Dynamic Surface Tension: A Key Parameter for Excellent Ink Jet Preparations

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Abstract

The concept of concentrated pigment preparations (pre-dispersions) for inks employed in digital printing, such as ink jet, is increasingly becoming popular in the market. The static surface tension is often given as a quality parameter of these preparations and inks based thereon. However, wetting processes in ink jet, for example, wetting of the printhead interior, drop formation, or interaction with the substrate, generally occur within a very short time (microsecond to millisecond time scale, which is far outside of equilibrium for most cases).[1]

Therefore, these ultrafast wetting processes can be understood with the help of the dynamic surface tension rather than by measuring the static surface tension. DSTM (dynamic surface tension measurements) provides a modern tool for a clever selection of appropriate dispersants with a good dynamic wetting behavior. It also allows the formulation of optimized pigment preparations employing these dispersants, thus enabling the manufacturing of high-quality pigmented inks for high-performance ink jet printing.

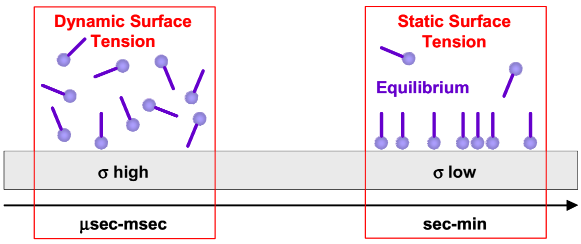

Figure 1. Comparison between dynamic and static surface tension

DSTM—Principle

The bubble pressure is monitored during a time interval starting with the time when the bubble first emerges from the orifice until bubble release, and the dynamic surface tension σ_d is calculated based on the difference between P_{max} and hydrostatic pressure P_0 and the capillary radius. Upon increasing the gas flow (bubble rate), the surface age of the bubbles is decreased, and thus, the time for the surfactant molecules to migrate to the bubble surface and to absorb is short. Consequently, the coverage of the surfactant on the surface becomes more and more incomplete and the surface tension increases with decreasing bubble age.

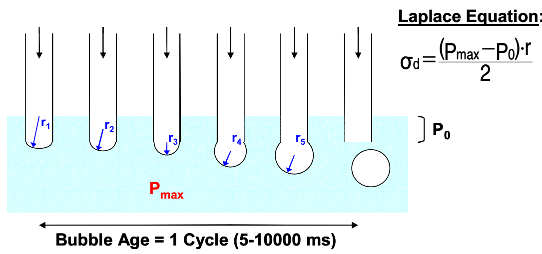

Figure 2. Principle of dynamic surface tension measurements with the maximum bubble pressure method

Choice of the Appropriate Surfactant

a) Oligomeric Surfactants

The dynamic surface tension of a surface-active compound depends on several parameters, such as

- concentration
- molecular weight
- polarity/charge
- chemical structure
- diffusion coefficients, etc.

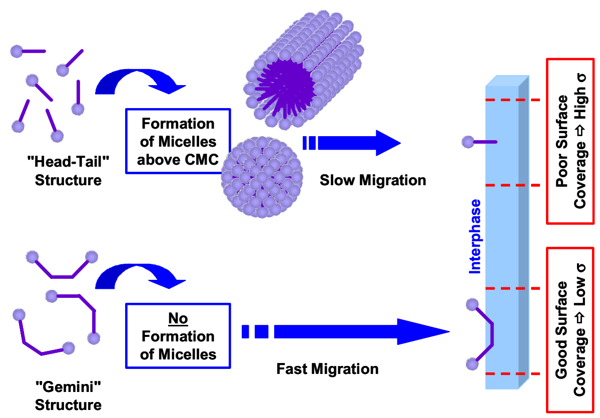

Figure 3. Influence of surfactant structure on diffusion coefficients and surface coverage per unit: "head-tail" vs. "gemini" structure (CMC = critical micelle concentration)

To understand the relationship between surfactant structure and the dynamic wetting behavior is important for optimizing pigment preparation and ink jet ink properties, choosing the right surfactant in the appropriate concentration.

An oligomeric "head-tail" surfactant may form micelles or vesicles with a small diffusion coefficient. In addition, such molecules normally have a small surface coverage, leading to a higher surface tension, especially at low surface ages (Chart 1).

