Breaking the Pigment-to-Binder Ratio Paradigm of Metallic Pigments: Concomitantly Promoting Pigment-Binder Bonding and Metallic Pigment Orientation

Christopher Hilbrich and Devin Schmitt

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Abstract

Aluminum PVD (Physical Vapor Deposition) effect pigments afford highly reflective surfaces, combined with large surface area, resulting in excellent optical performance in many applications with low binder content. In applications requiring high mechanical performance, higher binder content is typically utilized out of necessity, resulting in degraded optical characteristics (gloss, clarity, etc.). Good mechanical performance in high binder systems is a result of strong binder cohesion and increased binder intercalation. Pigment orientation is also paramount to improving optical characteristics. Our focus is a modification of the PVD pigment to promote both orientation and strong pigment-binder bonding, effectively reducing the necessity for binder intercalation. This allows for the use of a higher pigment-to-binder ratio, improving optical characteristics while maintaining good mechanical performance. We show that pigments can be uniquely modified per binder system class (urethanes, acrylics, etc.) to provide their best optical and mechanical performance.

Introduction

Physical vapor deposition (PVD) is a process by which metals are deposited under vacuum as a thin film onto a carrier substrate coated with a releasing agent. The metal film is then removed from the releasing agent and processed further into a finished dispersion [1]. This process generates very thin, flat metal flakes with exceptional reflective properties desirable in numerous end-use markets including graphic arts, coatings, and cosmetics.

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Inks developed with metallic PVD pigments are typically formulated with the aim of producing a glossy, mirror-like appearance. While it is possible to accentuate this effect through increased pigment loading, this often comes at the expense of adhesive properties of the applied film. This concept is illustrated in Figure 1 utilizing a nitrocellulose binder system. The sample shown on the left was prepared with a high loading level of binder, while the sample on the right was prepared from the same material with a high pigment concentration.

High binder vs high pigment applications

The sample on the right (high pigment) clearly exhibits superior gloss and clarity, but with poor adhesion exemplified by a simple tape test. In contrast, the sample on the left (high binder) passed the adhesion test but is notably duller in appearance. Balance must therefore be achieved between the respective pigment and binder levels in a system in order to optimize both optical and mechanical performance [2].

There is a wide array of binder systems available for ink formulation, each differing with regard to both chemical class and specific composition. Therefore, a single pigment dispersion may exhibit vastly different performance across a variety of binders. While there is no one-size-fits-all solution to this, it is possible to apply unique chemical modifications to PVD pigment dispersions that can enhance affinity toward a given system, thereby providing an additional pathway to further optical and mechanical enhancement.

The purpose of this paper will be to demonstrate that it is possible to achieve strong optical performance at low binder concentrations while maintaining adhesive integrity. This is accomplished through chemical modification of the pigment to promote compatibility within the binder system of choice.

Experimental Procedure

Seven aluminum PVD pigment dispersions were evaluated across multiple binder systems at varying pigment-to-binder ratios. The selected pigment dispersions included standard and next-generation products as well as experimental-grade materials, each with unique chemical modifications aimed at enhancing flake performance. All aluminum flakes had optical densities of approximately 1.9(1). Pigment dispersions were all processed to a particle size of 10(0.5) µm with 10.0(1)% non-volatile matter (NVM) in ethyl acetate solvent. An overview of the samples chosen for evaluation is provided in Table 1. The control (Sample 1) and next generation product (Sample 2) are commercially available Metalure Q310105AE and C21010AE, respectively.

Sample	Sample Description
1	Standard Grade Control
2	Next Generation
3	Experimental
4	Experimental
5	Experimental
6	Experimental
7	Experimental

Table 1: *Sample descriptions*

Three common classes of binder were utilized for experimentation: acrylic, nitrocellulose, and polyvinyl butyral (PVB). Ladder studies were designed to target pigment-to-binder ratios between 0.33 and 3.00, resulting in binder-heavy and pigment-heavy formulations, respectively. Ratios were calculated based on the solids content of the respective components. Two different formulation methods were implemented to achieve the desired loading ratios (Tables 2 & 3). In method 1, the total weight of each pigment dispersion was increased with each step in the ladder, while the weight of the binder was decreased. Though ink viscosity increased with higher pigment-binder ratios, this method allowed for a workable ink consistency across all tested binder systems and was employed for the bulk of the testing. Approximated pigment-binder solids ratios are provided in Table 2.

