

## Rheological Investigations on the Drying Behaviour of Polymer Dispersions and Paint Films

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### ABSTRACT

A new method to determine the drying behaviour of paints is presented. For this purpose a new measuring geometry for a rheometer has been developed, which offers a good sensitivity and does not influence the drying process itself. The measuring setup is described and exemplary measuring results on paint formulations with different binders are presented in this paper.

### INTRODUCTION

Among the technical challenges which have arisen due to the switch from solvent to waterborne paints - driven by the regulatory push towards a more sustainable coatings industry - the control over the drying and film forming process of paint dispersions has been a matter of intense investigation in recent years.

Advanced analytical methods and imaging techniques have been used to gain insights into the mechanisms driving the film forming process and to identify factors which influence open time<sup>1</sup>. Regardless of existing sophisticated analysis, we still see the need for a simple and easily accessible method which allows for quantitative differentiation of drying behaviour of aqueous paints and, moreover, one that will help formulators to select the most favourable ingredients for specific products and applications. This is particularly relevant for the identification of additives for the prolongation of open time, which refers to the period of time remaining

after paint application to make corrections without leaving visible defects in the film. This part of the painting process is still a challenging task due to the lack of an objective and stable method for its evaluation. The current ASTM D7488 method relies on subjective visual assessment of repainted marks on drawdown paint film<sup>2</sup>. In practice, this method is not reproducible and consistent, due to non-standardized factors such as the force applied during brushing, among other things. It often fails in performance differentiation when comparing the effect of paint additives on drying. Breivogel and Ottens proposed a method to deduce the open time from the properties of a fully dried paint film<sup>3</sup>.

A more intuitive, but less sophisticated method to characterize the drying of paint films can be provided by a rheometer, using a needle affixed to the classic plate geometry, which slowly rotates through the paint film. This has been described in previously published literature<sup>4</sup>. The main disadvantage of this method is that it relies only on a one-point measurement and therefore may be sensitive to film inhomogeneities.

### MATERIALS AND METHODS

#### Measuring geometry and method

The new system consists of 12 evenly distributed pins attached to a ring, each of them 2 mm thick, as shown in Fig. 1. The larger number of pins provides a higher

torque response and therefore a higher sensitivity towards viscosity changes in the film during drying. It also reduces the influence of inhomogeneities in the paint film thanks to the multiple point measurement technique in comparison to the one-point measurement. Moreover, undisturbed water evaporation from the film is guaranteed due to the open design of the measuring system, as the pins are attached to a ring and not to a condensation-prone plate which might create a local humidity environment.

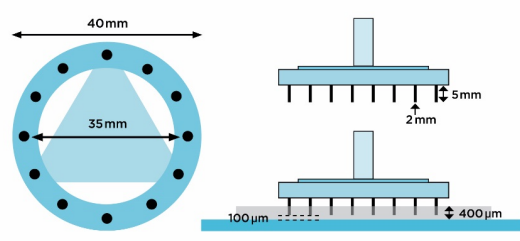


Figure 1. Novel rheological measuring system 12 pins fixed on a ring

This novel measuring system has been used to investigate the influence of several Clariant additives on the drying process of aqueous polymer dispersions and paints.

In a typical measurement procedure, a paint film was drawn down on a glass plate using a 400  $\mu\text{m}$  applicator blade and immediately transferred to a Thermo Scientific™ HAAKE™ MARS™ 60 rheometer. The glass plate was placed on a flat support and fixed with a metallic ring, as shown in Fig. 2. After starting the measurement, the pins penetrated into the paint film leaving a 100  $\mu\text{m}$  gap between the head of the pin and the glass plate. The ring was then rotated at a constant speed of 0.01 rpm for the duration of the measuring period, which was typically between 30 to 60 minutes. During measurement, the increase in torque over time was recorded as an indicator for the drying of the film. For each sample the measurement was repeated three times and the final torque shown as the average value of the three measurements. All

averaged measurements were conducted at similar temperature ( $\pm 1\text{ }^\circ\text{C}$ ) and relative humidity ( $\pm 2\%$ ), which were directly tracked during the experiments.

