# Model Emulsion System for Studying Pigments Distribution

*AN Zdravkov*, *D Senatore*, *J Laven*, *RATM van Benthem*, *WK Wijting* and *G de With*
*Coatings Technology Group, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

In this work we show that when producing an emulsion with typical mean drop size of 5 μm, it is possible to generate or not a large number of negatively charged small drops (smaller than 1 μm in diameter). The existence of the small charged drops is attributed to fact that the induced electrostatic repulsive force can be large enough (at pH > 9) to oppose the compressive forces during turbulent emulsification. Preliminary microscopic observations show that small drops can contribute to better distribution of $TiO_2$ particles during the film drying of the emulsion coating.

## 1 Introduction

Drying of water-borne emulsion films on a substrate has recently gained a considerable interest both because of the practical interest of producing environmentally friendly coatings and because of the fundamental interest for better understanding the complexity of the observed phenomena[1-5]. One of the main problems in the emulsion formulated paints is related to the pigments distribution during drying. After film application, the water evaporates and the pigments, which are originally stabilized in the aqueous phase, may become unstable and aggregate. The complexity of phenomena involved in the emulsion coating formulation (including pigments and additives) and the process of film drying itself makes the overall process difficult to investigate. That is why in this work a substantial effort is made to design a model emulsion that is used for studying effects of different parameters, such as pH, presence of electrolytes and surfactants on the "fate" of pigments distribution during film drying. The design of such model emulsion requires a detailed knowledge of the mechanisms of drop break-up and coalescence, and of the forces acting between the drops during the applied hydrodynamic conditions (in our case turbulent conditions).

## 2 Materials and methods

For producing an emulsion a commercially available sunflower oil (AH, Zaandam, The Netherlands) was used as a dispersed phase, deionized Millipore water (Milli-Q water purifying system) as a continuous phase and two types of surfactants Triton X-100 (Sigma and SigmaUltra, Sigma-Aldrich Co.) as emulsifiers. Water solutions of the two types Triton X-100 with concentrations 2 wt% were prepared and used in emulsification experiments (see Table 1). For producing a suspension $TiO_2$ particles (surface compounds Al and Zr, Kronos 2190, Kronos, Germany) were used as dispersed phase and deionized Millipore water (Milli-Q water purifying system) as a continuous phase. To ensure stable suspension only suspensions with 1 wt% of $TiO_2$ pigments were produced. In all experiments an aqueous NaOH solution with concentration of $1\times10^{-3}$ M was used; ensuring in this way an aqueous solution with pH = 11 before adding a surfactant or pigment particles (Table 1).

**Table 1** Materials, characteristics and experimental conditions.

| Emulsion (suspension) | Triton X-100 type | Initial Solution pH/conductivity , μS.cm⁻¹ | Supernatant, pH/conductivity, μS.cm⁻¹ |
|---|---|---|---|
| EmTrX100 | Sigma | 8/73 | 6/60 |
| EmTrX100U | SigmaUltra | 11/150 | 9/60 |
| SuspTiO$_2$ | - | 11/230 | 9/80 |

All emulsions were produced at dispersed phase volume fraction of 40 % by using a standard laboratory homogenizer (Ultra Turrax T25, Germany). The two phases, with total volume of 50 ml, were put in an emulsifying vessel with four baffles and emulsified at 7 400 rpm for 2 min, ensuring in this way a homogeneous mixing flow (determined by visual observations). The $TiO_2$ suspension was homogenized by using an ultrasound bath for 1-2 hours every day for a period of one week, until a constant value of pH (pH= 9) of the suspension supernatant was obtained.

The drop size distribution (DSD) of an emulsion was determined by using a laser diffraction particle size analyzer (Beckman-Coulter LS 230) combined with a polarized light detection system that allows determining sizes in the range 0.04-2000 μm. $TiO_2$ particles size distribution (PSD) was determined by using dynamic light scattering apparatus (Malvern 4700 DLS, Malvern Instruments Ltd, UK).
The $\zeta$ - potential of the emulsion drops and of $TiO_2$ particles as a function of pH was monitored by using a zetasizer (Nano Series, Malvern Instruments Ltd, UK) combined with multy-purpose titrator (MPT-2, Malvern Instruments Ltd, UK).

