# Design Considerations for Matte-Coated Microporous Media for Pigmented Inks

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## Abstract

Today, excellent images can be obtained with narrow-format printers that employ either dye- or pigment-based ink-jet inks, when jetted onto coated media. With the considerable interest in archival properties of the resulting prints, the impetus for utilizing pigmented inks has increased, and pigmented-ink technology is evolving rapidly. Furthermore, there is continued interest in microporous receivers, primarily for reasons of print productivity and performance. However, there is not much information in the open literature regarding the design of microporous receivers for pigmented inks.

The goal of this work is to determine the relationships between microporous receiver-layer properties and important aspects of print performance. An experimental screening design that involved evaluation of five parameters at four levels in sixteen experiments (Hyper-Greco Latin Square Design) was utilized. Receiver layers were coated at the laboratory scale using silica type, PVOH type, silica-surface treatment, latex type and coating composition as the experimental factors. The layers were then printed with EPSON narrow-format, pigmented-ink printers (2000P, C80) and responses such as visual appearance, color gamut and drytime were measured. Strong main effects were observed, particularly for silica surface treatment and PVOH type (degree of hydrolysis). The silica type was also important. Based on composite measures of the responses, the best formulations were noted.

## Introduction

Ink-jet technology continues to undergo rapid evolution. There is currently keen interest in the archivability of the printed image. Pigment-based inks generally are considered to offer better light-fastness and gas-fastness, and the potential for better water-fastness, than dye-based inks. However, the achievable color gamut for pigment-based inks often is not as great as that for dye-based inks. In addition, there is a trend for consumer printing towards inks that can be used with plain, uncoated paper. As reported last year[1], a few years ago EPSON introduced the StylusPhoto 2000P, a desktop printer that utilizes a 5 color and 1 black pigmented-ink set. These inks are reported to be micro-crystal (small particles) and encapsulated in resin, and have 200+ year archivability. In 2001, EPSON launched the Stylus C80, which employs a 3 color and 1 black pigmented-ink set. These pigmented inks are claimed to be resin-encapsulated and to demonstrate 70-year archivability. This printer and ink combination is designed for improved performance on plain paper. The pigment particles within the ink for this printer are coated with a hydrophilic resin so as to interact unfavorably with surface-sized (hydrophobic) paper, to maximize "hold-out" at the paper surface and give high optical density. Although the exact chemistries of these two ink-sets is unclear from the published reports, the availability and low cost of these printers makes them well-suited to be part of an experimental study focused on the interaction between pigmented inks and media.

At the same time, there is little information in the open literature concerning the design of media for pigmented-ink based printers, and development of ink-receptive layers with improved performance is also an active area of interest. While most work is focused on glossy ink-receptive layers, there are considerable challenges with design of media for that segment. In this study, we chose to focus on matte ink-receptive layers, and to determine what factors in the coating layer are important for good printability with the above pigment-based inks sets.

## Experimental

In order to screen a large experimental space with as few experiments as possible, a Hyper-Greco Latin-Squares experimental design (DOE) was chosen. With this design, five experimental factors at four levels were screened in sixteen experiments, as shown in Tables 1a and 1b. The four silicas were all commercial products from GRACE Davison commonly used in ink-receptive media, and these were chosen to provide a matrix of important properties such as particle size, pore volume and surface chemistry (SYLOJET® P405: nominal 5 micron particle size, 2.1 $cm^3/g$ pore volume, 300 $m^2/g$ surface area, pH 3.5; SYLOJET® P412: nominal 12 micron particle size, 2.1 $cm^3/g$ pore volume, 300 $m^2/g$ surface area, pH 3.5; SYLOID® W300: nominal 5 micron particle size, 1.1 $cm^3/g$ pore volume, 300 $m^2/g$ surface area, pH 9.0; SYLOID® W900: nominal 12 micron particle size, 1.1 $cm^3/g$ pore volume, 300 $m^2/g$ surface area, pH 9.0). The W300 and W900 are unique, hydrogel-type silicas. With regard to surface chemistry, additional materials were added to the formulations so as to further modify the nature of the silica surface such that the resulting surface charge was either cationic or anionic. Thus, two cationic materials (one of which was the inorganic aluminum chlorohydrol, SYLOJET® A200 from GRACE Davison, and the other was polymeric in nature) and one anionic additive were employed. Since the silica surface is normally anionic at the pH of these formulations, four of the experiments were conducted with no surface-modifying additive. A two component binder system was chosen, comprised of the water soluble binder poly(vinylalcohol) [PVOH] and the emulsion binder poly(vinylacetate) [PVA]. The poly(vinylalcohols) were also chosen so as to provide a matrix of properties, and were from Celanese. Thus, Celvol 107 (fully-hydrolyzed, low molecular weight), Celvol 205 (partially-hydrolyzed, low molecular weight), Celvol 325 (fully-hydrolyzed, intermediate molecular weight), and Celvol 523 (partially-hydrolyzed, intermediate molecular weight) were chosen as the main binder components. The PVA latexes were also chosen to cover a range of properties, and all were nominally nonionic. The latexes were none, AirFlex 110 ($T_g$ = 4°C, particle size 300 nm), AirFlex 315 ($T_g$ = 18°C), and Vinac XX-210 ($T_g$ = 35°C, particle size 1.4 microns). For experiments with the non-zero latex setting, the PVOH to latex ratio was held constant at 0.42. Finally, four silica to total binder ratios were chosen, ranging from 40:60, 50:50, 60:40 to 70:30.

