Jettability and Stability of Inkjet Inks for Textile Printing

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Abstract

To achieve highly reliable and productive inkjet printing systems for textiles, we have developed a black dye dispersed ink that meets the requirements of dye safety, image stability/durability, storage stability, and, most challenging, jettability. Jettability in this ink was achieved by using a wetting agent to strengthen surface energies and decrease the flocculation that causes structural viscosity. The result was Newtonian fluid behavior that allows superior jettability.

Introduction

Inkjet printing, with its low printer and running costs, its wide variety of compatible recording media, and its many other attractions, has proliferated in consumer and commercial markets alike. Of special note among emerging commercial applications is textile inkjet printing as a digital method of printing samples, designs, and coupons, and, for outdoor use, printing signage, flags, and banners [1].

Although textile and paper inkjet printing share the same basic technologies, textile inkjet printing inks must be designed specifically for the substrates and delivery mechanisms with which they are matched. This means fiber-specific colorants chosen for such fabrics as cotton, silk, and polyester.

Preferred with polyester fabrics are dispersed dye inks in the form of hydrophobic dyes dispersed to small crystalline form in an aqueous medium. After printing with such dye inks, polyester fabrics are heated and the dyes melt, sublime, and/or dissolve into the fabric's fibers, where they fix.

For this application, dispersed dyes must meet four requirements. First, safety requires that the dyes not be toxic, carcinogenic, or otherwise hazardous to health, especially because these dyes will often come into direct contact with human skin. Second, image stability requires that the dyes provide images that resist such agents of degradation as light, water, perspiration, and rubbing. Third, ink storage stability requires that these dyes remain in dispersed form, without aggregation and/or agglomeration, for a matter of years. If dispersed dye particles were to aggregate or agglomerate during storage, the larger particles thus formed would settle into a sediment, leading to filter and print head clogging and to inferior color reproduction. Fourth, jettability requires that the ink exhibit the behavior of a Newtonian fluid.

While the burden of satisfying these demands falls directly on the design of the dyes involved, only a small range of dyes exist to be chosen from, and therein lies the challenge. This paper presents our efforts to achieve safety, image stability, storage stability, and jettability in a black dispersed dye ink.

Experimental

Preparation of black inks

Yellow, magenta, and cyan dyes were dispersed independently with a beads mill disperser to yield commensurate dispersions. The three dispersions were then mixed to produce three black inks.

Evaluation of mutagenicity

The mutagenicity of the inks was tested through conventional AMES testing with *Salmonella typhimurium* TA98, *Salmonella typhimurium* TA100, and *E.Coli WP2uvrA/*pKM101.

Evaluation of dye surface energies

Each dye was palletized, and its contact angles with water, nitromethane, and diiodomethane were measured with a CA-V contact angle meter (Kyowa Interface Science Co., Ltd.). The surface energies of the dyes were calculated from the contact angles via Young-Fowkes equilibrium.

Evaluation of ink properties

Each ink was centrifuged at a common speed, and the absorbance of the supernatant was measured at intervals with a U-3200 spectrophotometer (Hitachi). The sedimentation property of each ink was expressed as the ratio between the initial and the centrifuged absorbencies. The viscoelasticities of the inks were measured with an MCR 300 modular rheometer (Physica Messtechnik GmbH). Light fastness, water fastness, and the fastness of color against perspiration, washing and laundering, and rubbing were evaluated according to corresponding Japan Industrial Standards. The firing velocity of each ink was measured at intervals with a Konica Minolta's shear-type inkjet head. The jettability was expressed as the ratio between the initial and the intermittent firing velocity.

Results and Discussion

Dye safety

Dye safety was of paramount concern. We evaluated the mutagenicity of selected stable dyes, and most tested positive in AMES testing. Unfortunately, no black dye tested negative, but we did find yellow, magenta, and cyan dyes that satisfied dye safety as well as specifications of color, image stability, and durability. Thus we produced black dye from a combination of yellow, magenta, and cyan dyes.

