as follow:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$$

Considering these non-polar, polar and hydrogen components, each particle or solvent can be represented by a point in a 3D-space with these components as coordinate values named HP coordinates. The stability of the particle under study is evaluated considering a range of solvents with known HPs exhibiting large variation in these 3D-space and followed by a ranking of the tested solvents as good or poor stabilization media. The border between good and poor solvents allows to build a sphere with a center corresponding to the HP coordinates of the particle as well as a radius R_0. If a solvent is situated inside the sphere of the particle, **it can be considered as a good stabilization media**.

Inversely, a solvent situated outside the sphere should poorly stabilize the suspension. Considering the distance R_a between the determined HP coordinates of the particle ($\delta_{D,p}$; $\delta_{P,p}$; $\delta_{H,p}$) with the one of another solvent ($\delta_{D,s}$; $\delta_{P,s}$; $\delta_{H,s}$), it is quite easy to estimate the Relative Energy Difference, named RED, which indicates if the chosen solvent should give a stable (RED < 1) or an unstable suspension (RED ≥ 1) as follow:

$\mathrm{RED} = \frac{R_a}{R_0}$ with

$$R_a = \sqrt{4.(\delta_{D,p} - \delta_{D,s})^2 + (\delta_{P,p} - \delta_{P,s})^2 + (\delta_{H,p} - \delta_{H,s})^2}$$

Reminder on the technique

TURBISCAN® technology is based on Static Multiple Light Scattering and consists of sending a light source on a sample to acquire a backscattered and transmitted signal all over the height of a sample in its native state.

By repeating this measurement over time at adapted frequency, the instrument enables to monitor physical stability of a sample without dilution.

To compare the stability of different suspensions in a quantitative way, the TURBISCAN Stability Index (TSI) can be used. The TSI is a number calculated at time t by summing up all temporal and spatial variations in a considered zone:

$$TSI(t) = \frac{1}{N_h} \sum_{t_i=1}^{t_{max}} \sum_{z_i=z_{min}}^{z_{max}} |BST(t_i, z_i) - BST(t_{i-1}, z_i)|$$

More information on the TSI can be obtained from the application note 0220_F_Tubiscan Stability Index (TSI). The real advantage to use the TURBISCAN technology in the Hansen approach is **to discriminate in an accurate way the tiny stability variation of solvents tested as good dispersion media**, which is quite difficult by conventional observation. Such measurements allow generating a **Hansen sphere which is more precise and restrictive** than the ones obtained through visual characterization of samples as it is classically realized.

Methods for evaluating suspension stability

The TiO_2 particles was dispersed by means of the ultrasonic probe Sonotrode in 18 different solvents listed in the following Table 1. Following the dispersion step, the sample was immediately closed, and its stability was measured during 30 minutes at 25 °C in a TURBISCAN® Tower.

To score the different solvents, the TSI scale is used as it described in a quantitative way the stability evolution of suspensions. Obtained results are presented in Figure 1. The solvent was scored from 4 when a totally unstable suspension is obtained (TSI>10), to 1 for the obtainment of a suspension with a high stability (TSI<0.5).

Table 1. List of the 18 solvents tested to build the TiO_2 Hansen sphere

Solvents	δ_d	δ_p	δ_h
DMSO	18.4	16.4	10.2
Ethanol	15.8	8.8	19.4
γ-Butyrolactone	18	16.6	7.4
N,N-Dimethyl Acetamide	16.8	11.5	9.4
Dichloromethane	17	7.3	7.1
1,4-Dioxane	17.5	1.8	9
Ethyl Acetate	15.8	5.3	7.2
Methanol	14.7	12.3	22.3
N-Methyl-2-Pyrrolidone	18	12.3	7.2
Propylene Glycol	16.8	10.4	21.3
Water	15.5	16	42.3
Tetrahydrofuran	16.8	5.7	8
Acetonitrile	15.3	18	6.1
Chloroform	17.8	3.1	5.7
Toluene	18	1.4	2
Dimethoxymethane	15	1.8	8.6
Heptane	15.3	0	0
p-Xylene	17.8	1	3.1

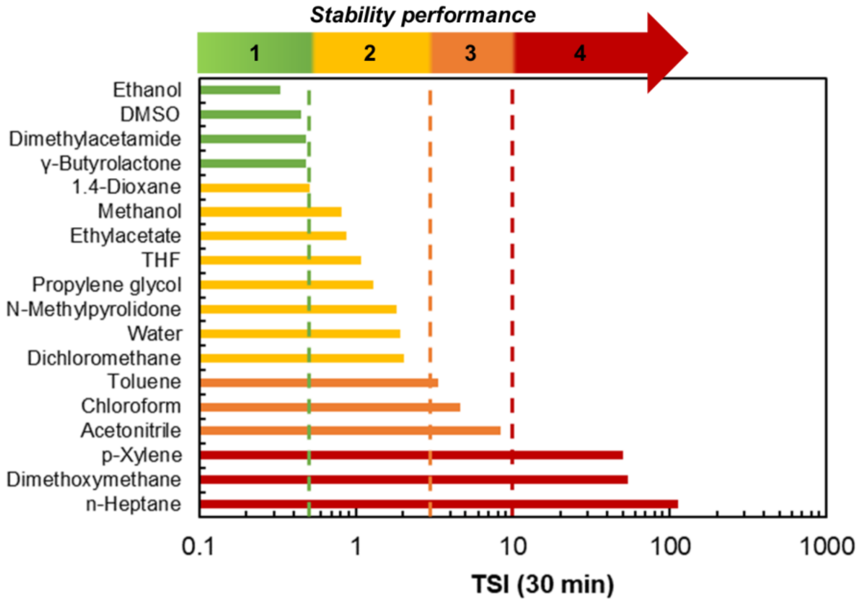

Figure 1. TSI obtained at 30 minutes for the 18 solvents tested to stabilize TiO_2 particles

Calculation of HP stability sphere

Having the TSI values allows scoring each solvent toward its ability to stabilize TiO_2 particles and so building the corresponding Hansen sphere by repeated calculation and iteration using an adapted software like HSPiP as highlighted by Figure 2. From the localization of the sphere centre by the software, the HP of TiO_2 particles are easily obtained as well as the stability sphere radius.