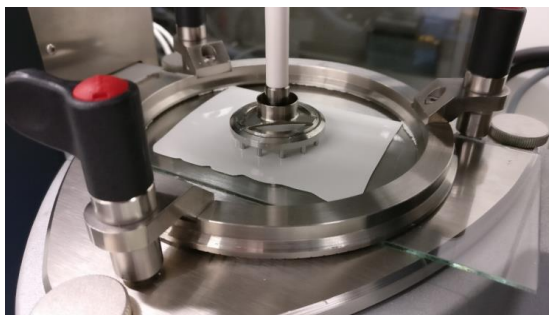


Figure 2. Glass plate with paint film fixed on rheometer during measurement with the new 12 pin ring geometry

## Materials

Four commercial aqueous polymer dispersions used as binders for paints were selected for comparative measurements (P1 – P4). Binders P1 and P4 are both stabilized by surfactants only whereas P2 and P3 are stabilized by different combinations of surfactants and polymeric compounds. Whereas P2, P3 and P4 are based on vinyl acetate-ethylene, P1 is made from acrylates. In order to fairly compare the drying speed of the binders, the solids content of all four dispersions was adjusted to 45% through dilution with deionized water. At this concentration, the viscosity of the dispersions was still suitable to draw down stable 400  $\mu\text{m}$  wet films.

## RESULTS

The pure binders gave significantly different results (Fig. 3). Interestingly, both binders P2 and P3 show a very similar drying profile. Despite having similar small particle sizes and zeta potential values, the binders stabilized only by surfactants, P1 and P4, show rather different drying behaviours. P1 already shows a steep increase in film

viscosity after 10 minutes whereas for the binder P4 the increase in torque takes place after roughly 50 minutes.

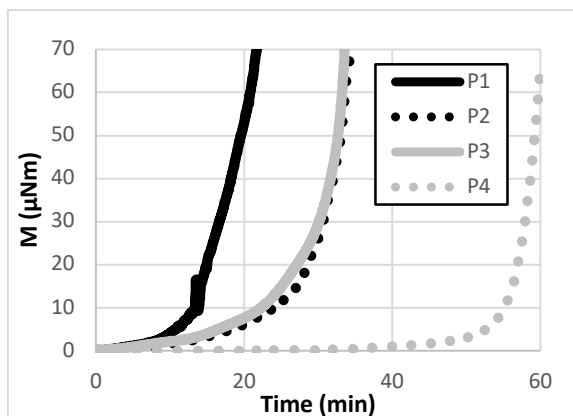


Figure 3. Drying of films of all 4 binders at 23 °C and 59 % relative humidity

#### Pure binders with additives

In order to illustrate how the new measuring method can be used to assess the way in which additives might affect drying behaviour of the binders, the effect of supplementing two additives in 1 wt% to the polymer dispersions was investigated. A well-established open time extender additive was chosen as additive A1 and additive A2 was tested as potential alternative. The results are shown in Fig. 4 to 7. The purple curve shows the drying of the binder as a 45% aqueous dispersion with the red curve showing the effect caused by the addition of 1wt% of additive A1 and the green curve, the effect generated by additive A2. Interestingly, each binder is affected by the additives in a different manner. In comparing surfactant-stabilized binders, additive A2 has a major impact over A1 in the drying behaviour of binder P1 whereas the opposite is true for the binder P4. This observation suggests that specific additive-binder interactions may be responsible for the prolongation of the low viscous range before a steep increase in torque occurs, indicating the start of the film formation. For binder P2 similar ability to retard the increase of film

viscosity is seen for both additives, although the increase of viscosity is steeper in the case of additive A1 than for additive A2. In the case of binder P3, the additives are not able to influence the drying behaviour, thus suggesting that this is strongly controlled by the protective colloid-surfactant mixture already used to stabilize the polymer dispersion, and that this mixture may hamper further interactions between the polymer particles and additional additives.

