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Effects of Surfactant, Propylene Glycol, and Incorporation Sequence on the Properties of Eco-Friendly Aqueous Sublimation Transfer Inkjet Inks

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ABSTRACT

The effects of a nonionic surfactant, propylene glycol, and surfactant incorporation sequence on the dispersion behavior, stability, and rheological properties of aqueous sublimation transfer inkjet inks were systematically investigated. Dispersion evolution during jar milling was monitored by turbidity measurements and validated by dynamic light scattering and UV-Visible spectroscopy. Surfactant and humectant accelerated the initial stage of particle size reduction, whereas the formulation containing neither additive ultimately achieved the smallest particle size after prolonged milling (151 vs. 317 nm). This behavior indicates that improved wetting dominates the early stage of milling, whereas the final particle size is governed by the balance between wetting, capillary-assisted agglomerate fracture, and Ostwald ripening. Formulations containing propylene glycol also exhibited inferior ultimate dispersion efficiency. Freeze–thaw testing revealed that the combined presence of surfactant and propylene glycol reduced dispersion stability, particularly when the surfactant was added after milling, highlighting the destabilizing role of non-adsorbed surfactant. All formulations followed the Ostwald–de Waele power-law model ($R^2 > 0.99$), while the additive-free formulation exhibited the strongest shear-thinning behavior ($n = 0.785$ versus 0.90 ± 0.075). These findings demonstrate that under the investigated formulation conditions, surfactant incorporation sequence is an important processing variable affecting milling efficiency, dispersion stability, and rheological performance. Prog Color Colorants Coat. 20 (2027), 353-365© Institute for Color Science and Technology.

1. Introduction

Pigment-based inkjet inks are increasingly favored over dye-based counterparts due to their superior resistance to light and chemical degradation. The performance of these inks, however, is highly dependent on the quality of the mill-base-a concentrated pigment dispersion subsequently combined with other components to produce the final ink [1, 2]. As the primary dispersion of pigment particles, the mill-base plays a critical role in controlling particle size, dispersion stability, rheological properties, surface tension, and optical behavior of the finished formulation [3].

A fundamental requirement for inkjet inks is achieving pigment particle sizes below 200 nm with a narrow distribution. Larger particles or coarse aggregates can cause nozzle clogging, unstable jetting, and

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compromised print quality [4-6]. Beyond printability, fine and uniform particle sizes are essential for maximizing color strength and saturation, since smaller particles favor light absorption over scattering [6, 7]. Consequently, the predominant production route for nanometric pigment dispersions involves wet milling in the presence of polymeric dispersants and surfactants [8].

During wet milling, particle size reduction markedly increases the surface area of pigment particles, thereby enhancing interparticle Van der Waals interactions and promoting a tendency toward re-agglomeration. To counteract this undesirable effect, the use of polymeric dispersants and surfactants is essential. These additives adsorb onto particle surfaces and generate repulsive forces-either electrostatic or steric in nature-that prevent particles from approaching each other too closely [9-11]. The efficiency of polymeric dispersants, however, is strongly influenced by their chemical structure, molecular weight, and production process variables, including the sequence in which formulation components are incorporated into the mill-base [12].

Beyond particle size, rheological properties and surface tension are also critical for inkjet performance, as they directly influence droplet formation and jetting stability. Ideally, inkjet inks should exhibit sufficiently low viscosity and near-Newtonian flow behavior to facilitate stable droplet generation and accurate deposition [5, 13]. The influence of rheological characteristics on jetting depends on the balance among viscous, inertial, and capillary forces and may manifest in variations in droplet velocity, tail formation, and satellite-droplet formation [5, 13]. Deviations from near-Newtonian behavior caused by strong interparticle interactions can adversely affect jetting performance, highlighting the importance of characterizing and appropriately tuning the rheological behavior of inkjet inks [14]. Surface tension must also be maintained within an optimal range, determined by both ink properties and printhead design, to balance droplet formation with the prevention of leakage or satellite droplet formation [13, 15]. Moreover, interfacial properties can significantly influence wet milling behavior, as described by capillary penetration models such as the Washburn equation [16].

In addition to achieving appropriate particle size, rheological properties, and surface tension, aqueous inkjet inks must maintain long-term colloidal stability to ensure reliable performance during storage and application. This requires not only appropriate selection of formulation components but also careful consideration of their incorporation during processing. Our previous studies investigated the effects of polymeric dispersant characteristics and concentration, milling aids, and surfactant-related formulation parameters on the dispersion and performance of sublimation transfer inkjet inks [12, 17, 18]. However, the influence of propylene glycol on dispersion evolution during milling, particularly in combination with a nonionic surfactant, has not been systematically investigated. Moreover, the effect of surfactant incorporation history has not been distinguished from that of its final concentration in the formulation.