Image stability and durability

A dye's stability and durability against light, water, perspiration, and rubbing determines the image stability and durability of the inkjet-printed textile image. We examined the dyes' stability ratings in conventional screen-printing systems, and chose stable yellow, magenta, cyan, and black dyes. Table 1 presents the results that confirmed the image stability and durability of these dyes in inkjet textile prints.

Table 1 Durability and stability ratings

	Y	M	C	K
Light	7	7	7	7
Water	4-5	4-5	4-5	4-5
Perspiration/Acid	5	5	5	4
Perspiration/Alkali	5	5	5	4
Rubbing	5	4-5	4-5	4-5

Storage stability

Because our black ink was formulated from yellow, magenta, and cyan dyes, the rapid adsorption and desorption exchange of dispersants tended to lead to the sedimentation of dye particles. However, by adopting an appropriate single dispersant and an auxiliary agent, we reduced sedimentation [2].

Jettability

For a specific amount of inkjet ink to be jetted stably, it is preferable that the ink be a Newtonian fluid. When we increased dye content to obtain high density prints, however, the ink tended to display non-Newtonian behavior because of the increased interaction between dye particles. Such non-Newtonian behavior interferes with stable jetting, especially when jetting smaller droplets at high-speed. Overcoming this problem is essential.

Fig. 1 shows the viscoelasity of the storage-stable black ink, where the horizontal axis indicates shear rate and the vertical axis indicates the viscosity of the ink. The ink showed non-Newtonian behavior, namely that the viscosity of the ink was high at low shear rate. This suggested that the ink possessed structural viscosity.

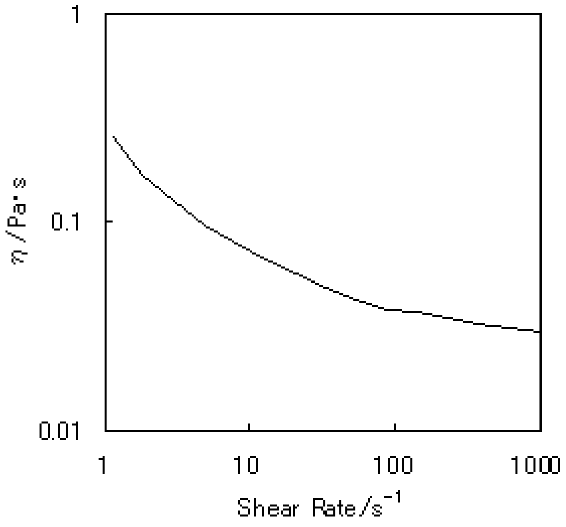

Figure 1. Shear rate dependence of viscosity

To clarify the phenomenon, we measured the shear rate dependence of shear stress of the yellow, magenta, and cyan dispersions, and found that one of them, incorporating dye D, displayed non-Newtonian behavior. The flow curve of Fig. 2 shows the relationship, where the horizontal axis indicates shear rate and the vertical axis indicates shear stress. In Fig. 2, the ascending curve did not fit with the descending curve, suggesting that the dispersion had a thixotropic property. The same dispersion was further investigated and angular frequency dependencies were measured. Fig. 3 shows the angular frequency dependencies of the storage modulus and the loss modulus of the dispersion, where the horizontal axis indicates angular frequency and the vertical axis indicates the modulus. In Fig. 3, the slope of the storage modulus G' flattened in the low frequency region. This suggested that the dispersion itself also possessed structural viscosity.