The formulations were prepared at nearly constant calculated fluid-phase occupied volume (and not constant total solids) of 30%. With no interactions between components in the fluid phase, the viscosities for formulations at constant occupied volume should be nearly the same unless there are significant particle packing effects. Coatings were prepared on polyester substrate (Mellinex 534) in order to ensure that there were no substrate effects, such as absorbance of ink liquids. Two levels of coating thickness were evaluated by using applied wet film thickness of 24 microns and 40 microns. Coatings prepared from these are referred to subsequently as 24 wet-film thickness (WFT) and 40 WFT, respectively.

The formulation pH, viscosity (Brookfield LV-2 spindle at 60 RPM) and solids were measured prior to application. Once applied, the coatings were cured at 105° C for 3 min. All sixteen coatings, for both wet-film thick nesses, showed good physical integrity (good adhesion to substrate, no chalking, no curl, etc.). SEM photographs showed that coatings prepared at 24 WFT barely covered the substrate uniformly. Hence, coatings prepared at this wet-film thickness represent the lower acceptable limit of thickness given the particle sizes of the silicas employed (5-12 microns). Surface roughness was measured using a Zygo Optical Profilometer. Coated sheets were printed with the EPSON 2000P and C80 printers in Archival Matte mode using test patterns drafted in CorelDraw. Drytime was measured by printing a pattern of green blocks with varying halftone fill (0% to 100% for each of the yellow and cyan colors for a nominal total of 0% to 200% fill) and then by measuring the offset to a transfer sheet applied at fixed interval and with fixed force to the receiver layer after printing. The overall appearance of C, M, Y, R, G, B and K 100% fill areas was assigned a number of 1, 2 or 3 depending on the degree of ink coalescence, with a 1 representing extreme coalescence, a 2 representing modest coalescence, and a 3 representing little to no coalescence. Text appearance was similarly rated. Color gamut (vector sum of C, M, Y, R, G, B CIE L*a*b* values) was calculated as described before[2]. Other responses such as ink bleed and black optical density were also evaluated.

**Table 1a. Factor Combinations for DOE.**

| | C1 | C2 | C3 | C4 |
|---|---|---|---|---|
| **R1** | A1a | B3d | C4b | D2c |
| **R2** | B2b | A4c | D3a | C1d |
| **R3** | C3c | D1b | A2d | B4a |
| **R4** | D4d | C2a | B1c | A3b |

**Table 1b. Description of Factors**

| | Factor |
|---|---|
| **R1** | Silica 1 |
| **R2** | Silica 2 |
| **R3** | Silica 3 |
| **R4** | Silica 4 |
| **C1** | Cationic 1- A200 |
| **C2** | Cationic 2 |
| **C3** | Anionic 1 |
| **C4** | Anionic 2-none |
| **A** | PVOH 1 |
| **B** | PVOH 2 |
| **C** | PVOH 3 |
| **D** | PVOH 4 |
| **1** | Latex 1- none |
| **2** | Latex 2 |
| **3** | Latex 3 |
| **4** | Latex 4 |
| **a** | Silica/Binder 1 |
| **b** | Silica/Binder 2 |
| **c** | Silica/Binder 3 |
| **d** | Silica/Binder 4 |

The data were analyzed using MiniTab statistical software. The basic approach was to calculate averages for the responses for the different settings of the factor of interest, and to determine the significance of the difference between the averages using analysis of variance (ANOVA). Probabilities for the null hypothesis (that there is no difference between averages) were used as a measure of the significance of the effect. Probabilities $< 0.10$ were considered to be highly significant. In addition to the individual responses, composite responses were calculated in the following way. First, the individual responses were normalized by linear interpolation to a scale of 0.1 to 0.9.