Accordingly, the present study systematically investigates the individual and combined effects of propylene glycol and a nonionic surfactant on the dispersion efficiency, particle-size evolution, surface tension, rheological behavior, and storage and freeze-thaw stability of aqueous sublimation transfer inkjet dispersions. Particular attention is given to the role of surfactant incorporation sequence during milling. To isolate the influence of processing history, the surfactant was incorporated either at the beginning of milling or at the final stage of milling, while maintaining the same final formulation composition. This experimental design enables the effects associated with formulation composition to be distinguished from those associated with processing history and provides insight into whether the role of a surfactant in a wet-milled pigment dispersion is determined solely by its concentration in the final formulation or is also influenced by the stage of dispersion at which it is incorporated.

2. Experimental

2.1. Materials

A slightly anionic polymeric dispersant, TEGO® Dispers 750 W (40 wt. % active content in water), was employed as the primary stabilizing agent for pigment dispersion. Propylene glycol (purity ≥99 %, Merck) was used as a humectant. Oleic acid ethoxylate (6 moles, KEOL6) was provided by Kimyagaran Emrooz company as a surfactant, and Disperse Blue 359 (D.B.359) was supplied by Tiankum Company as a well-known disperse dye in sublimation transfer inkjet inks. All chemicals were utilized as received without any additional purification.

2.2. Characterization

Surface tension was determined using the Wilhelmy plate technique with a Krüss tensiometer. It was measured five successive times for each sample, and the reported value represents the arithmetic mean. The deviation among successive measurements was less than 0.1 mN m^{-1}. Particle size distribution was analyzed by dynamic light scattering (DLS) with a Horiba SZ-100 instrument. Rheological behavior, including viscosity and ink flow characteristics, was measured using a Physica MCR300 (Anton Paar) equipped with a concentric cylinder geometry. The viscosity measurements were validated, with an error margin below 0.5 mPa·s. In the present study, steady shear-rate sweeps were selected primarily to characterize the shear-dependent viscosity and flow behavior of the mill-base formulations and to quantitatively compare their deviation from Newtonian behavior. Turbidity during milling and storage was monitored using a Hach 2100N turbidimeter to assess milling efficiency and ink stability. All turbidity measurements were performed in triplicate. The reported values correspond to the arithmetic mean of the three measurements, and the measurement repeatability was found to be within ±3 NTU. All formulations were prepared using Disperse Blue 359 as the colorant; therefore, all mill bases exhibited a blue appearance. Differences in optical properties among the formulations were evaluated by a Bio Spec-1601 double-beam UV-Visible spectrophotometer, which provided insights into the light absorption characteristics of the ink. Dispersion stability was further examined through freeze–thaw cycling. Pigment dispersions were sealed and subjected to storage at -9 °C for 24 hours, followed by heating at 50 °C for 24 hours [19]. Freeze–thaw stability was evaluated by comparing turbidity values before and after the treatment. It should be mentioned that the freeze-thaw experiment was conducted as a comparative stress test to evaluate the relative susceptibility of the investigated mill-bases to freeze-induced destabilization. Given that the objective was to compare the effects of formulation composition and surfactant incorporation sequence rather than to qualify the long-term freeze–thaw durability of a finished inkjet formulation, a single freeze–thaw cycle was employed. These repeated measurements were performed on the same prepared sample and therefore represent instrumental repeatability rather than independent experimental replication.

2.3. Preparation of ink dispersions

Pigment dispersions were prepared by first formulating a mill base consisting of pigment, polymeric dispersant, propylene glycol, and deionized water. Two different formulation strategies were examined to evaluate the effect of component incorporation_sequence on dispersion behavior.

In the first approach, the surfactant was added directly to the mill base prior to the milling process, allowing it to participate in dispersion during particle size reduction. In the second approach, the surfactant was introduced at the very late moments of the milling process, just before completion of the milling process, serving as a post-dispersion additive. This was done to find out whether the presence of surfactant in the formulation, even after the completion of the milling process, can improve the state of dispersion or not. In both cases, the compositions were adjusted to maintain consistent solid content across all samples.

Milling was carried out under controlled conditions using a jar mill to ensure comparable mechanical energy input for all formulations. After pre-mixing the formulations, 25 g of the mill base was poured into the milling vessel containing 190 g of zirconia grinding media (0.8-1 mm diameter). Milling was conducted using a jar mill at 175 rpm for 168 hours (one week). It should be mentioned that at the beginning of the milling, samples were under a wetting control regime and had high viscosities. Accordingly, for the first 24 hours, milling was conducted at 100 rpm for all samples to avoid centrifugation. After that stage and the viscosity drop of the samples, the milling was continued at 175 rpm. Because the dispersion was performed using a low-energy jar mill operating at moderate rotational speeds, the process was expected to induce particle deagglomeration without causing significant chemical degradation or structural modification of the disperse dye. Accordingly, the present study focuses on changes in dispersion state rather than chemical stability. The surfactant concentration was fixed at 0.1 g per formulation based on the optimum concentration identified in our previous study [12]. This concentration was therefore kept constant in the present work to isolate the effect of surfactant incorporation sequence while avoiding the introduction of surfactant concentration as an additional experimental variable.