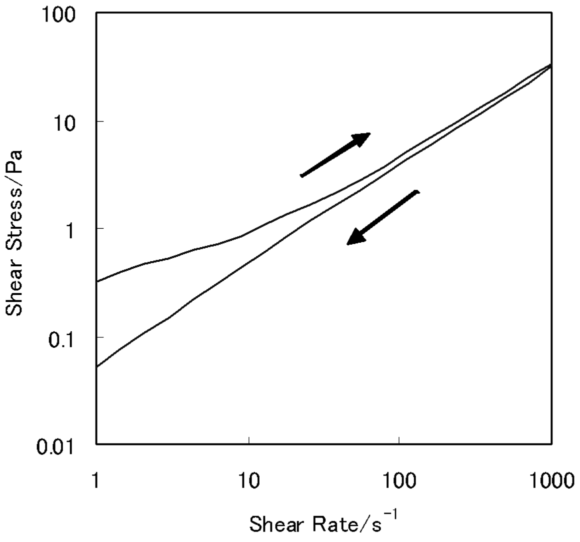

Figure 2. Flow curve for dispersion of dye D

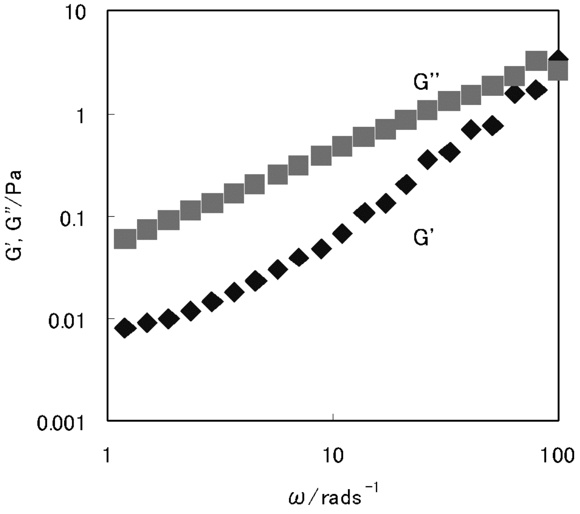

Figure 3. Angular frequency dependencies of storage modulus (G') and loss modulas (G") for dispersion of dye D

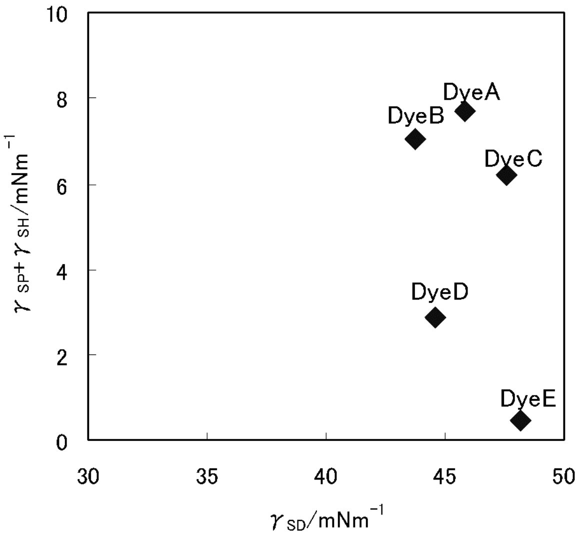

Figure 4. Surface energies of dyes

The aggregation and flocculation of dispersed particles may cause such structural viscosity. We studied the shapes of dispersed particles of dye D via electron microscope and found neither the needle- nor plate-like shapes that promote aggregation. Rather, the particles were globular in shape, suggesting that the dispersed dye particles interacted gently to form flocculation, resulting in structural viscosity. In fact, the structural viscosity broke down with high shear stress and the viscosity decreased in the high shear rate region, as seen in Fig. 1.