The normalized individual responses were then used to calculate the nth root of the product of n individual responses. Thus, a composite score was calculated as the cube root of the product (normalized color appearance score*normalized text appearance score*normalized drytime score). This method enabled the best overall formulations to be found, based upon the composite responses.

## Results

### *Effect of Coating Thickness and Printer*

Printouts were prepared using the C80 and 2000P printers for both levels of coating thickness. For the case of the C80 printer and 24 WFT, it was observed visually that there were some relatively good as well as some relatively bad prints. For the 2000P printer, all of the 24 WFT coatings had very bad print appearance. Similarly, for the 40 WFT coatings, the appearance of the printouts from the C80 printer were better than for the thinner coatings, but there still was a range in performance. For 2000P printouts on the thicker coatings, some of the prints had good appearance and some bad.

Each sheet was given a rating for color and text as described above, and was evaluated for drytime. A composite score based on these three responses was calculated for each formulation, and overall averages for the effects of printer and WFT were calculated. Comparisons between averages for printer and WFT were then made using ANOVA. The effect of printer on the average composite ranking was highly significant (P = 0.034) with the C80 printer giving the higher score. Similarly, the effect of WFT was also highly significant (P = 0.000) such that the thicker films gave better print performance on average. The implications of these findings are the following: (1) Either the ink-set or the ink-laydown (3+1 color for the C80 versus 5+1 color for the 2000P), or both, must be significantly different between these printers. The challenge that this situation poses for the development of media intended to be compatible with both printers is obvious; (2) The print performance is highly dependent on coating thickness, and the 2000P requires a thicker coating to achieve acceptable print performance.

### *Top Formulations based on Composite Responses*

One of the more important results of this screening approach is the ability to readily identify combinations of factors that produce desirable results. Shown in Tables 2a and 2b are the highest two composite scores, calculated for each printer and WFT (minimum possible score = 0.1; maximum possible score = 0.90). With this analysis, the top formulations can be identified and common features between them appear. A blank cell in these tables indicates a score less than those shown.

**Table 2a. Top Formulations based on Composite Scores for 24 WFT.**

| Mix | Silica | Surf. Mod. | C80 | 2000P | C80+2000P |
|---|---|---|---|---|---|
| 1 | P405 | Cat. 1- A200 | | | |
| 2 | P405 | Cat. 2 | | | |
| 3 | P405 | Anionic 1 | | | |
| 4 | P405 | An. 2-None | | | |
| 5 | P412 | Cat. 1- A200 | | | |
| 6 | P412 | Cat. 2 | | | |
| 7 | P412 | Anionic 1 | | | |
| 8 | P412 | An. 2-None | | | |
| 9 | W300 | Cat. 1- A200 | 0.76 | 0.71 | 0.74 |
| 10 | W300 | Cat. 2 | | 0.71 | 0.74 |
| 11 | W300 | Anionic 1 | | | |
| 12 | W300 | An. 2-None | | | |
| 13 | W900 | Cat. 1- A200 | 0.78 | | |
| 14 | W900 | Cat. 2 | | | |
| 15 | W900 | Anionic 1 | | | |
| 16 | W900 | An. 2-None | | | |

**Table 2b. Top Formulations based on Composite Scores for 40 WFT.**

| Mix | Silica | Surf. Mod. | C80 | 2000P |
|---|---|---|---|---|
| 1 | P405 | Cat. 1- A200 | | |
| 2 | P405 | Cat. 2 | | |
| 3 | P405 | Anionic 1 | | |
| 4 | P405 | An. 2-None | | |
| 5 | P412 | Cat. 1- A200 | | |
| 6 | P412 | Cat. 2 | | |
| 7 | P412 | Anionic 1 | | |
| 8 | P412 | An. 2-None | | |
| 9 | W300 | Cat. 1- A200 | | 0.81 |
| 10 | W300 | Cat. 2 | | |
| 11 | W300 | Anionic 1 | | |
| 12 | W300 | An. 2-None | | |
| 13 | W900 | Cat. 1- A200 | 0.80 | 0.87 |
| 14 | W900 | Cat. 2 | | |
| 15 | W900 | Anionic 1 | 0.79 | |
| 16 | W900 | An. 2-None | | |

