Metal working fluids
Stability measurement with Turbiscan®
at each product life stage

Introduction

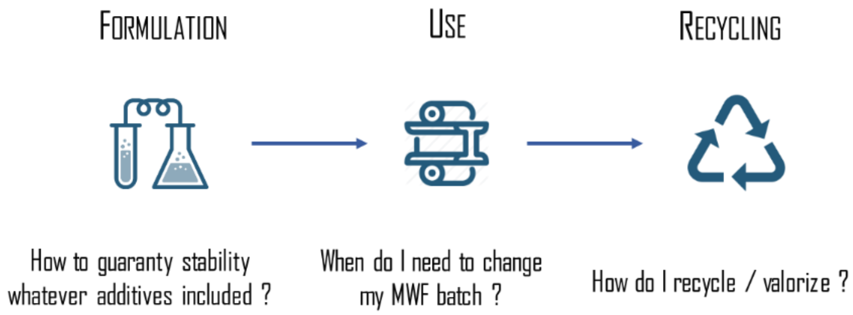
Metal Working Fluids (MWF) are engineered fluids made to optimize metalworking operations as rolling, drawing, grinding, cutting… They are complex formulations with multiple purposes: reducing friction, mitigate heating degradation, flush away residues, protect from corrosion, achieve desired surface finish…MWF formulations can contain tens of ingredients, the major one being oil, water and emulsifiers supplemented by a large range of additive like corrosion inhibitors, lubricity additives, defoamers, biocides, anti-mist agents, dyes, extreme pressure agent, metal deactivators, wettings agents, antioxidants… As a result, optimization of MWF is elevated at the level of science and stability is a critical parameter to be probed at every stage of the product line

KEY BENEFITS

FAST

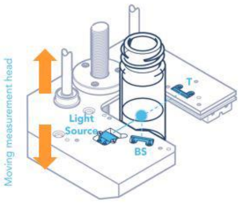
NO DILUTION

SENSITIVE



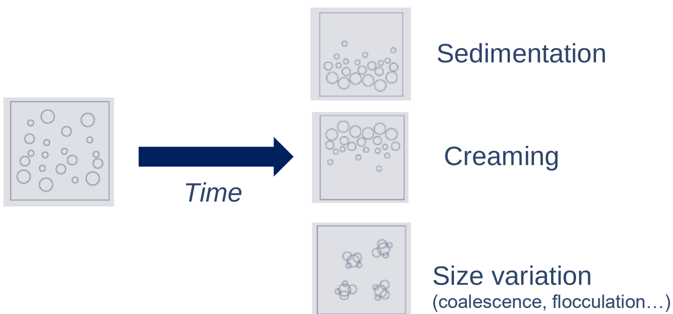
Reminder on the technique: Static Multiple Light scattering

Turbiscan® technology, based on Static Multiple Light Scattering (SMLS), consists on sending a light source (880nm) on a sample and acquiring backscattered (BS) and transmitted (T) signal over the whole sample height. By repeating this measurement over time with adapted frequency, the instrument enables to monitor physical stability, because the signal is directly linked to the particle concentration (ϕ) and size (d) by the Mie theory:



$$BS = f, \phi, d, n_p, n_f$$

Major part of MWF are emulsions whose efficiency is directly correlated to their state and stability and are, by nature, unstable colloidal systems. Destabilization can take the form of coalescence, flocculation, creaming, sedimentation… and can originate from various causes (lack of surfactant, chemical contamination etc.).



Turbiscan® and Turbiscan® Stability Index (TSI) are ‘must have’ tools for formulators for fast and quantitative formulation screening in order to speed up product development or control quality test. Turbiscan technology have been used for decades by formulators to enhance and monitor stability of MWF and it is now recognized as a standard analysis.

Stability Prediction thanks to Turbiscan Stability Index (TSI)

The Turbiscan® Stability Index (TSI) has been introduced for a fast, robust and objective quantifying of sample evolution over time in one single click. The TSI is a dimensionless number that is a result of summing all occurring destabilization phenomena in the sample that can be measured by noticeable change of the backscattering or transmission signal intensity along the sample height. These signal variations are directly linked to any destabilization in the sample, thus the higher the TSI value, the lower the stability.

2 emulsions (O/W 10% + 1% Xanthan) with additional emulsifiers have been tested:
- Tween® 80 (HLB = 15)
- Tween® 65 (HLB = 10.5)

Samples were analysed with Turbiscan® technology for 3 days at RT. Figure 2 represents the backscattering in function of sample of height obtained for one of the emulsions. Each scan is represented by a colour, first in blue last in red. Thanks to the evolution of the backscattering, destabilization phenomena can be identified and quantified. For these formulations, the phenomena detected show coalescence (particle size variation), without any particle migration during the analysis time. Meanwhile, visual observation does not show any variation.