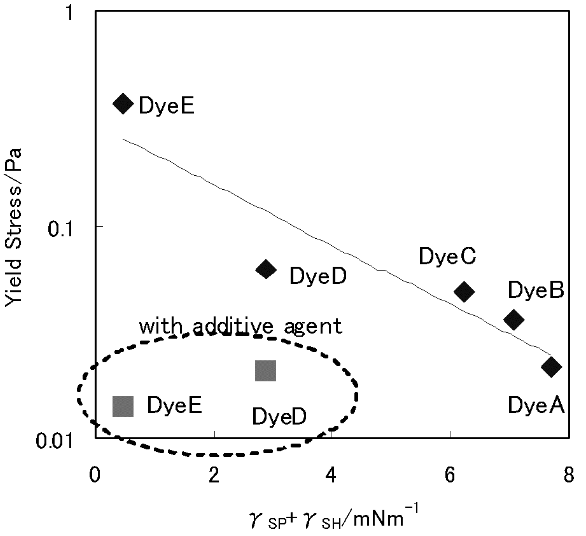

Figure 5. Yield stresses and surface energies

To investigate flocculation, we studied five dye dispersions. Fig. 4 shows the surface energies of the five dispersed dyes, where the horizontal axis indicates dispersion force, i.e. the hydrophobicity of the dye surface, and the vertical axis indicates the sum of polar and hydrogen bonding forces, i.e. the wettability of the dye. We analyzed the relationship between the dyes' surface energies and flocculation and found that wettability correlated well with flocculation. In Fig. 5, we plotted yield stress against hydrophobicity, where the horizontal axis indicates the sum of polar and hydrogen bonding forces and the vertical axis indicates the yield stress of the dispersion, which we viewed as an index of flocculation calculated from Casson's plot. In Fig. 5, the yield stress was low in the region exhibiting high sums of bonding force, suggesting that flocculation was caused by the polar and hydrogen bonding forces of the dye's surface being weak.[3] To strengthen these forces, we dispersed our two least wettable dyes, dyes D and E, in combination with a wetting agent. As seen in Fig. 5, the yield stresses of dyes D and E dropped sharply with the addition of the wetting agent, suggesting an improvement in the wetting ability of the dyes.

Guided by these results, we dispersed dye D with the wetting agent, formulated a black ink with two other dye dispersions, and evaluated the viscoelastic property of the ink. As seen in Fig. 6, structural viscosity broke down and the viscosity of the ink dropped dramatically and flattened across all shear regions. This low viscosity black ink achieved stable jetting even at high speeds.

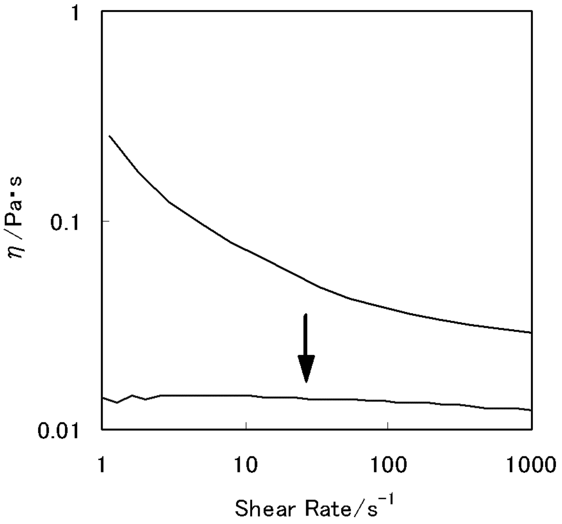

Figure 6. Effect of the wetting agent on viscosity

Conclusion

Newtonian behavior is essential to stable jetting. We found that the surface energy of dispersed dyes affected the viscoelasity of an ink; dyes with poor surface energies yielded structural viscosity that led to poor jetting. The addition of a wetting agent improved wettability significantly, allowing the design of a black dispersed dye ink for textile inkjet printing that was safe, that was highly resistant to light, water, perspiration, and rubbing, that had high storage stability, and that provided highly stable jetting.

References

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Author Biography

Hitoshi Morimoto received his B.S. (1991) and his M.S. (1993), both from Ehime University. He joined Konica Corporation in the same year, where he developed digital materials for silver photographic systems. Since 1995 he has focused on the development of inkjet materials.