Silica Nanoparticles: Design Considerations for Transparent and Glossy Inkjet Coatings

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Abstract

Inkjet technology is finding utility in a variety of applications ranging from advertising, packaging, proofing, and the in-home printing of photographs. In many applications transparency of the inkjet coating is a critical parameter. Transparent media is widely used for graphic displays, window advertisements, and backlit applications. Ink receptive transparent coatings are also critical in glossy photographic media, especially transparency of the topcoat in multiple layer architectures. A transparent and glossy top layer is highly desirable and in most cases clarity correlates with gloss. It is generally accepted that a high degree of topcoat transparency translates to high printed color optical density.[1]

Silica nanoparticles are used in highly pigmented topcoats to create a porous structure, which traps the colored elements of the ink and lets the carrier liquid pass through to the underlying absorptive layer. In some cases nanoparticles are used in clear films to improve its mechanical properties.

This paper describes two studies. Study I investigated the impact of the properties of silica nanoparticles on the clarity, gloss and printability of inkjet coating films. An experimental design was used to evaluate silica nanoparticles in combination with various binders. In Study II we explored the impact of acetoacetylated polyvinyl alcohols combined with different silicas on the transparency and gloss of the film.

Introduction

The inkjet market continues to grow. The digital camera market is also expanding quickly in all regions of the world. According to InfoTrends/CAP Ventures' research, nearly 80 million inkjet devices were installed in 2003, making inkjet the dominant printer technology in the desktop arena.[2] The media market is dominated by photo papers, greeting card stock, and label supplies. The use of pigmented or microporous coatings is becoming the preferred technology for producing high quality "instant dry" glossy inkjet paper. A typical inkjet coating formulation includes silica or alumina pigments as key components. The optical properties, transparency, gloss and printability of microporous inkjet media are strongly dependent on the type of pigments used in the coating.

Modern pigments provide unique pore structures and surfaces for the adsorption of dyes and/or color pigments resulting in properties like excellent image density, outstanding resolution and instant drying.

This paper gives an overview of the physical and chemical properties of synthetic silica nanoparticles and their effect on the performance of the inkjet media. Particle size, surface charge, pigment to binder(s) ratio, binder type are correlated with media properties like gloss, ink absorption, and image quality.

Experimental

Study I: Impact of Silica Nanoparticles Properties on the Clarity, Gloss and Printability of Inkjet Coating Films

In order to screen a large experimental space with as few experiments as possible a Hyper-Greco-Latin Squares (HGLS) design of experiment (DOE) was chosen.[3] With this design four factors at three levels were screened in nine experiments as shown in Tables 1a and 1b. HGLS designs are especially useful in the initial stages of formulation studies, directing focus to the best choices of formulation ingredients.

Inkjet coatings were prepared using silica nanoparticles and various binders. All silica nanoparticles used for Study I were commercially available grades from Grace Davison with a cationic surface treatment: SYLOJET® 4000C (particle size <90 nm, organic cationic treatment), SYLOJET® 4001 (particle size <90 nm, inorganic cationic treatment) and LUDOX® CL-P (particle size 22 nm, inorganic cationic treatment). Cationically modified silica nanoparticles are widely used in glossy topcoats due to their glossing potential and compatibility with cationic additives. Polyvinyl alcohol (PVOH) was used as a binder on its own or in combination with latex. PVOH grades used for this study were chosen from Celanese Corporation and Nippon Gohsei Limited. Two grades from Nippon Gohsei are chemically modified (acetoacetylated grade Z-100 and quaternary amine grade K-210) and Celvol® 523 from Celanese is a non-modified grade (partially-hydrolyzed, medium molecular weight). Latexes were obtained from Specialty Polymers, Inc. Both latexes were cationic styrene acrylates that mainly differed in T_g (H1Q027: T_g =17°C, particle size ~0.18 µm and H1Q061: T_g=65 °C, particle size ~ 0.22 µm).

Formulations were prepared at total solids content of 28%. The pigment to binder ratio was varied as described in Table 1b. For experiments using latex, the PVOH to latex ratio was held constant at 9. The formulations were coated on polyester substrates (Melinex® 454 clear film and Melinex® 534 opaque white film) at a wet film thickness (WFT) of ~80 microns. The transparency of the coating applied on the clear film was determined by placing the coated film on top of a black surface and measuring black optical density. Higher optical density was interpreted as higher transparency. Uncoated clear film was used as a reference. Gloss was measured on the coating applied to opaque film with BYK-Gardner gloss meter at 60° angle.