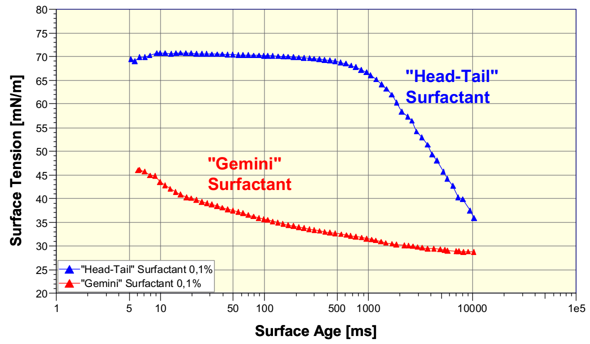

Chart 1. Dynamic surface tension of a "head-tail" and a "gemini" surfactant (each 0.1% in aqueous solution)

In contrast, "gemini" surfactants do not form micelles and can have a larger surface coverage, which is demonstrated by a low dynamic surface tension even at low concentrations.

b) Polymeric Surfactants

Table 1 compiles static surface tension data for different amphiphilic random co-polymers with either different ratios of the hydrophobic (A) to the hydrophilic (B) moiety or different substitution patterns.

Table 1. Chemical description and static surface tension of different amphiphilic co-polymers

Polymer	A/B	Substitution	Static Surface Tension [mN/m]
1	1/1	none	49
2	2/1	none	45
3	2/1	Benzyl Ester	41
4	2/1	2-Ethylhexyl Ester	35
5	2/1	Lauryl Ester	35

Chart 2 shows the plot of the dynamic surface tension versus surface age for these polymers. With increasing hydrophobic character of the polymers either by varying the A/B ratio or by additionally introducing hydrophobic ester groups, the diffusion constants, and thus the dynamic wetting ability, can be increased. Interestingly, the lauryl ester and the 2-ethylhexyl ester end up with the same static surface tension although they exhibit a completely different dynamic wetting behavior.

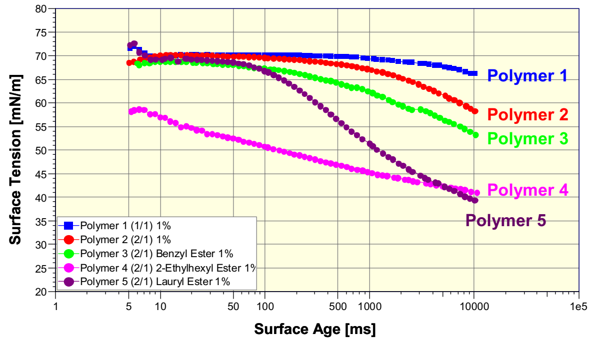

Chart 2. Dynamic surface tension of several amphiphilic co-polymers (each 1% in aqueous solution)

Pigment Preparations

To satisfy the stringent demands of modern, high-performance ink jet printing, several parameters of the pigment preparation and the resulting ink need to be optimized (Figure 4).[2] One of the key parameters is the dynamic surface tension.

To investigate the influence of different types of surfactants in aqueous pigment dispersions, pigment preparations based on *Colour Index* P.Y. 155 were prepared and the static and the dynamic surface tension were measured (Table 2, Chart 3).

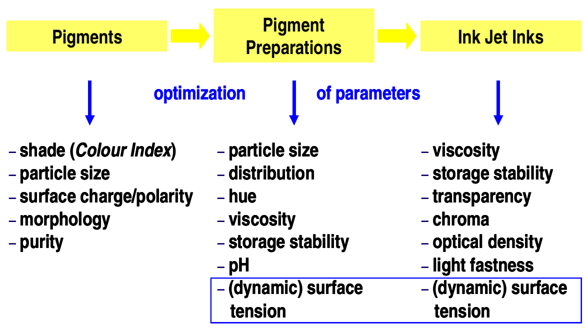

Figure 4. Numerous parameters have to be optimized for high-quality pigment preparations and ink jet inks based thereon

Table 2. Dispersant system and static surface tension of Preparations 1 to 3 (2% P.Y. 155)

Preparation	Dispersant System	Static Surface Tension [mN/m]
1	0.25% Polymer	60
2	0.25% Polymer + 0.1% Surfactant	50
3	0.25% Polymer + 0.1% Wetting Agent	36

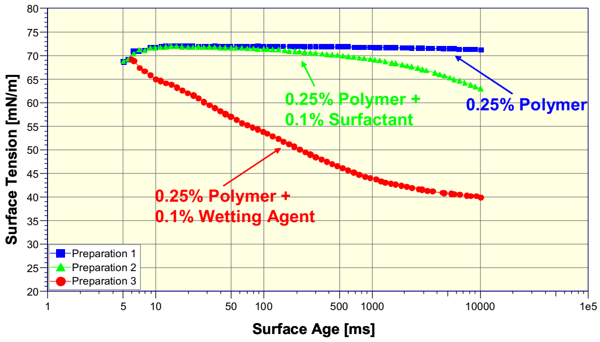

Chart 3. Dynamic surface tension of aqueous pigment preparations based on Colour Index P.Y. 155 (2% pigment content) employing different dispersant systems