Target Pigment-Binder Ratio	Acrylic		Nitrocellulose		Polyvinyl Butryal (PVB)	
	Pigment Solids (g)	Binder Solids (g)	Pigment Solids (g)	Binder Solids (g)	Pigment Solids (g)	Binder Solids (g)
0.33	0.75	2.28	0.31	0.94	0.31	0.94
0.50	1.00	1.95	0.44	0.88	0.44	0.88
1.00	1.40	1.43	0.75	0.75	0.75	0.75
2.00	1.80	0.91	1.14	0.59	1.14	0.59
3.00	2.00	0.65	1.41	0.47	1.41	0.47

Table 2: *Pigment-binder ratios, pigment solids, binder solids, and binder type of method 1*

In the second method the weight of pigment dispersion was held constant and the binder system was diluted with each step of the ladder. The same quantity of pigment and diluted binder solution was used for each formulation, resulting in a constant pigment volume loading in the ink. However, the ink viscosity decreased with increasing pigment-binder ratio. The acrylic binder was chosen as a representative sample, as it was the only system with a high enough starting viscosity to maintain drawdown film consistency upon dilution. Table 3 shows the approximate pigment-binder solids content of the two methods.

Target Pigment-Binder Ratio	Acrylic (Increased Pigment)		Acrylic (Diluted Binder)	
	Pigment Solids (g)	Binder Solids (g)	Pigment Solids (g)	Binder Solids (g)
0.33	0.75	2.28	1.25	3.75
0.50	1.00	1.95	1.25	2.50
1.00	1.40	1.43	1.25	1.25
2.00	1.80	0.91	1.25	0.63
3.00	2.00	0.65	1.25	0.41

Table 3: *Pigment-binder ratios, pigment solids, and binder solids of acrylic binders of method 1 vs method 2*

As rheological properties varied between all binders, pigment dispersions, and loading levels, viscosity was not controlled throughout experimentation. Binders were diluted as necessary to achieve workable starting point NVMs.

Inks were prepared and applied in duplicate via automatic drawdown onto Leneta opacity charts using a wire wound rod. Samples were deposited at a wet film thickness of approximately 40 µm and dried between 60-140°F, per drying

requirements of the binder system. All samples within a given binder system set were dried under the same conditions. A minimum of 16 hours elapsed between sample drying and final evaluation.

Samples were analyzed for both optical performance (60° gloss) and adhesive properties. Gloss measurements were collected using a BYK Micro Tri-Gloss Meter using an average of five points per card and data are reported as an average of two cards. Adhesion was evaluated using a tape test method. Transparent 3M Scotch tape was applied firmly across a single drawdown sample from each set and swiftly removed, with any residual product sticking to the tape indicating adhesion failure.

Results and Discussion

Gloss measurements collected from each binder set versus pigment-binder ratio using method 1 are shown in Figures 2-4 below. Solid lines represent full adhesion, while a dashed line represents the point where adhesion failure occurred. Thus, adhesion failure is in the range represented by the dotted line.