Table 1a: Factor Combinations for DOE (Study I)

	C1	C2	C3
R1	A1	B3	C2
R2	B1	C1	A3
R3	C3	A2	B1

Table 1b: Description of Factors (Study I)

R1	SILICA 1: SYLOJET® CL-P
R2	SILICA 2: SYLOJET® 4001
R3	SILICA 3: SYLOJET® 4000C
C1	PVOH1: CELVOL® 523
C2	PVOH 2: NIPPON GOHSEI Z-100
C3	PVOH 3: NIPPON GOHSEI K-210
A	LATEX 1: H1Q061
B	LATEX 2: H1Q027
C	LATEX 3: NONE
1	PIGMENT/BINDER RATIO 1: 85/15
2	PIGMENT/BINDER RATIO 2: 90/10
3	PIGMENT/BINDER RATIO 3: 95/5

Print properties were determined on the coatings (24 microns WFT) and applied to a base layer consisting of Grace Davison's SYLOJET® 733C (particle size ~330 nm, cationic organic surface treatment) and binders based on an internal reference formula. The applied topcoats were dried at 100 ºC. Coated double–layer sheets were printed with the Epson Stylus® 870 dye inkjet printer in Premium Glossy Photo Paper mode at 720 dpi using test patterns drafted in CorelDraw®. Coalescence and bleed were evaluated visually on 100% fill areas of primary and secondary color patterns and ranked using a scale of 0.1 to 0.9 (0.1-worst, 0.9-best). Optical densities were measured on cyan, magenta, yellow and black with an X-Rite® Spectrophotometer. All print properties (coalescence, bleed and optical densities) were combined in one score with each factor holding equal weight and compared against gloss or transparency.

Study II: Impact of Acetoacetylated Polyvinyl Alcohols on the Transparency and Gloss of Films in Combination with Different Silicas

As a next step, we looked at modified acetoacetylated binders in combination with our pigments. The following binder grades from Nippon Gohsei were chosen: Z-100, Z-200, Z-210, Z-320 and Z-410. The grades differed in degree of hydrolysis, molecular weight, modification level, etc. For simplicity, all combinations were tested at an 80/20 pigment to binder ratio. Single layer coatings were prepared and applied as described earlier. Transparency and gloss were the only responses studied in this set of experiments.

Results

Study I Results Summary

In general, all combinations with SYLOJET® 4001 and 4000C exhibited noticeably higher optical densities than combinations with LUDOX® CL-P. When trade-offs among several responses must be considered in the analysis, one approach used in HGLS designs is to develop a composite index that reduces several responses into a single one. First, individual responses (print quality scores, gloss and transparency) were normalized by linear interpolation to a scale of 0.1 to 0.9. The normalized individual responses were then used to calculate the square root of the product (print quality and transparency or print quality and gloss) of the two individual responses. The three responses obtained for each individual factor were averaged and are reported in Table 2a.

As a next step analysis of variance (ANOVA) was conducted to determine the significance of difference between the averages of each factor. Probabilities for the null hypothesis (that there is no difference between averages) were used as a measure of the significance of the effect. Probabilities < 0.05 were considered highly significant. P-values for the effect of factor type on composite scores are listed in Table 2b. Data were analyzed using statistical software from MINITAB®.

Table 2a: Average Composite Scores for Print Quality and Transparency or Gloss (Study I)

FACTORS	Average Composite Score	
	Print Quality and Transparency	Print Quality and Gloss
SYLOJET®CL-P	0.47	0.23
SYLOJET®4001	**0.74**	**0.74**
SYLOJET®4000C	0.45	0.37
CELVOL® 523	0.51	0.41
Z-100	**0.60**	**0.48**
K-210	**0.61**	**0.46**
H1Q061	**0.60**	**0.51**
H1Q027	0.53	0.39
NONE	0.56	0.44
(85/15)	0.51	0.38
(90/10)	0.53	0.43
(95/5)	**0.63**	**0.54**

Table 2b: Probability for Null Hypothesis for the Effect of Factor Type on Composite Score (Study I)

FACTOR TYPE	P-Values	
	Print Quality and Transparency	Print Quality and Gloss
Silica	0.012	0.004
PVOH	0.793	0.914
Latex	0.887	0.856
P/B Ratio	0.694	0.772

One of the important results of this screening approach is the ability to identify combinations of factors that produce desirable results. The highest composite score indicates the best overall performance. Best performers for each factor group are highlighted in Table 2a. Overall the SYLOJET® 4001 performed significantly better than the other two silicas, as shown by p-value in Table 2b. If the averaged composite scores are very similar within a factor group, the effect of this factor on the overall performance is not significant, as was confirmed using analysis of variance (ANOVA).