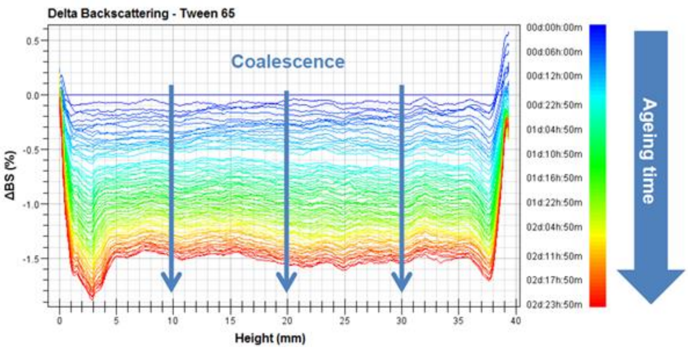


Figure 1. ΔBS (%) scans over 24h @RT for the Tween 65 supplemented sample. Change in signal are characteristic of emulsion destabilization

Beyond characterizing destabilization phenomenon, TSI offers a quick and robust way to analyse destabilisation kinetics in the samples versus ageing time. Computed from individual scans, it constitutes a reliable way to rank the formulations and are compared to formulation without the extra stabilizing agent.

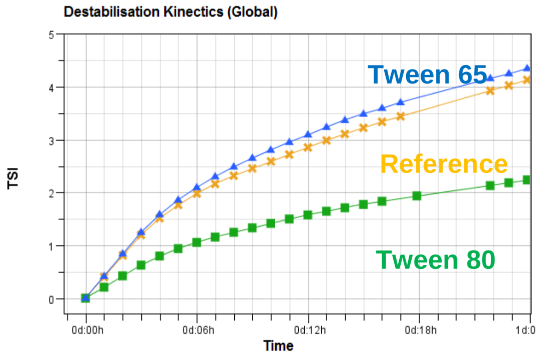


Figure 2 : TSI for the reference emulsion and the 2 emulsions with surfactant

Figure 2 shows TSI for the samples analysed and after **10 hours** differences in the stability evolution can be observed. Tween 65 has no influence on the stabilization of the emulsion (compared to the reference sample), and its HLB is not high enough to play a stabilising role. However, Addition of Tween 80 (HLB 10.5) decreases significantly the kinetics of coalescence and thus increases the stability of the emulsion and is a good candidate for extra stabilization.
The TSI is becoming more and more THE criteria used to compare sample stability evolution, extensively used in research and development, quality control and academic researches

One of the very first paper about the use of Turbiscan for MWF stability analysis was published in 2006 by YP.Zhao "*Monitoring and Predicting Emulsion Stability of Metalworking Fluids by Salt Titration and Laser Light Scattering Method*". The study demonstrated the interest of using the Turbiscan and the time saving compared to visual observation. Turbiscan measurements were able to predict emulsion stability after only 8 hours compared to 12 days at 54°C and 4 months at RT, so up to 300 time faster than naked eye. Although long established, we give in the following paragraphs recent literature to illustrate advantages of MWF testing with Turbiscan®.

Optimizing surfactant / base oil toward enhanced stability

Reference: Norrby, (2017) T et al. Group I Replacement Fluids – a Hydraulic Fluid Formulation and Compatibility Study. Tribologie + Schmierungstechnik, Vol. 64, No. 1, 31-41

MWF formulation ingredients must be optimized toward enhanced stability. In the Norrby's study, base oil/surfactant with varying HLB (Span 80 and Tween 80 mix) with butyldiglycol are formulated and tested. Emulsion characterization is performed both by using TSI calculus after 10 min and mean particle size of fresh, day 1 and day 7 formulations. Figure 3 gives the results obtained with a Nynas T22 naphtenic oil.

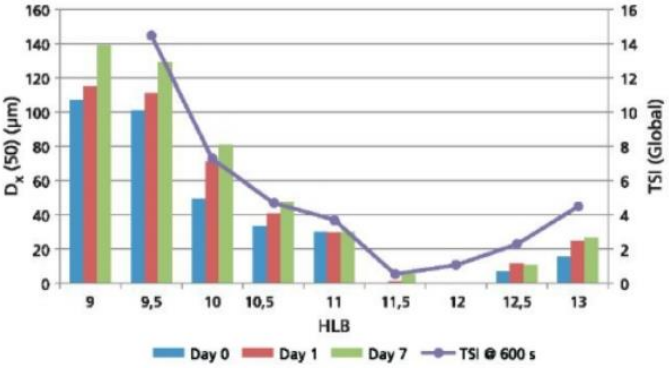


Figure 3: mean DSD evolution over 7 days versus TSI (10 min) for a NYNAS™ T 22 based milky emulsion.