To isolate the influence of formulation strategy and processing sequence, this concentration was kept constant throughout the investigation. The detailed

compositions of all prepared samples are summarized in Table 1.

It is noteworthy that S4 and S5 formulations are absolutely identical. They differ by the components' addition sequence. In S4, all the components are added during the pre-mixing stage, while in S5, the surfactant was kept out and added just at the very late stage of the milling process. This is more clearly demonstrated in Table 2.

3. Results and Discussions

3.1. Dispersion progress by milling

The key performance attributes of inkjet inks-including droplet formation, transfer to substrates, droplet-substrate interactions, and color strength-are governed by parameters such as ink density, surface tension, and rheological properties. However, these factors ultimately depend on the state of dispersion, defined by pigment particle size, its temporal evolution, and interparticle interactions. Consequently, investigations into inkjet ink formulation must carefully examine how formulation variables influence dispersion. To this end, we assessed changes in the dispersion state at selected stages of the milling process. Because the primary particles of the employed disperse dyes are smaller than 200 nm, fragmentation of larger aggregates reduces visible light scattering, as particles below this threshold do not scatter visible light. Thus, turbidity was expected to decrease with particle-size reduction during milling [17, 20, 21]. Turbidity measurements were conducted after 24 h and 168 h of milling to represent initial and final dispersion efficiencies, respectively. During the initial stage of milling, the relatively high viscosity of the suspensions restricted the rotational speed of the jar mill to 100 rpm, as higher speeds resulted in partial centrifugation of the grinding media and reduced milling efficiency. As the pigment agglomerates became progressively wetted and dispersed, the viscosity decreased substantially, enabling the rotational speed to be increased to 175 rpm. This transition was completed within the first 24 h for all formulations. Therefore, 24 h was selected as a representative boundary between the initial viscosity-limited stage and the subsequent stage, in which higher milling intensity could be applied, and particle size reduction proceeded under more favorable grinding conditions.

Table 1: Sample formulations.

Sample name	Tego Dispers 750W (g)	KEOL6 (g)	PG (g)	D.B.359 (g)	Water (g)
S1	3.75	–	–	2	8.25
S2	3.75	–	2	2	6.25
S3	3.75	0.1	–	2	8.15
S4	3.75	0.1	2	2	6.15
S5	3.75	0.1	2	2	6.15

Table 2: Experimental design illustrating the formulation composition and addition sequence of the investigated samples.

Sample name	Propylene glycol	Surfactant	Surfactant addition order
S1	–	–	–
S2	✓	–	–
S3	–	✓	Before milling
S4	✓	✓	Before milling
S5	✓	✓	After milling

To obtain a preliminary assessment of the short-term dispersion stability during the early stage of milling, aliquots collected after 24 h of milling were diluted to 0.66 % to bring turbidity values into a measurable range. Stored under ambient conditions, their turbidity was measured after 3 and 48 h. These relatively short monitoring times were selected because the dispersions still contained comparatively large particles at this stage, making any instability-induced turbidity changes more likely to occur over short time scales. The objective of these measurements was therefore to compare the relative stability trends of the formulations during the early stages of dispersion development rather than to evaluate their long-term storage stability. Likewise, the 24 and 168 h measurements were selected as representative initial and final stages of the process and were not intended to constitute a detailed milling-kinetics study or to establish a continuous kinetic model. The results are summarized in Table 3.

Since lower turbidity corresponds to smaller particle size, sample S3 demonstrated superior milling efficiency compared to the other formulations. Samples S2 and S4 showed slightly higher and lower efficiencies, respectively, relative to S1. These results suggest that the incorporation of a small amount of surfactant enhances dispersion during the early stages of milling, whereas the simultaneous addition of surfactant and humectant negatively impacts efficiency. Storage behavior after 24 h of milling revealed distinct trends. In samples S1–S3, turbidity initially increased within the first 3 h, followed by a slight decrease, indicating particle growth due to aggregation and subsequent sedimentation under gravity. Notably, particle growth in S3 was considerably less pronounced than in the other samples. In contrast, S4 deviated from this pattern, showing no turbidity increase during storage, which can be attributed to its larger particle size and faster sedimentation.