Preparation 1, solely containing the polymeric dispersant (0.25%), shows no significant dynamic wetting behavior. Preparation 2, additionally containing 0.1% of a surfactant, shows only a small effect, decreasing the surface tension to below 70 mN/m only at surface ages higher than 500 ms. In contrast, Preparation 3, additionally containing 0.1% of a wetting agent instead, exhibits excellent wetting action even at low surface ages.

Taking into consideration these findings, pigment preparations for ink jet printing can be optimized such as those shown in Table 3. The pigment preparations all exhibit excellent flowability properties due to their low viscosity, which does not significantly increase upon storage at elevated temperature, proving the shelf-life stability of the preparations.[3]

Table 3. Optimized aqueous pigment preparations for ink jet printing (physical data represent typical values)

Colour Index	Pigment Content	d_{50} [nm][a]	Viscosity [mPas]
P.Y. 155	20%	100	14.4
P.R. 122	20%	88	16.5
P.B. 15:3	20%	79	22.9

[a]**measured by capillary hydrodynamic fractioning (CHDF)**

Chart 4 shows the dynamic surface tension curves for the cyan pigment preparation based on *Colour Index* P.B. 15:3. Before optimization of the formulation, the surface tension in the relevant time frame (below 100 ms) is relatively high, whereas after modification, an excellent wetting can be observed even for small surface ages.

It is noteworthy that the modified pigment preparation has a kind of "bump" in the curve. Due to multiple surfactants typically being present in an ink, competing effects can cause the surface tension decrease with surface age, then increase and then decrease again as one surfactant reaches the surface only to be displaced and replaced by another.

A standard test ink prepared from the unmodified cyan preparation shows irregular printouts with a number of nozzles failing due to insufficient wetting and ink flow in the cartridge interior. In contrast, the ink prepared with the optimized pigment preparation gives regular printouts of excellent quality.

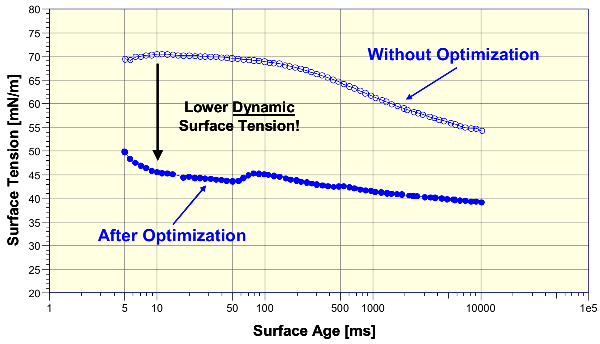

Chart 4. Dynamic surface tension of the cyan pigment preparation (2% pigment content) before and after optimization

Conclusions

Wetting processes in ink jet occur in a very short time (milliseconds to microseconds). DSTM is a tool to better understand these processes and to differentiate between dispersants and "fast" wetting agents with a good dynamic wetting characteristic. By choosing the appropriate surfactant system in the optimum concentrations, one can enhance the performance of pigmented inks in modern ink jet printing.

References

1. K.-H. Schweikart, B. Fechner, H.-T. Macholdt, "DSTM, A Modern Method for Optimizing Pigment Preparations for Ink Jet", Proceedings ECC: The Power of Ink Jet, 15-26 (2004).
2. K.-H. Schweikart, J.-P. Lerch, U. Rohr, H.-T. Macholdt, "Nano-color Pigments for Water-based Ink Jet Inks", Proceedings ECC: The Power of Ink Jet, 17-26, (2003).
3. Pigment preparations for water- and solvent-based ink jet inks: for details see brochure "The Source of Ink Jet Printing Excellence", Frankfurt (Germany), September 2004, DP8518E (Clariant).

Biography

Karl-Heinz Schweikart is a member of Market Segment Non-Impact Printing at Clariant GmbH, Pigments & Additives Division and responsible for the development of aqueous pigment preparations for ink jet applications.

He holds a Ph. D. in chemistry awarded by Eberhard-Karls-Universität Tübingen (Germany) in 2000. Before joining Clariant in 2001, he had a postdoctoral position at North Carolina State University in Raleigh (USA), working in the group of Prof. Jonathan S. Lindsey in the field of organic chemistry/molecular electronics.