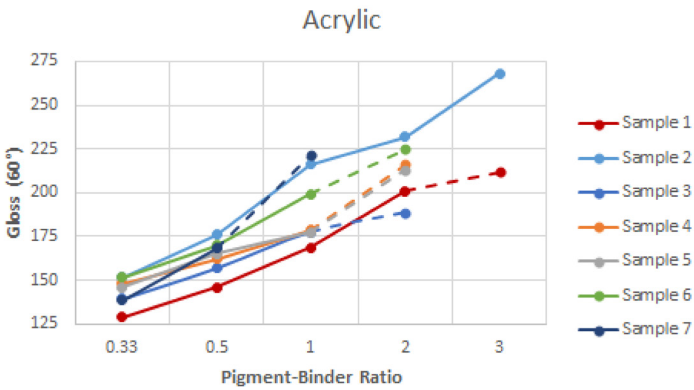

Figure 1: *Acrylic drawdown 60° gloss – method 1*

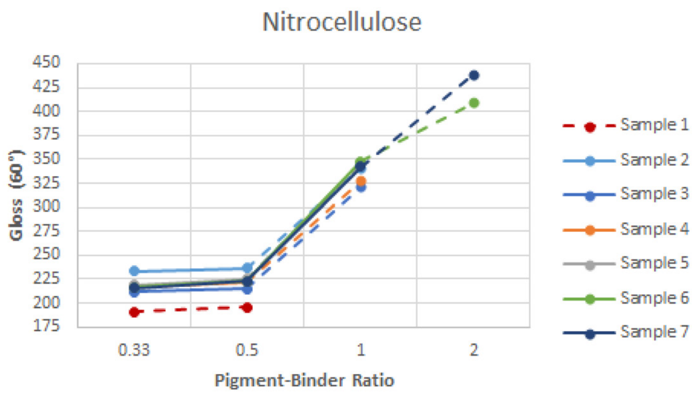

Figure 2: *Nitrocellulose drawdown 60° gloss – method 1*

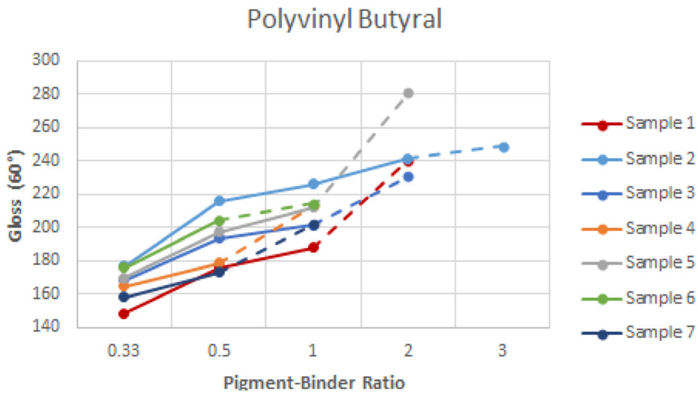

Figure 3: *PVB drawdown 60° gloss – method 1*

Gloss values were found to increase with elevated pigment-to-binder ratios. This occurrence was noted in all samples across all three binder systems and continued even after the point of adhesion failure. In the case of the nitrocellulose system, gloss values appeared to reach a plateau at a ratio of 2.00. Adhesion performance varied between samples and systems, due largely due to the interactions between each uniquely modified pigment and the different chemical properties of the binders. Therefore, optimal sample performance in this study can be represented by the highest ratio at which a successful adhesion test was collected (Table 4). It is worth noting that the next generation Metalure C21010AE sample exhibited superior gloss and no adhesion failure across all pigment-to-binder ratios evaluated in the acrylic system.

Sample	Acrylic		Nitrocellulose		PVB	
	Pigment-Binder Max Adhesion	Max Gloss (60º)	Pigment-Binder Max Adhesion	Max Gloss (60º)	Pigment-Binder Max Adhesion	Max Gloss (60º)
1	2.00	201	0.33	191	1.00	188
2	3.00	268	0.33	237	2.00	242
3	1.00	178	0.50	215	1.00	202
4	1.00	179	0.50	222	0.50	179
5	1.00	178	0.50	225	1.00	212
6	1.00	199	1.00	348	0.50	205
7	0.50	168	1.00	343	0.50	173