As noted earlier, turbidity was also measured after one week of milling to evaluate the ultimate dispersion efficiency of the different formulations. The results, presented in Table 4, indicate that S1 achieved the lowest turbidity and therefore the smallest final particle size, clearly outperforming S3 despite the latter exhibiting a faster initial rate of particle size reduction. Samples S2 and S5 showed nearly identical turbidity values, whereas S4 exhibited the highest turbidity, corresponding to the largest final particle size among the investigated formulations.

The distinct functions of the two surface-active components should be considered in interpreting this behavior. TEGO® Dispers 750 W acts primarily as the polymeric dispersant and stabilizing agent, providing surface coverage and steric and/or electrosteric stabilization of the newly generated particle surfaces during milling. KEOL6, in contrast, is a relatively low-molecular-weight and highly mobile nonionic surfactant. Its principal contribution during the early stage of milling is therefore expected to be associated with rapid migration to the particle–liquid interface, reduced surface tension, and enhanced particle wetting and liquid penetration into pigment agglomerates. Hence, when both surfactant and polymeric dispersant are present from the beginning of the milling process, the surfactant may improve the wetting and therefore the initial particle size reduction.

Table 3: Turbidity of samples after 24 hours of milling at various sampling-to-measurement intervals.

Sampling to measurement interval (h)	Turbidity (NTU)				
	S1	S2	S3	S4	S5
0	2493±3	2460±3	2311±3	2539±3	2457±3
3	2535±3	2470±3	2314±3	2531±3	2471±3
48	2483±3	2448±3	2272±3	2509±3	2453±3

Table 4: Turbidity of samples after 168 hours of milling.

	Sample name				
	S1	S2	S3	S4	S5
Turbidity (NTU)	785±3	1214±3	1076±3	1418±3	1269±3

Over prolonged milling, however, competition between the two surface-active species for interfacial sites may occur and could modify the effectiveness of polymeric dispersant adsorption. This possibility is considered a plausible interpretation rather than a directly measured adsorption mechanism.

The observed influence of propylene glycol on the final particle size may be interpreted in light of Ostwald ripening phenomena. Previous studies on wet milling processes have shown that, when the dispersed particles possess a finite solubility in the continuous phase, Ostwald ripening can become increasingly significant as particle size approaches the submicron range, where the large specific surface area results in a substantial increase in surface free energy. Under such conditions, smaller particles tend to dissolve preferentially and redeposit onto larger particles, thereby counteracting further particle size reduction and limiting the ultimate efficiency of the milling process [22, 23].

Propylene glycol is known to enhance the solubility of hydrophobic disperse dyes in aqueous media [24]. Therefore, increasing the propylene glycol content may accelerate dissolution-reprecipitation processes and promote Ostwald ripening during prolonged milling. This interpretation is consistent with the progressively poorer ultimate dispersion efficiency observed for formulations containing propylene glycol, particularly S4, which exhibited the highest final turbidity despite containing the surfactant that facilitated rapid initial dispersion [22]. These findings suggest that, although propylene glycol serves an important role as a humectant, its presence may adversely affect the minimum attainable particle size if enhanced dye solubilization contributes to ripening-driven particle growth.

The behavior of the surfactant-containing formulations suggests the existence of two competing effects during the milling process. On the one hand, surfactant addition accelerated the initial rate of particle size reduction, as evidenced by the rapid turbidity decrease observed for S3. On the other hand, prolonged milling resulted in a larger final particle size compared with the surfactant-free formulation S1. This behavior may be attributed to a combination of enhanced solubilization of disperse dye molecules, promoting Ostwald ripening, and modifications in interfacial phenomena governing agglomerate fracture during wet milling.

The influence of surfactant on the wetting and penetration behavior of pigment agglomerates can be described using the Lucas–Washburn equation (Eq. 1):

$$\frac{dV}{dt} = \frac{\pi R^2 \sigma \cos\theta}{4\eta L} \quad (1)$$

Where V is the volume of penetrated liquid, t is time, R is the capillary radius, σ is the liquid surface tension, θ is the contact angle between the liquid and the capillary wall, η is the liquid viscosity, and L is the penetration length. Surfactant addition simultaneously decreases the surface tension of the medium and improves wetting, resulting in a lower contact angle and hence higher cosθ. Consequently, the overall penetration behavior depends on the balance between these competing effects through the σ.cos θ term [15, 16]. The rapid initial dispersion observed for S3 suggests that improved wetting and liquid penetration into porous agglomerates was the dominant factor during the early stages of milling, facilitating deagglomeration.

As milling progresses and particle size decreases, the role of liquid penetration becomes less dominant, and particle breakage is increasingly governed by the efficiency of stress transmission during bead–particle collisions. In this regime, adsorption of surfactant molecules at newly generated surfaces may modify interfacial mechanics and influence how mechanical energy is dissipated during collisions, potentially reducing the efficiency of further particle fracture.