The emulsion and $TiO_2$ suspension were always mixed at ratio 1:1. After that the mixture was applied on a glass substrate by using a wire applicator, in this way ensuring around 50 μm initial thickness of the applied film. The process of drying and pigment distribution was monitored by optical microscopy (Polyvar - Leica, Rijswijk, The Netherlands).

## 3 Results and discussion

Apparently, surfactant Triton X-100 Sigma lowers the pH more than SigmaUltra most likely because it consists of more additives (see Table 1). As a result of this, for emulsion EmTrX100 the value of the pH at the end of the emulsification process is 6 while for emulsion EmTrX100U it is 9 (see Table 1).
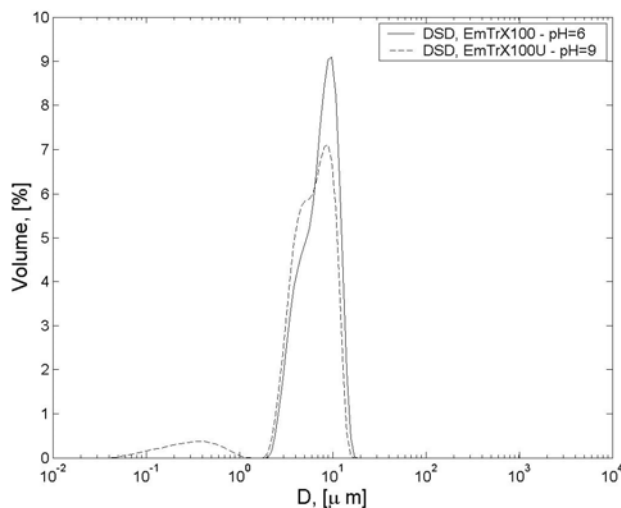


**Fig. 1** Volume drop size distribution (DSD) of two emulsions produced at two different final pH values; pH = 6 and pH = 9. In the case of pH = 9 there is a stable fraction of small drops.

In Fig.1 the volume drop size distributions of the two emulsions are shown. One can see that for emulsion EmTrX100U a fraction of small drops in the DSD is present (see Fig.1). In order to find out why the small drops in this case are present a titration experiment with them is performed (see Fig. 2). In Fig.2 the $\zeta$-potential of the small drops as a function of the pH is shown. At pH = 9 the value of the $\zeta$-potential of the small drops is approximately -17 mV, while at pH = 6 it is around -9 mV.
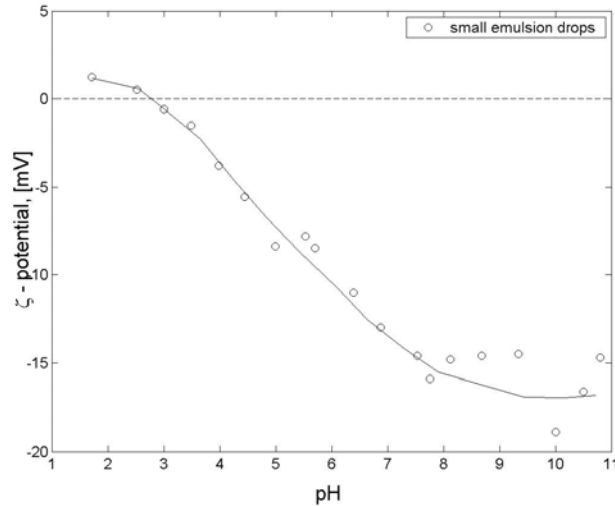
**Fig. 2** The $\zeta$ - potential of the small drops from Fig.1 versus pH. Titration experiments done with 0.7M, $HNO_3$ and ionic strength, $I = 1 \times 10^{-3}$ M. The solid line is drawn to guide the eye.

Using the classical DLVO theory[6] one can calculate based on the conductivity measurements (see Table 1) that the inverse screening length $\kappa^{-1}$ is around 20 nm. Then, assuming that the $\zeta$-potential is a good estimate of the surface potential, the repulsive force, $F_{rep}$, can be calculated as a sum of repulsive electrostatic and attractive van der Waals part. On the other side one can estimate the hydrodynamic viscous force[7, 8], $F_v$, induced by the turbulent eddies larger than the small drops of emulsion EmTrX100U. The values of these two opposing forces are presented in Table 2.