Table 4: *Maximum gloss with respect to successful adhesion*

Table 4 shows the gloss associated with the highest pigment-binder ratio achieved without adhesion loss. The highest performing samples associated with each binder system are highlighted in green for clarity. In the acrylic system, Sample 2 (next-generation C21010AE) was the top performing material. Within the tested pigment-binder ratio range, Sample 2 exhibited an overall gloss improvement of approximately 77%, while maintaining adhesive integrity across all pigment- binder loading levels. Sample 2 also produced the best results in the PVB system, with an approximate 36% gloss improvement over the tested range up to adhesion failure. In the nitrocellulose system, both Samples 6 and 7 (experimental) displayed similar and superior performance in the series with a gloss improvement of approximately 60% prior to adhesion failure in the tested pigment-binder ratio range. In this instance, Samples 6 and 7 continued to adhere a full step beyond all other samples in the set. Relative to the control, the top performing samples displayed gloss improvements of 33% (Sample 2), 82% (Sample 6 & 7), and 29% (Sample 2) in the acrylic, nitrocellulose, and PVB binder systems, respectively.

In some cases, adhesion is less important than absolute optical performance; thus, samples from each binder system that produced the best optical results across all pigment-binder loading levels were isolated and compared against the control material (Sample 1). Results are shown in Figures 5-7.

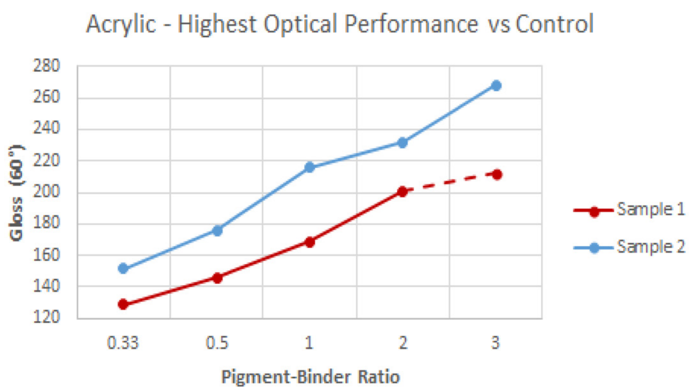

Figure 4: *Acrylic drawdown - highest optical performance vs control – method 1*

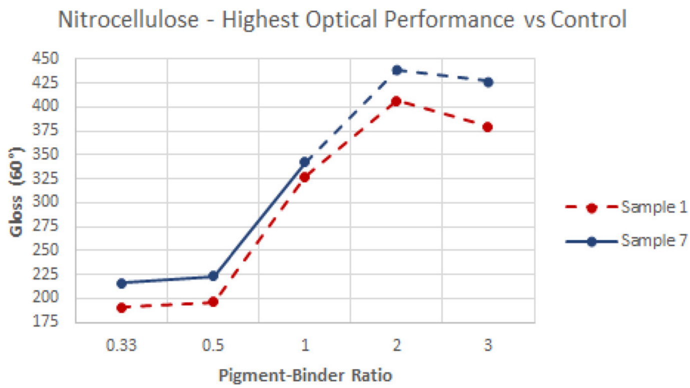

Figure 5: *Nitrocellulose drawdown - highest optical performance vs control – method 1*

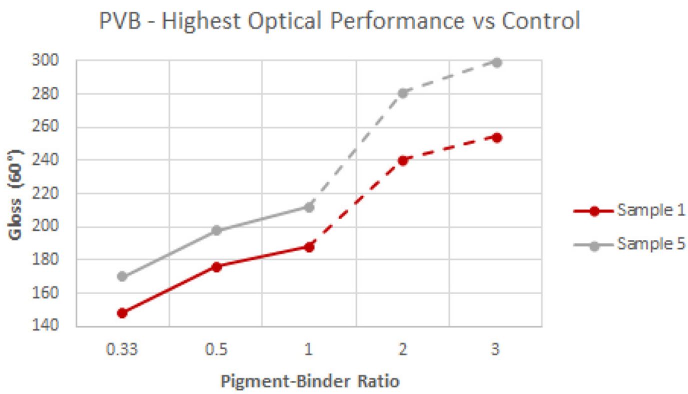

Figure 6: *PVB drawdown - highest optical performance vs control – method 1*

Various samples produced the highest gloss values in each binder system. Recall that Table 4 shows the highest performance while maintaining adhesion across all