In addition, capillary pressure (P_c) within partially wetted porous agglomerates can be expressed as (Eq. 2):

$$P_c = \frac{2\sigma \cos\theta}{R} \quad (2)$$

Capillary forces generated during liquid infiltration may contribute to internal stress development within agglomerates and assist their mechanical breakdown during early milling stages. However, excessive reduction in surface tension may reduce capillary pressure, thereby diminishing this contribution to agglomerate fracture [25]. In other words, while surfactant addition improves wetting and accelerates initial deagglomeration, it may simultaneously reduce capillary-driven contributions to agglomerate disruption during milling. This shift in the balance of mechanisms can limit further particle size reduction at later stages. Although capillary pressure and its contribution to the

pigment coarse breakdown were not measured directly, the consistency of the observations suggests that it would be a reasonable interpretation. This interpretation is consistent with established industrial practice, where surface-active agents are often introduced after the primary grinding stage to optimize final ink properties while minimizing adverse effects on milling efficiency [26, 27].

To validate the proposed underlying reason for the above observations, surface tension was measured after completion of milling, as shown in Table 5. As expected, S1-prepared without surfactant or humectant-exhibited the highest surface tension, whereas S4 and S5, both containing surfactant and humectant, showed the lowest values. A notable distinction emerged between S4 and S5, despite their identical components: the order of addition significantly influenced the outcome. In S4, surfactant introduced during the premix stage had sufficient time to adsorb onto pigment surfaces, while in S5, surfactant added at the end of milling remained largely unadsorbed in the medium, thereby reducing bulk surface tension. This explains the markedly lower surface tension observed in S5 compared with S4. Furthermore, the slight difference between S2 and S3 highlights the superior efficiency of surfactants in lowering surface tension relative to co-solvents and humectants; indeed, 0.71% surfactant reduced surface tension more effectively than 14.3% humectant. It should be noted that the measured surface tensions correspond to mill bases rather than finished inks. Final adjustment of surface tension is performed during the let-down stage to satisfy the requirements of the intended inkjet printhead.

To further substantiate the turbidity-based interpretations of particle size, direct measurements were performed using dynamic light scattering (DLS), as shown in Figure 1. The results closely mirrored the turbidity trends: S1 exhibited the smallest particle size with the most uniform distribution, whereas S4 displayed the largest particles and the broadest, least uniform distribution. Samples S2 and S5 showed nearly identical particle sizes and distributions, consistent with their comparable turbidity values. Considering that S2 and S5 are almost the same except for the incorporation of surfactant into S5 at the end of milling, it can be deduced that reducing surface tension after completion of milling has no considerable effect on the particle size. Conversely, S4 and S5, which have the same final formulations, behave completely differently in DLS and turbidity, further supporting this idea.

Table 5: Surface tension of samples after 168 hours of milling.

	Sample name				
	S1	**S2**	**S3**	**S4**	**S5**
Surface tension (N/m)	39.43	37.318	36.503	33.612	29.439

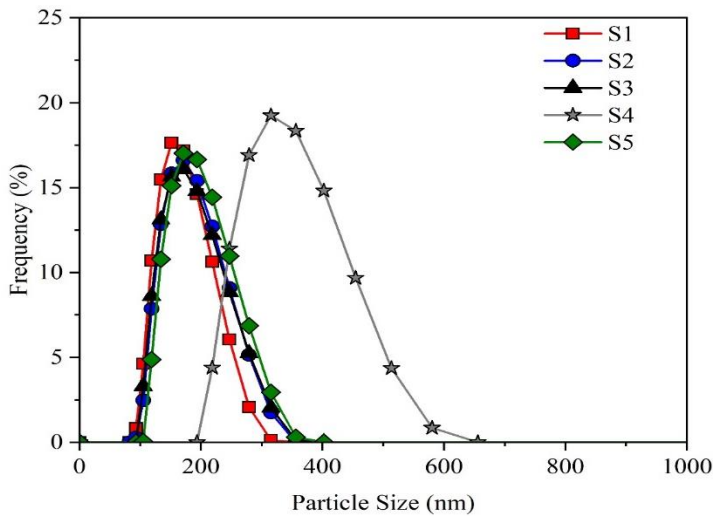


Figure 1: Particle size distribution of samples obtained by DLS.

An essential property of inkjet inks that is strongly influenced by particle size is their optical behavior, particularly color strength. As pigment aggregates are further broken down, light absorption becomes dominant over scattering, thereby enhancing color intensity. Therefore, the interaction of the pigment dispersion samples with visible light can provide great insight into their state of dispersion. To evaluate this effect, UV-Vis spectra of the samples were recorded (Figure 2). The results were consistent with turbidity and DLS measurements: S1 exhibited the highest blue light transmission at approximately 455 nm, reflecting its superior dispersion. Samples S2 and S5 showed nearly identical optical responses, while S3 occupied an intermediate position. In contrast, S4 demonstrated the lowest transmission, in agreement with its larger particle size and poorer dispersion quality.