TSI and mean drop size correlates very well and there is a global correlation between the particle size and the emulsion stability. For emulsion prepared with HLB between 11.5-12, Turbiscan® provides more precise and global overview of the stability and results are obtained in only **10 minutes.**

Optimizing formulations for hard water condition

Reference: *Slinkman, (2018). Design of experiment reduces development time for higher-performing metal-cutting fluids. Tribology & Lubrication Technology, 74(1), 26-32.*

One of the main problems when formulating a new MWF is to make it as resilient as possible to hard water/electrolyte destabilisation. Indeed, divalent cations are known to be emulsions breakers through interaction with emulsifiers leading to lime formation. In this study, design of experiment (DOE) is used to find the best formulation regarding:

- Enhanced emulsion stability in hard water
- Auto-emulsification capability
- Limited foam production

Stability measurement with naked eye does not provide quantitative data (a must for DOE) and are too long for fast optimization. On the opposite, Turbiscan® analysis quantifies destabilization and is used to rank the formulations (9 tests, **24 hours** analysis at 50C–Figure5) by following backscattering evolution in the middle of the sample in function of time (linked to particle size variation)

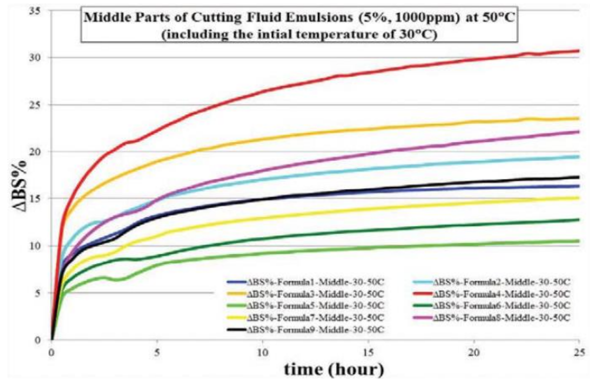


Figure 4: backscattering variation (%) in function of time for 9 sample tests

Results obtained with the Turbiscan are used as in input for DOE software in order to provide the optimum formulation. Turbiscan evolution of the optimum formulation is compared to the control formulation (figure 6).This optimization leads to a drastic reduction of signal change (~15 %) in the middle of the sample compared to the original formulation (figure 6), measured in only **24 hours** and thanks to the quantitative measurement of the stability by following the evolution of the Turbiscan signal.

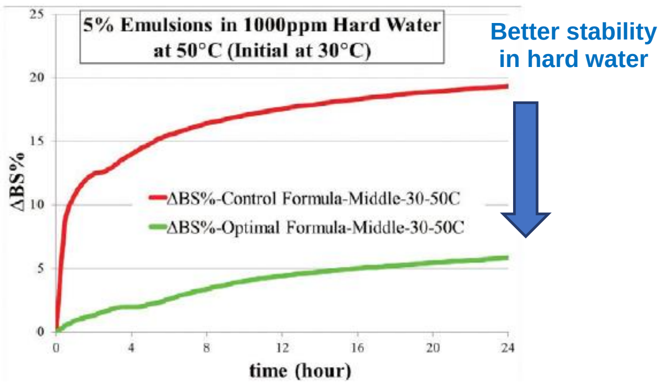


Figure 6: Evolution of the backscattering signal of the reference MWF compared to the DOE optimized new formulation.

Backscattering signal as reliable indicator of MWF efficiency

Reference: *María Matos et al. (2012) Extending the Useful Life of Metalworking Fluids in a Copper Wire Drawing Industry by Monitoring Their Functional Properties, Tribology Transactions, 55:5, 685-692*

We showed above how stability tests conducted with Turbiscan® could guide formulators to optimize their formula and to save time. One remaining question is, when used, when do MWF need to be discarded/changed? This question sounds economically critical as the batch volume involved are huge and because inefficiency of fluid could lead to quality issues.