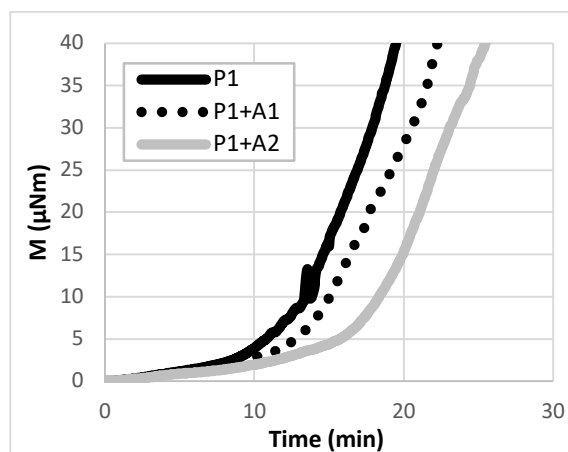


Figure 4. Drying of binder P1 without additive and with 1% of additives A1 and A2 at 23 °C and 59 % rel. humidity

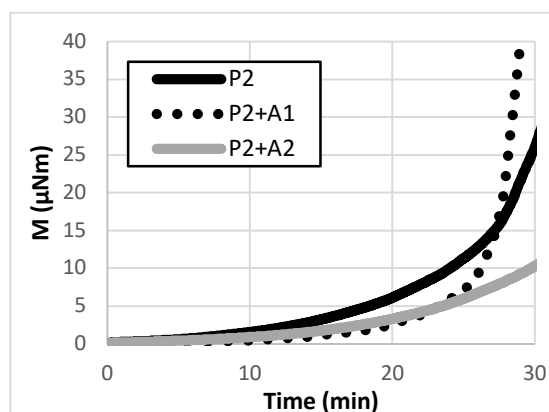


Figure 5. Drying of binder P2 without additive and with 1% of additives A1 and A2 at 23 °C and 59 % rel. humidity

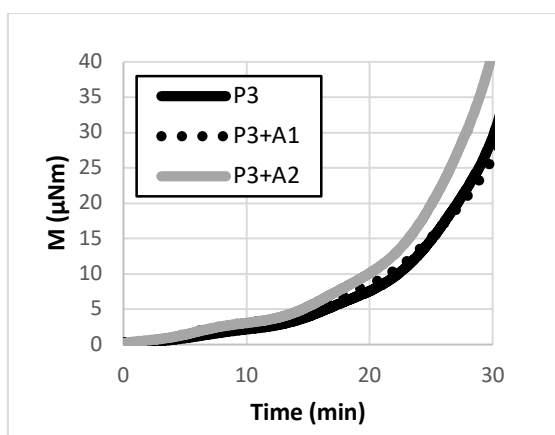


Figure 6. Drying of binder P3 without additive and with 1% of additives A1 and A2 at 23 °C and 59 % rel. humidity

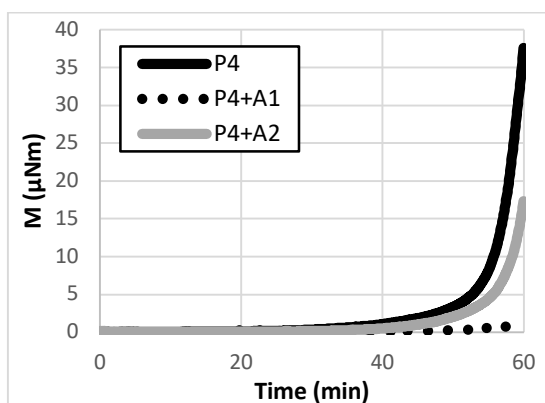


Figure 7. Drying of binder P4 without additive and with 1% of additives A1 and A2 at 23 °C and 59 % rel. humidity

#### Additives and binders in paint formulations

Finally, the new methodology was tested on paint formulations. Binder P4 was added to two paint formulations with high and low pigment volume concentration (PVC) respectively described in Table 1 and Table 2. Three samples were tested based on this formulation, containing 1wt% of additive A1 or A2 or a blank sample completed with deionized water.