3.2. Dispersion stability

Dispersion involves three fundamental steps: wetting, distribution, and stabilization of pigment particles [28, 29]. Although the state of dispersion is crucially important, a pigment dispersion can only be considered a decent sample for being used in real applications only when it shows appropriate stability. Otherwise, the prepared dispersion undergoes flocculation and particle size growth, which can be followed by sedimentation. To assess this aspect, they first investigated under static conditions by storing them at ambient conditions for a prolonged time and monitoring their turbidity meanwhile.

As can be seen in Figure 3, the static condition cannot show this differentiation since it is too mild. Only a subtle fluctuation in the turbidity of samples during storage time has been seen, which was slightly more prominent for S5. It can be attributed to the interaction between non-adsorbed surfactant molecules and the particle interface. In order to further accentuate the differences among samples, freeze-thaw (F-T) test was employed. Accordingly, samples were subjected to one cycle of the F-T test, and turbidity was measured before and after treatment (Table 6). The results showed that turbidity increased by approximately 100 NTU in all samples, except for S5, which exhibited nearly double this increase. It is also noteworthy that the presence of propylene glycol has no appreciable effect on the samples' performance during the F-T test, while it is a well-known approach in latex systems to incorporate somewhat around 150 g/lit of low vapor pressure solvents like glycols into them to improve their behavior under F-T conditions. This pronounced instability in S5 -even in the presence of propylene glycol- can be attributed to the addition of surfactant at the end of milling, leaving a significant fraction of molecules unadsorbed in the medium. These free surfactant molecules are prone to micelle formation, which can destabilize dispersions by promoting particle flocculation through mechanisms such as depletion-induced aggregation and Ostwald ripening that are more significant under the severe conditions of the F-T test [30-32]. These mechanisms, however, were not directly measured and should therefore be regarded as plausible interpretations. The results therefore highlight a trade-off associated with post-milling surfactant incorporation. While this approach can minimize the adverse influence of surfactant on ultimate particle-size reduction, the present results indicate that it may adversely affect freeze-thaw stability, particularly when a substantial fraction of the added surfactant remains in the continuous phase. Therefore, post-milling surfactant incorporation should be carefully controlled to achieve the desired balance between milling efficiency and dispersion stability. The freeze-thaw experiment should be interpreted as a comparative stress test based on a single cycle, rather than as a complete assessment of multi-cycle freeze-thaw durability.

It should be noted that the stability evaluation performed in this study was intended to assess the overall colloidal stability of the dispersions. Distinguishing reversible flocculation from irreversible aggregation would require additional characterization techniques beyond the scope of the present work. Nevertheless, both phenomena are undesirable in inkjet applications because they may impair jetting reliability and increase the risk of nozzle clogging.

Table 6: Influence of freeze-thaw treatment on turbidities of samples.

Stage of measurement	Turbidity (NTU)				
	S1	S2	S3	S4	S5
Before F-T	785±3	1214±3	1076±3	1418±3	1269±3
After F-T	878±3	1312±3	1194±3	1500±3	1462±3

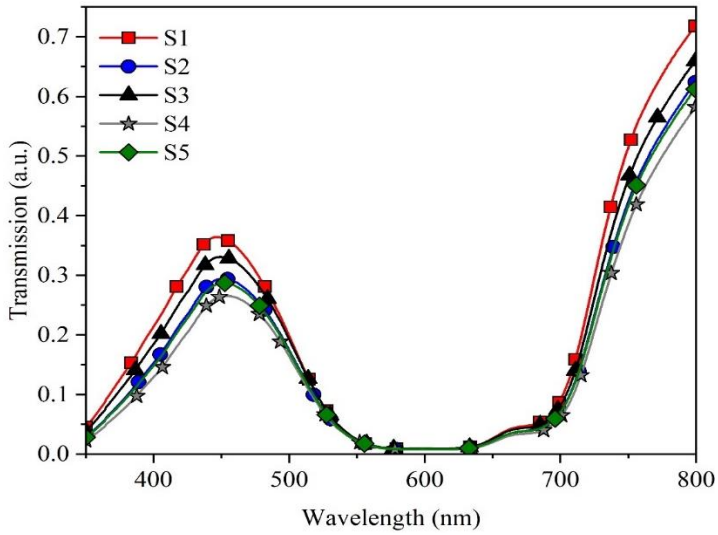


Figure 2: UV-Vis spectra of samples.