**Table 2** Forces acting on the small drops (smaller than 1 $\mu$m in diameter)

| Emulsion type | $F_v$, N | $F_{rep}$, N |
|:---:|:---:|:---:|
| EmTrX100 | $7 \times 10^{-12}$ | $7 \times 10^{-12}$ |
| EmTrX100U | $7 \times 10^{-12}$ | $3 \times 10^{-11}$ |

Comparing the forces acting during the emulsification in both types of emulsions one can see that in the case of emulsion EmTrX100 the viscous compressive force is from the same order of magnitude as the repulsive electrostatic force, therefore the small drops will have tendency to coalesce. In contrast, in the case of emulsion EmTrX100U, $F_{rep}$, is by factor 3 larger than $F_v$ so the small drops will be more stable.

In Fig. 3 the particle size distribution of $TiO_2$ particles at pH = 11 is shown. At this pH the mean particle size is 226 nm. Although, all the microscopic observation are done with emulsion/suspension mix with pH around 9, from the titration experiments presented on Fig. 4 one can see that $\zeta$-potential at pH = 9 is the same as it is at pH = 11. Therefore, it is reasonable to expect that the mean particle size at pH = 9 will be around 226 nm, as well.

Preliminary observations of emulsion/suspension film drying on glass substrate show that the system that consist of small drops is giving a more homogeneous pigment distribution than the system without small drops. This is most likely because the small drops can act as dispersants.
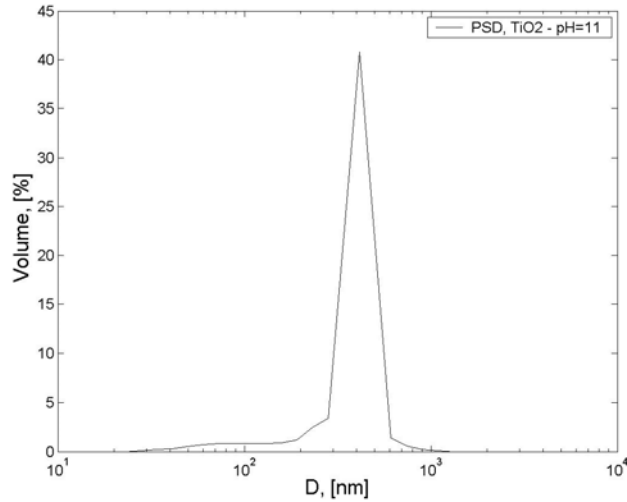
**Fig. 3** Volume particle size distribution (PSD) of TiO$_2$ particles at PH = 11.
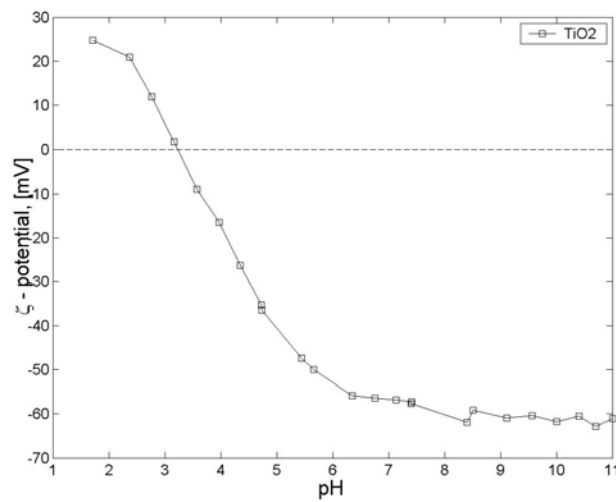


**Fig. 4** $\zeta$- Potential of TiO2 particles. Experiments on titration with 0.7M, HNO$_3$ at ionic strength, I = 1$\times$10$^{-3}$M.

## 4 Conclusions

In conclusion we have proved that in basic conditions (pH > 9) a fraction of large number of small drops is present. The existence of this large number of small charged drops can have a significant effect on the water-borne emulsion coating formulation as well as on the pigments distribution during drying. For example these small drops will increase the viscosity of the paint and consequently can change the drying process.

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