It can be seen from the tables that the high pH silicas SYLOJET® W300 and SYLOJET® W900 are the silicas that appear in the top formulations. In addition, the cationic surface treatment involving SYLOJET® A200 appears in several of the top formulations. For 24 WFT, Mix 9 is the best for each individual printer and for both printers taken together, and would be a good starting point for optimization. Previous experience has shown that the P400 silicas give excellent performance with dye-based inks, and so the silica properties optimum for pigments are likely different than those optimum for dyes. This type of information enables additional experimentation to be better directed towards development of optimum media performance.

***Effect of Individual Factors on Composite Responses***

It is also of interest to examine the average effects of the individual experimental factors on the composite responses for both printers and WFT. As described above, the averages for the responses of interest were calculated for each of the experimental factors, and the results compared using ANOVA analysis. Shown in Table 3 are the probabilities (P) for the null hypothesis (that there is no difference between averages) that are considered to be highly significant ($P < 0.10$). A cell without a value indicates that $P > 0.10$. Column 3 in the Table was calculated using a composite score that involved the product of responses from both printers, so it represents an "overall" score.

**Table 3. Probabilities for Null Hypothesis for the Effect of Individual Factors on Composite Responses.**

| WFT | 24 | 24 | 24 | 40 | 40 |
|---|---|---|---|---|---|
| Factor | C80 | 2000P | C80/2000P | C80 | 2000P |
| Silica | | | | | |
| Silica pH | | | | | |
| Silica size | | | | | |
| Surf. Mod. | 0.006 | | 0.090 | 0.040 | |
| Cat./An. | 0.077 | 0.021 | 0.023 | | 0.054 |
| PVOH | | | | | |
| Deg. of Hyd. | | 0.021 | 0.045 | | |
| Mol. Wt. | | | | | |
| Latex Type | | | | | |
| Silica:Binder | | | | | |

It can be seen from the Table that the nature of the surface modification exerts a highly significant effect on the composite response for the C80 printer, such that on average the SYLOJET® A200 surface modifier gives the best performance. For the 2000P printer, the surface modification is important, but more specifically, the sign of the surface modification (cationic versus anionic) is most important, with cationic surface modification giving the best performance on average. Also, it can be seen that for the 24 WFT coatings, the nature of the PVOH, and in particular the degree of hydrolysis, has a strong effect on the composite response such that partially hydrolyzed PVOH gives the best performance on average. It is interesting that for the 40 WFT coatings, the significance of the effect of degree of PVOH hydrolysis is much lower. The implication is that this particular factor is important under the most severe conditions, but is "washed-out" under less severe conditions.

***Effect of Individual Factors on Individual Responses***

It is also of interest to evaluate the effect of individual factors on individual responses. Summarized in Table 4 are the factors that had a significant ($P < 0.10$) effect on the noted individual responses.

For example, for the 24 WFT coatings, the particle size of the silica had a significant effect on the color gamut for the C80 printer, such that the smaller the particle size, the higher the gamut. From a mechanistic point of view, this may be the result of better pigment "hold-out" at the surface of the receptor because of narrower inter-particle pores for the smaller particle silicas. As noted above for the composite responses, the nature of the surface modification is also important for both printers for several of the individual responses involving print appearance, with the cationic surface modifiers giving better performance on average than the anionic surface modifiers. Interestingly, the anionic surface modifier resulted in much lower formulation viscosities on average, which suggests that the interactions in the fluid phase are less significant in the anionic systems, even though the binder system is nominally nonionic. The degree of PVOH hydrolysis also affected the print performance for both printers as noted above, with partial hydrolysis on average giving the best performance. The latex type influenced the drytime for the C80 printer, with AirFlex 315 giving the best drytime on average. This latex has $T_g$ intermediate to the other latexes used in this study, while the particle size is unknown. It is likely that the latex particle size is an important parameter for this particular response. Finally, the coating composition was important for the 2000P drytime, such that higher silica levels yielded better drytime.