In the work from Matos et al., fluids used in copper wire drawing, smoothing and casting have been checked and followed over 2 years. They identified Turbiscan® measurement as a good indicator of MWF efficiency as backscattering signal evolve sharply when emulsion need to be discarded as illustrated in figure 7, representing a 3 days analysis with the Turbiscan of a fresh and a used emulsion

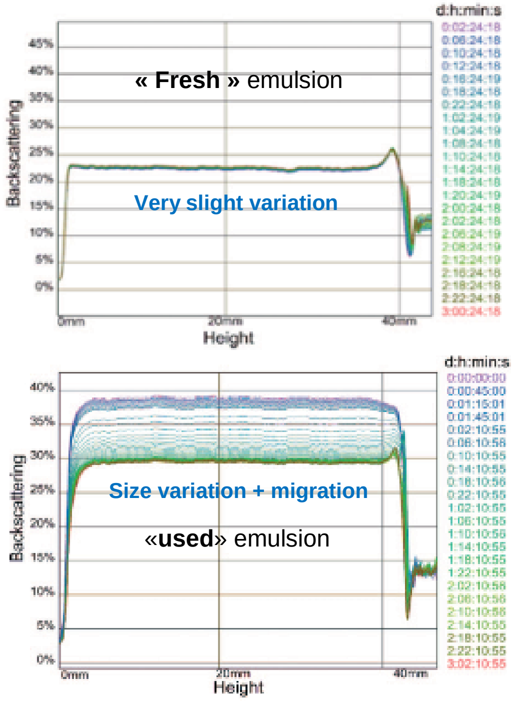


Figure 7: Backscattering signal obtained from wire drawing emulsion after (top) and before (bottom) their replacement.

This work paves the way for a quality control routine involving testing of the solution with Turbiscan®. Looking at the slope of backscattering evolution as a function of time (figure 8) and after only **10 hours** of measurement, it is possible to define if the batch must be discarded.

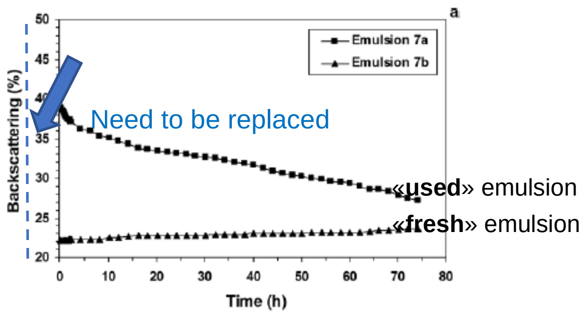


Figure 8: Backscattering (%) evolution in function of time for a fresh and used emulsion.

Designing recycling strategies with Turbiscan

***Reference**: Pacholski et al. (2019) Turbiscan Lab® Expert analysis of the chemical demulsification of oil-in-water emulsions by inorganic salts. Separation Science and Technology : 1-12.*

MWF need to be replaced periodically and "dirty" MWF still contains value. In order to be recycled, individual ingredient need to be segregated. In the work of Pacholski et al., chemical destabilization by salt addition is used to separate oil of the emulsion. Turbiscan measurements allow to optimize salt dosage toward the highest recovery rate and fastest destabilization. Figure 9 shows results obtained with $Al_2(SO_4)_3$. From the transmittance level slope evolution (bottom) it is possible to find the optimal salt dosage (the higher is not the better). Moreover, quality of the separation can also be monitored as the closest to the level of pure water it gets, the better the demulsification is.

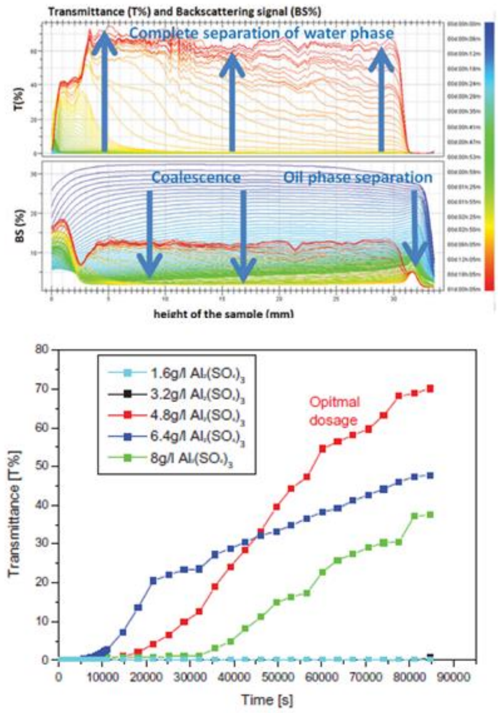


Figure 9: Top - Destabilization kinetics with 4,8g/l $Al_2(SO_4)_3$ Bottom- Evolution of mid-tube level of transmission for $Al_2(SO_4)_3$ salt addition.

Conclusion

In this application review we showed how Turbiscan® range and TSI offer straightforward ways for formulators to optimize and assess quality of MWF emulsions. Native and undisturbed sample analysis with Static Multiple Light Scattering embedded in Turbiscan® range allows to take the right decision at each step of the product life, from formulation to recycling.