As can be seen from Table 2b, silica choice plays the most significant role. At the same time binder composite scores indicate a small effect of binders on overall performance; however the effect of binder should not be underestimated. This became more apparent in Study II where we looked at combinations of silica nanoparticles with acetoacetylated PVOHs from Nippon Goshei that differed in degree of hydrolysis, molecular weight and modification level.

Study II Results Summary

Figures 1 and 2 show the impact of different binders on transparency and gloss for different silica types, which varied in particle size and size distribution. Results from the second study indicate that:

- Overall, the data shows an inverse gloss to transparency relationship.
- SYLOJET® 4001 seems to be the least affected by changes in the binder properties.
- Effect of each binder is directionally similar for all silicas. Magnitude of effect depends on silica type.

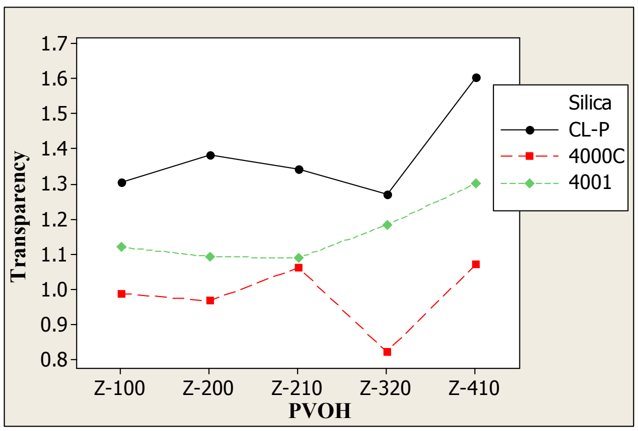

Figure 1. Interaction Plot for Transparency: Z grades and Silicas (Study II)

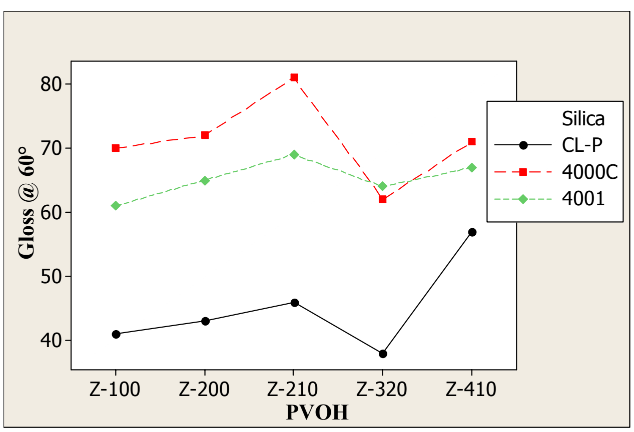

Figure 2. Interaction Plot for Gloss: Z grades and Silicas (Study II)

Conclusions

Experiments showed that all silicas in our studies were compatible with binders tested and resulted in coatings with good properties.

Study I showed that large particle size silicas (SYLOJET® 4001 and 4000C) had positive affect on printability, especially optical density. Analysis of print quality, transparency and gloss indicated that SYLOJET® 4001 was the silica with the best statistical overall performance in this study. Binder type had only minor impact on the results; the inclusion of small amounts of latex also had only a minor influence on the properties measured.

As our second study shows, interactions between silica and binder can occur and cause unexpected reduction in gloss and transparency. As an example, the interaction between silica and Z-320 resulted in some cases in lowest transparency and gloss. Also the inversed relationship between gloss and transparency indicates that optimization of the pigment system will depend on the relative importance of each property in the target formulation.

The intention of this work is to give the formulator guidance in using our nanoparticle silica products. Overall formulating glossy inkjet coatings is a complicated task. Optimizing all properties simultaneously can be difficult and compromises are often required.

References

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Author Biography

Natalia Krupkin received her B.S. degree in Chemical Engineering from the Ukrainian Polytechnical Institute in 1985 and M.S. degree in Chemical Engineering from the Johns Hopkins University in 1995. She joined W.R. Grace and Co.-Conn in 1988 working in the Corporate Research Center first and then in the Silicas/Adsorbents group of Grace Davison. She is currently a Technical Service and Application Development Group manager in the Digital Media Solution group. She is a member of ACS.