three test systems. When optimized for adhesion, Sample 2 (next generation) produced the best results in both the acrylic and PVB systems, while Samples 6 and 7 (experimental) performed the best in the nitrocellulose system. Disregarding adhesion and focusing solely on overall optical improvement produces slightly different results. Sample 2 continues to display superiority in the acrylic system with an overall gloss increase of around 77% within the tested pigment-binder ratio range. In the nitrocellulose system, experimental-grade Sample 7 produced the best optical measurements with an improvement of approximately 98% within the tested range. In the PVB system however, Sample 5 (experimental) was now noted to be the best optical performer, exhibiting a gloss increase of about 76% within the measured pigment-binder ratio range. The top performing samples in this data set displayed gloss improvements of 26% (Sample 2), 8% (Sample 7), and 18% (Sample 5) over the control in the acrylic, nitrocellulose, and PVB binder systems, respectively.

The difference in outcomes between the two PVB system data sets suggests that the unique chemical modifications present in each pigment dispersion can contribute heavily toward the ability to achieve optimal optical properties in a binder system of choice. There were no instances in which the standard-grade control produced the best results. Additionally, all highest optical performers were found to be comparable or better to the control in terms of adhesion.

Formulation methods 1 and 2 (increased pigment and diluted binder, respectively) were compared using the acrylic binder system. Results are shown in Figure 8 below:

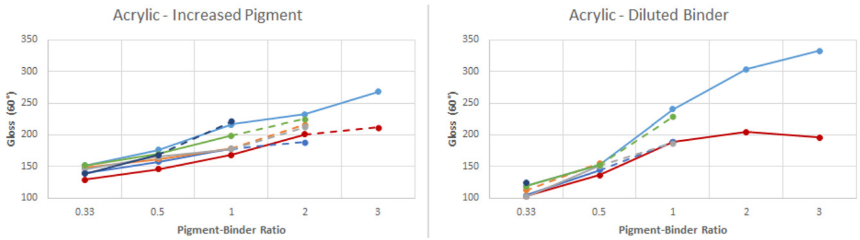

Figure 8: *Acrylic drawdown 60° gloss – method 1 vs method 2*

In the diluted binder formulation, Sample 2 was once again found to produce the highest gloss while maintaining full adhesion across all pigment-binder ratios. The gloss improvement in this formulation was approximately 179%, compared to the 77% noted using the increased pigment formulation. The difference in final gloss measurements for Sample 2 between the two formulations was around 24%. This suggests that performance can be further optimized through variation in formulation technique. Sample 1 (control) improved in terms of adhesion but appeared to reach a plateau with regard to gloss at a pigment-binder ratio of 2.00. All other samples exhibited adhesion degradation in the diluted formulation.

Conclusions

Multiple aluminum PVD pigment dispersions were evaluated across different binder systems at varying pigment-to-binder ratios. Results suggest that optical performance may be dramatically improved while maintaining adhesive integrity through optimization of the pigment-binder ratio and chemical modification of the pigment to complement the desired binder system. The highest gloss improvements per system relative to the control while maintaining adhesion are as follows:

- Acrylic - 33% gloss increase up to pigment-binder ratio of 3.00 with Sample 2 (next-generation C21010AE)
- Nitrocellulose - 82% gloss increase up to pigment-binder ratio of 1.00 with Samples 6 and 7 (experimental)
- PVB - 29% gloss increase up to pigment-binder ratio of 2.00 with Sample 2 (next-generation C21010AE)

In many binder systems, appropriate chemical modification of the pigment may allow for further improvement of optical performance post-adhesion failure. In the case of the PVB binder system for instance, Sample 5 (experimental) exhibited the overall highest optical performance, contrary to the results factoring in adhesive integrity where Sample 2 was the top performing candidate. Performance may be further optimized through variation in formulation technique.

These concepts may be expanded into additional application methods (gravure, screen print, etc.) and binder systems for further evaluation. Eckart is currently evaluating spray formulation in additional binder systems using these methodologies.

References

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Acknowledgements

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