Table 1. Composition of a high pigment volume concentration paint

Compound	Content	Active content
Water	26.7%	100%
Thickener	0.3%	100%
Neutralizing agent	1.0%	50%
Dispersing agent	0.4%	45%
Defoamer	0.6%	100%
TiO <sub>2</sub>	10.1%	100%
CaCO <sub>3</sub> 0.3 µm	5.1%	100%
CaCO <sub>3</sub> 2.0 µm	8.1%	100%
CaCO <sub>3</sub> 5.0 µm	10.1%	100%
CaCO <sub>3</sub> 10.0 µm	5.1%	100%
Talc	8.1%	100%
Kaolin	3.0%	100%
Binder P4	20.2%	55%
Preservative	0.2%	2.5%

Table 2. Composition of a low pigment volume concentration paint

Compound	Content	Active content
Water	24.0%	100%
Neutralizing agent	2.4%	50%
Dispersing agent	0.2%	45%
Defoamer	0.2%	25%
TiO <sub>2</sub>	17.5%	100%
Binder P4	54.5%	55%
Preservative	0.2%	2.5%

In comparison to the pure P4 binder films shown previously in Fig. 7, the changes in film viscosity are detected at shorter times in the case of paints (Fig. 8 and 9). The trend observed fits with expectations – that the formulation with the highest pigment to binder ratio shows the fastest drying. The performance of the additives differs across the three systems. Although additive A1 was able to effectively stabilize the low viscous state of the film in the pure binder formulation, it shows an accelerating drying effect in the low PVC paint. In the high PVC paint, a similar retardation in the steep

increase of film viscosity is achieved by both additives A1 and A2, whereas in the low PVC paint additive, A2 slows the increase of film viscosity in comparison to the paint without an additive.

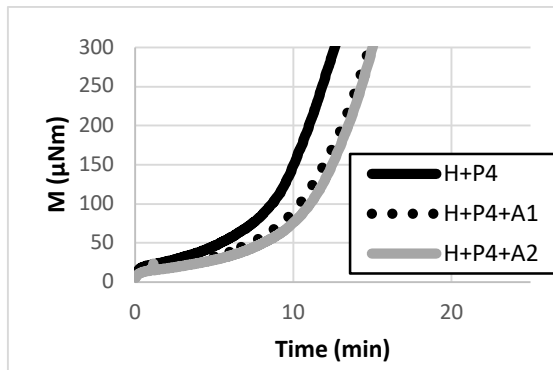


Figure 8. Drying of high PVC paint at 23 °C and 50 % rel. humidity

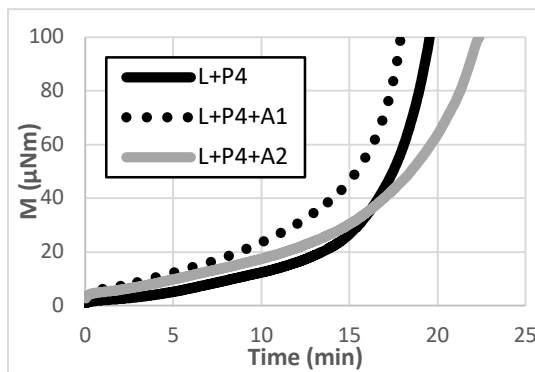


Figure 9. Drying of low PVC paint at 23 °C and 50 % rel. humidity

These observations indicate that in paint formulations the interplay of interactions between additives and the rest of the components such as binder particles, pigments and dispersing agents, may be crucial to determine the drying behaviour of the system. Further investigations of additive-pigment interactions may be required to get a better understanding of the role of additives during the drying of paint films.

## CONCLUSION

A simple rheological method based on a novel measuring system has been presented which enables the investigation in drying behaviour of aqueous paints. The new system is based on twelve pins equidistantly affixed on a ring geometry with an outer diameter of 40 mm, which is then attached to a highly precise air-bearing rheometer. The pins penetrate a freshly applied wet paint film of defined thickness and slowly rotate through it. The detected change in torque over time is directly related to a change in film viscosity and allows for detection of the formation of a high viscous close-packed arrangement of particles as a characteristic transition during drying. The method has been successfully tested in the characterization in drying behaviour of four commercial polymer dispersions and also in the investigation of the effect of two additives on the drying process of polymer dispersions. Furthermore, the method has been successfully used to evaluate the impact of additives on drying of high and low pigment volume. The new test system will help formulators to select easily and objectively the most favourable ingredients to optimize drying behaviour of aqueous paints.

## REFERENCES

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