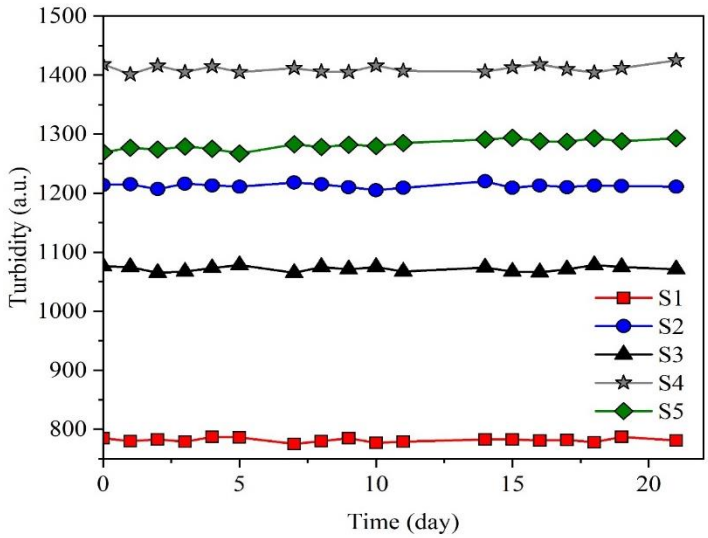


Figure 3: Turbidity of the samples during storage at ambient condition.

3.3. Rheological behavior

Precise droplet formation is essential for reliable inkjet printing, as it directly affects jetting performance, color reproduction, and image sharpness. Among the physicochemical properties governing droplet formation, surface tension and rheological behavior are predominantly important [32, 33]. Therefore, in addition to surface tension measurements, the rheological properties of the prepared dispersions were systematically investigated.

Rheological characterization was performed using a standard four-step protocol consisting of a pre-shear stage followed by a rest period to eliminate residual stresses and establish a comparable structural state for all samples. Subsequently, steady shear-rate sweeps were conducted over the range of 10–1000 s^{-1} (Figure 4). The resulting flow curves revealed clear differences among the formulations. Sample S1 exhibited the highest viscosity throughout the investigated shear-rate range and showed the most pronounced shear-thinning behavior.

To quantitatively compare the rheological behavior of the dispersions, viscosity data obtained from steady shear-rate sweeps (10–1000 s^{-1}) were fitted using the Ostwald–de Waele power-law model [34]. The power-law model is a widely used constitutive equation for describing the flow behavior of generalized Newtonian fluids, including many suspension-based systems. According to this model (Eq.3).

$$\tau = K\dot{\gamma}^n \quad (3)$$

Where "τ" is shear stress, "K" is the consistency index, "n" is the flow behavior index, andẏ" represents shear rate. The flow behavior index was used as a measure of deviation from Newtonian behavior, with n = 1 corresponding to an ideal Newtonian fluid and lower values indicating increasing shear-thinning character [34]. The coefficient of determination (R^2) was also calculated to evaluate the extent to which the experimental data could be described by the power-law model. As can be seen in Table 7, all formulations were well described by the power-law model, with R^2 values close to unity. Nevertheless, significant differences were observed in their flow behavior. While S2–S5 exhibited flow behavior indices between 0.89 and 0.91, sample S1 displayed a substantially lower value of 0.785, indicating a greater deviation from Newtonian flow and a more pronounced shear-thinning character. This rheological response, together with the relatively high viscosity of S1, suggests the presence of stronger interparticle interactions within the dispersion. Considering that S1 exhibited the smallest particle size according to DLS and turbidity measurements, its larger specific surface area likely increased the extent of particle–particle interactions, thereby contributing to the observed rheological behavior [9, 35].

Furthermore, the dispersant-to-pigment ratio employed in the formulation (≈75 %) may not have been sufficient to completely cover the enlarged surface area generated by the nanosized particles [12]. Under such conditions, exposed particle surfaces can promote attractive interactions and transient network formation. In the other formulations, the presence of surfactant and humectant may have partially compensated for this effect by occupying available surface sites and improving steric stabilization.

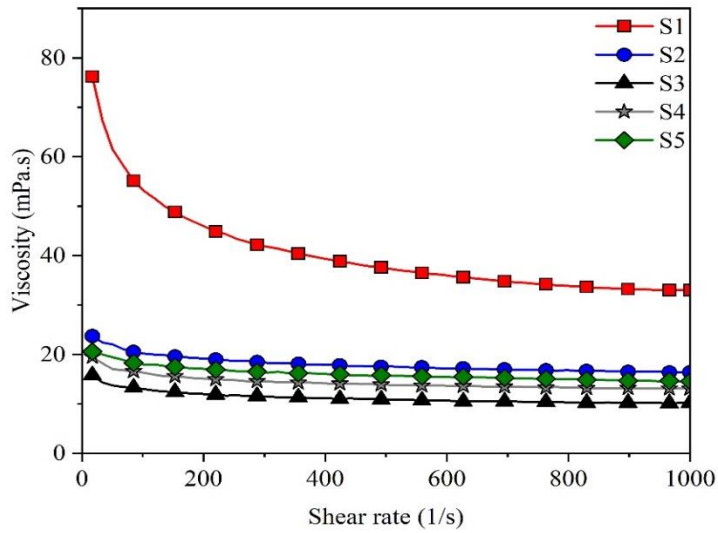


Figure 4: Viscosity as a function of shear rate of samples.

