Understanding the fascinating complexity governing the performance of crop protection flowable formulations – from coffee rings to collapse of arrested gels.

Authors: Malcolm A. Faers

Affiliations: Bayer CropScience K.K, Formulation Technology, Yuki, Japan.

Email: malcolm.faers@bayer.com

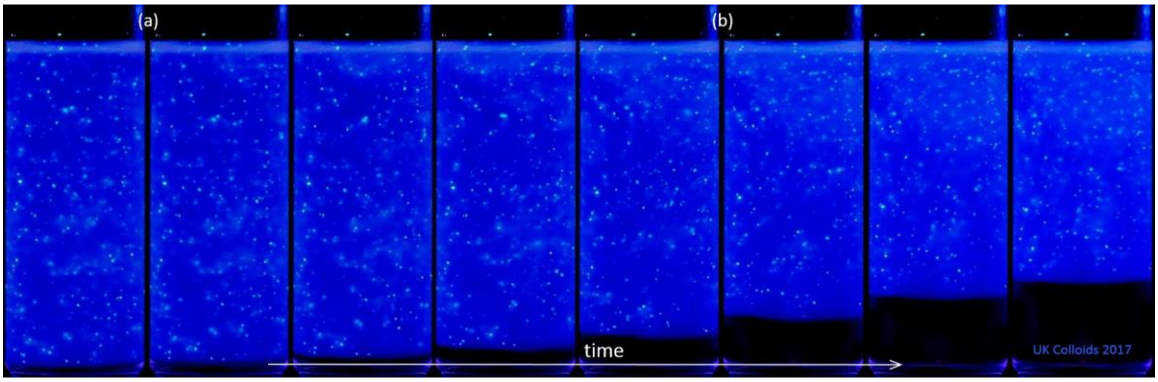
Abstract:

Designing crop protection formulations for spray application can be amongst the most complex formulation challenges that exists on account that the formulations have to fulfil such a diverse range of functions, they have to be robust for their manufacture, be stable for 2+ years, readily disperse in water in the spray tank, deliver the correct wetting, retention and coverage on crops, form spray deposits on leaves which enable the required biodelivery/bioavailability of the active ingredients and to be safe. Designing formulations to fulfil all these requirements while maximising the biodelivery of the active ingredient to the target and minimising off-target losses may appear an unmanageable challenge but if the steps are broken down and examined individually this challenge can then become attainable by intentional design rather than being treated pragmatically as an unknown 'black box'.

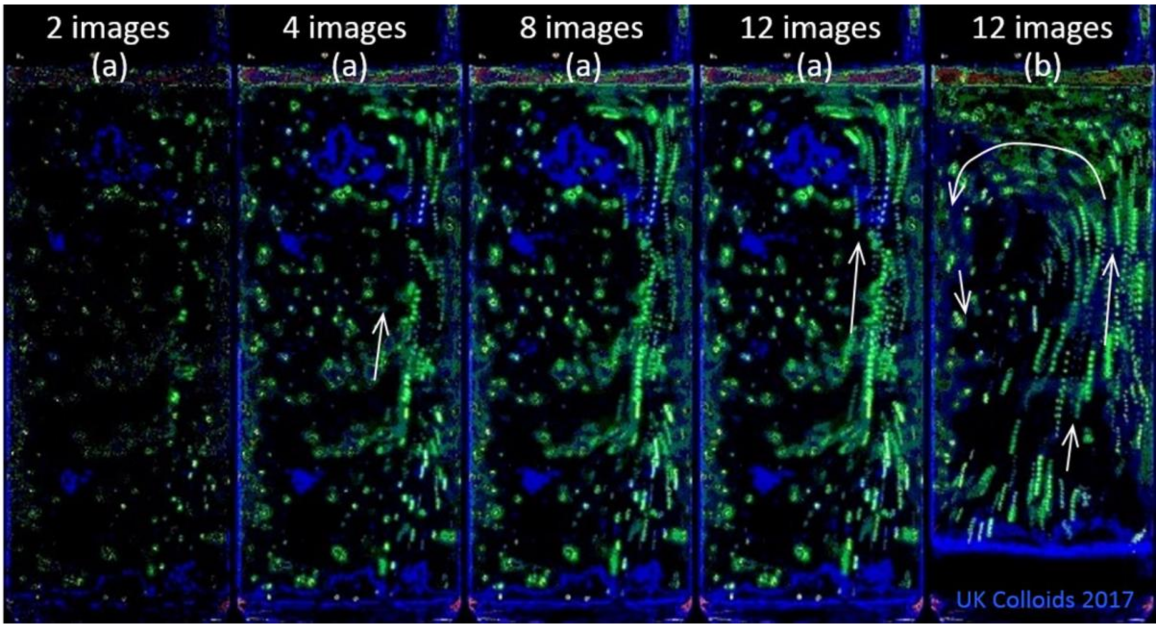
Many of these steps are governed by the science of colloids and interfaces/surfaces and there has been a dramatic advance in our understanding of these areas over the last 10 to 15 years to the point where we can start to understand from a scientific viewpoint how they all contribute to the performance of crop protection formulations. The focus of this talk is flowable formulations (SC, SE and OD) where many modern formulation opportunities and challenges exist, especially the understanding and prediction of their stability.

Building adjuvants and surfactants into dispersion formulations creates highly complex systems which are stabilised against gravitational separation by the formation of weak, reversible 'arrested gels'. These are optically opaque and difficult to study. However, by designing transparent refractive index matched model systems which represent the essential features detailed scientific investigations can be made. These model systems as well as real formulations are weak arrested gels which show both ageing of the gel network and delayed gravitational collapse. Collapse is a random process demonstrating both height and density dependence indicating it to be stress driven and therefore the mechanical properties (G', static yield stress) are important elements for the stability of the suspensions. Bespoke low invasive in-situ vane rheology allows the mechanical ageing of the network to be measured throughout the ageing and collapse process and curiously shows that the gel network increases in strength prior to collapse, demonstrating that the collapse is not due to weakening of the network but an increases in the internal stress in the sample. The inclusion of tracer particles reveals remarkably that internal structural changes on the macroscopic scale (as well as microscopic) occur for significant periods of time prior to collapse and ultimately when collapse occurs that it is a highly chaotic process driven by density unevenness in the sample.

Understanding the ageing processes is important for designing stable formulations and measurement of the evolving mechanical properties by low invasive vane rheology is a valuable predictive technique which can contribute to this.



Time-lapse image series showing changes in the interface height and internal movement both pre-collapse (a) and post-collapse (b). Sample: Depletion flocculated PDMS emulsion (ϕ 0.3) with HEC (1.4 g/L).



Composite images from regions (a) and (b) showing internal movement of tracer particles between successive images.

SC = Suspension Concentrate (aqueous suspension)
SE = Suspo-emulsion (aqueous suspension + emulsion)
OD = Oil Dispersion (non-aqueous suspension)