The values obtained are the following ones:

$$\delta_D = 16.4\ MPa^{1/2} \quad \delta_P = 14.1\ MPa^{1/2}$$

$$\delta_H = 14.0\ MPa^{1/2} \quad R_0 = 7.7\ MPa^{1/2}$$

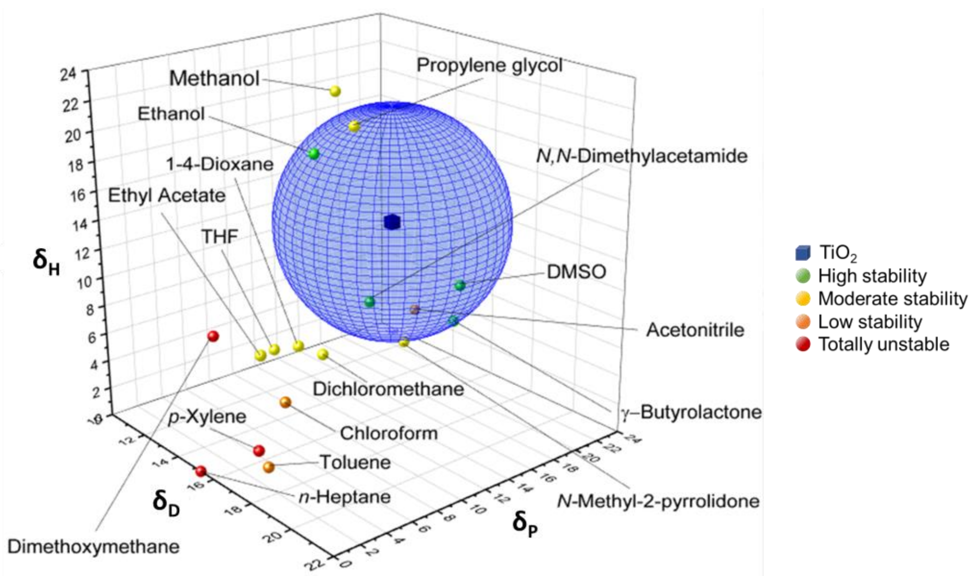

Figure 2. Hansen sphere obtained for TiO_2 particles (FIT=1, no solvent wrong in, no solvent wrong out)

From these values obtained for the TiO_2 particles and HP ones of other solvents available in the literature, it is quite easy to calculate the RED and predict if the selected solvents will be a good or a poor stabilization media. A classification of the solvent stabilization properties can be also predicted considering that **the lower is the RED value, the more stabilized suspension should be obtained**.

This is particularly interesting to design mixture of solvents which highlight an even better stability such as the Ethanol/DMSO mixture presented in the following Figure 3. Due to the specific positions of Ethanol and DMSO located at opposite borders of the TiO_2 Hansen sphere (see Figure 2), it is quite easy to formulate a mixture of these two solvents which is much closer to the sphere centre (*i.e.* the TiO_2 position in the Hansen space) and which provide a better suspension stability as presented by this figure (TSI = 0.29).

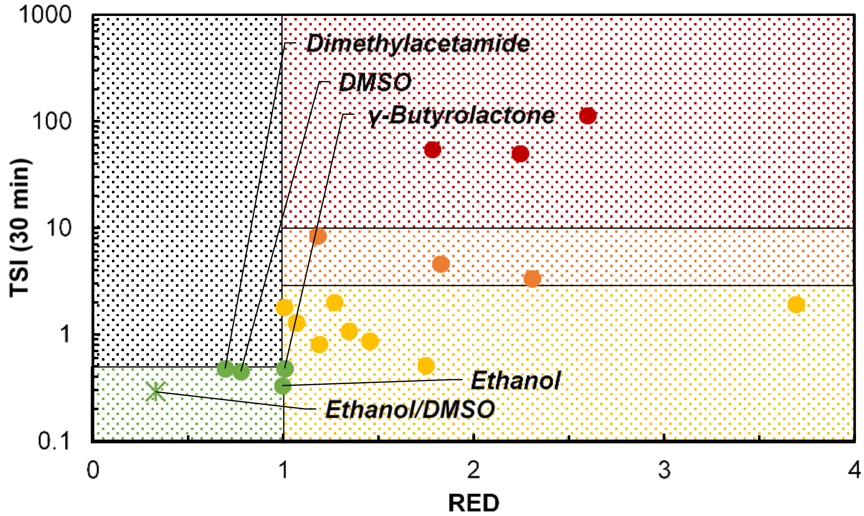

Figure 3. RED vs TSI values to investigate the stability benefits highlighted by the Ethanol/DMSO mixture suspension compared to other solvents

Conclusion

TURBISCAN® experiments have been performed **to quantify and compare** the effect of the stabilization media on the stability of different TiO_2 particle suspensions. The TURBISCAN® technology, through the calculation of the TSI, allows classifying the different solvents tested and is well adapted to the HP approach for **predicting new stabilization media**. This approach finds a direct application in **predicting better stabilization media, greener and cheaper solvents** to optimize particles formulation regarding the content of costly stabilizing additive or product regulatory requirements evolution. As the TURBISCAN® technology can either discriminate the stability and the dispersibility of particles, the HP approach could be also employed to characterize the dispersibility properties of solvents.