Table 7: Power-law fitting parameters obtained from steady shear-rate sweeps.

Sample name	Flow behavior index (n)	Coefficient of determination (R^2)
S1	0.78	0.999
S2	0.90	0.998
S3	0.91	0.993
S4	0.90	0.997
S5	0.89	0.996

Comparison of the rheological responses of samples S2–S5 provides additional insight into the role of formulation components. Sample S3 exhibited the lowest viscosity and the highest flow behavior index (n=0.91), indicating that the nonionic surfactant was more effective than propylene glycol in reducing interparticle interactions and promoting near-Newtonian flow. However, when both additives were simultaneously present, as in S4, the reduction in viscosity was less pronounced than expected from the effect of surfactant alone. This observation suggests that propylene glycol may have partially reduced the efficiency of surfactant adsorption or altered its interfacial arrangement on the particle surface, thereby limiting its stabilizing effect.

The comparison between samples S4 and S5 further highlights the importance of the formulation sequence. In S4, the surfactant was introduced during the premixing stage, allowing it to participate in particle wetting and adsorption throughout the milling process. In contrast, in S5, the surfactant was added after milling, reducing its opportunity for effective surface association with the pigment particles. Consequently, S4 exhibited lower viscosity and a flow behavior index closer to unity, indicating weaker interparticle interactions and improved colloidal stabilization. These findings demonstrate that not only the composition of the formulation, but also the sequence of component incorporation, plays a critical role in determining the rheological characteristics of sublimation transfer inkjet dispersions. It should also be emphasized that the rheological trends observed for the mill bases cannot, by themselves, establish the jetting or printing performance of the corresponding finished inks. Final printability depends on the properties of the complete ink formulation and on the specific printhead and operating conditions. Therefore, the present rheological results are interpreted as formulation-level indicators rather than direct evidence of printability.

Given that the formulations investigated in this study are mill bases rather than finished inkjet inks, the rheological properties discussed herein are intended to evaluate the influence of formulation variables on dispersion quality and processing behavior. Therefore, the present results should not be interpreted as direct evidence of inkjet printability. Preparation and printability evaluation of the corresponding finished inks, obtained after the let-down stage, are beyond the scope of the present work. It should also be emphasized that the proposed mechanisms are based on the combined interpretation of the measured dispersion, surface, and rheological properties and are not direct measurements of capillary stresses, dye dissolution–reprecipitation, or interfacial adsorption. Accordingly, these mechanisms should be regarded as plausible explanations of the observed formulation-dependent trends rather than as independently verified processes.

4. Conclusion

This study systematically investigated the effects of a nonionic surfactant, propylene glycol, and surfactant incorporation sequence on the dispersion, stability, rheological behavior, and processing characteristics of aqueous sublimation transfer inkjet mill-bases. Surfactant and propylene glycol accelerated the initial stage of particle-size reduction, whereas prolonged milling ultimately produced the smallest particles in the surfactant- and humectant-free formulation, reaching 151 nm compared with 317 nm for the surfactant-containing formulation. These results demonstrate that additives that promote early-stage wetting do not necessarily improve ultimate milling efficiency. The incorporation sequence of the surfactant was found to be a critical processing variable. Although the formulations had identical final compositions, changing the stage at which the surfactant was introduced substantially affected milling efficiency, dispersion stability, and rheological behavior. Post-milling addition preserved milling efficiency but resulted in greater susceptibility to freeze–thaw destabilization, whereas incorporation during milling provided more favorable stability but compromised the ultimate particle-size reduction. Rheologically, all formulations were well described by the Ostwald–de Waele model (R^2>0.99); except for the surfactant- and humectant-free formulation, the samples exhibited nearly Newtonian behavior (n≈0.9±0.075), while the latter showed pronounced shear-thinning (n=0.785). Overall, the findings demonstrate that surfactant performance in wet-milled aqueous dispersions depends not only on its final concentration but also on its incorporation history. Thus, processing sequence should be considered an independent formulation variable when optimizing sublimation transfer inkjet dispersions. From an industrial perspective, post-milling surfactant incorporation can provide a favorable compromise by

avoiding adverse effects on particle-size reduction; however, its potential impact on freeze–thaw stability should be considered during final formulation. To the best of our knowledge, this is the first systematic study demonstrating that the timing of surfactant addition, rather than merely its concentration, plays a decisive role in balancing milling efficiency, dispersion stability, and rheological performance in aqueous sublimation transfer inkjet mill-bases.

5. References

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