**Table 4. Significant Effects for Individual Responses for 24 WFT.**

| Factor | Effect |
|---|---|
| Silica | Size affects gamut for C80 (small is best) |
| | pH affects bleed for 2000P (high is best); |
| Surf. Mod. | Sign affects bleed for C80 and 2000P (cat. is best) |
| | Sign affects viscosity (an. is best) |
| | Sign affects C80 color and text (cat. is best) |
| | Sign affects 2000P text (cat. is best) |
| PVOH | Deg. Of Hyd. affects C80 color (partial is best) |
| | Deg. Of Hyd. affects 2000P color (partial is best) |
| Latex | Latex affects C80 drytime (AirFlex 315 is best) |
| Sil:Binder | Silica:Binder affects 2000P drytime (high is best) |

In Table 5 are summarized significant factors for the 40 WFT coatings. For the C80 printer, the silica type affected ink coalescence (high pH silicas were best on average) and also color gamut (the 5 micron silicas were best on average). Hence, for these measures of printability, SYLOJET® W300 is the material of choice. The surface modification is again important for these films, such that cationic is better on average for bleed with the 2000P printer. Interestingly, one of the anionic surface treatments gave the best performance for ink coalescence for the C80 printer. The latex was important for drytime with the 2000P printer such that the AirFlex 110 gave the best results on average, and finally, the silica to binder ratio was important for the C80 text appearance, such that the higher the silica content, the better the text appearance.

**Table 5. Significant Effects for Individual Responses for 40 WFT**.

| Factor | Effect |
|---|---|
| Silica | pH affects C80 color (high is best) |
| | Size affects C80 color gamut (small is best) |
| Surf. Mod. | Sign affects 2000P color bleed (cat. is best) |
| | Affects C80 color uniformity (An. 1 is best) |
| PVOH | |
| Latex | Latex affects 2000P drytime (AF110 is best) |
| Sil:Binder | Sil:Binder affects C80 text (high is best) |

## Conclusions

This study illustrates the power of a simple screening-type experimental design for the development of coating formulations for application with selected pigmented-ink printers. Five experimental factors were screened at four levels using only sixteen experiments. Strong main effects of the factors on a variety of responses were observed. The results enabled the identification of top formulations based on composite response scores, and these formulations likely represent excellent starting points for further development. Strong effects were also found for some of the factors on composite responses. In particular, the type and sign (cationic versus anionic) of added silica surface modifiers strongly affected formulation viscosity and print performance (drytime, color uniformity/ink coalescence and text quality). Strong effects of the factors on some individual responses were also found. The type of silica, silica particle size and percentage of silica in the coating compositions were important for some of the responses. Coatings based on SYLOJET® W300 and W900, particularly in combination with SYLOJET® A200 and partially hydrolyzed PVOH, on average gave very good print performance. The variation in print performance associated with these experimental factors highlights the strong interaction between pigmented inks and receptor layers. The variation in performance observed for the two printers in this study highlights the difficulty for media design for multiple printer platforms. It is hoped that this study illustrates the power of experimental design at the screening level to facilitate media development.

## References


1. M. Usui, H. Hayashi, K. Hara, T. Kitahara, Proc. IS&T's 18th International Conference on Digital Printing Technologies, pp 369-373 (2002).
2. D. Darwin, R. T. Taylor and P. Press, Proc. IS&T's 17th International Conference on Digital Printing Technologies, pp 116-119 (2001).


## Acknowledgements

The author would like to acknowledge the fine experimental work of M. Winters, M. Bendix, and B. Stief and would like to thank W. R. Grace & Co.-Conn. for encouragement and permission to publish this work.

## Biography

**David Chapman** received his B. S. degree in Chemistry from St. Lawrence University in Canton, NY in 1980 and a Ph.D. in Inorganic Chemistry from the University of Tennessee in Knoxville, TN in 1984. He began his industrial career with the Union Carbide Corporation in the Molecular Sieves Department, and since 1987, he has worked at W. R. Grace and Co.-Conn., first in the Corporate Research Group and then in the Silicas/Adsorbents group of Grace Davison. His current work focuses on sub-micron silica gel product development for microporous inkjet receiver layers.