

Metallic Donor for Direct Digital Halftone Proofing

*David A. Niemeyer
Eastman Kodak Company
Rochester, New York*

Abstract

A continuing trend in the printing industry is the increased use of specialty inks, not the least of which are the metallics. To achieve the desired specular reflection characteristics, metal flake pigments are used in the ink formulation. In order to provide a reasonable match to the expected printed product, a direct digital halftone color proofing was developed utilizing the same metal flake pigments as are used in typical lithographic inks. The use of non-volatile pigments necessitates the use of bulk transfer donor architecture. A two-layer film structure was developed wherein a metal flake pigment containing layer overlies an IR radiation sensitive propellant layer. Gasification of the propellant layer upon exposure by an 830 nm laser diode array provides the motive force to transfer the pigment layer from the donor to a receiver. Donor structure options, imaging mechanism sensitivities, and salient material properties are discussed.

Introduction

An ongoing trend in the printing industry is the increasing use of specialty colors. Specialty colors can increase color gamut, provide signature colors, and generate special effects. In the advertising and packaging marketplaces this translates into greater appeal and recognition. One example is the use of metallic inks. Although the particular color can be approximated by standard process color inks, the specular reflectivity characteristic that gives metallic colors their special appeal necessitates the use of metal flake pigments in the ink formulation. Another trend in the printing industry is the conversion from analog to digital workflows. As the adoption of digital workflows has increased in publication printing and spread to package printing, demand for specialty donors for direct digital proofing has also increased. In response, a metallic donor was developed for the Kodak Approval™ XP digital color proofing system. Several broad technologies have been used to generate direct digital color proofs, offering varying trade-offs of capability versus price. The Kodak Approval system is a high resolution system capable of true area modulation halftone printing using laser induced colorant transfer. Because the Kodak Approval system is capable of printing multiple colors at variable density at the same

location, multiple metallic need not be developed. Gold, bronze, copper, and the host of metallic reds, greens, and blues can be obtained by overprinting a brilliant silver. In order to provide a good match to the expected printed product, the metallic silver donor was formulated using an aluminum flake pigment as in typical lithographic inks.

Architecture

In the Kodak Approval system process, successive dye containing donor films are juxtaposed at 8 μm spacing against an intermediate receiver film and exposed through the base of the donor films with an 830 nm laser diode array. The multicolor dye image, along with the top layer of the intermediate, is laminated to a final receiver. The final receiver is, generally, a customer printing stock to which a dye receiving layer has previously been laminated. The mechanism of dye transfer is sublimation/volatilization. This mechanism is totally unsuited for the transfer of a non-volatile pigment such as aluminum flake and hence a different architecture was needed. A number of technologies have been developed for the laser induced bulk transfer of pigments. They include single-layer ablation,¹ assisted single-layer ablation,² propulsion,³ and various forms of melt transfer.^{4,6} Selection of a suitable technology for commercialization involves many factors not the least of which are efficacy, compatibility with the other materials and hardware of the system, and freedom to use. In laser induced transfer there is also the issue of managing the potential for color contamination from the IR absorber. A dye or pigment absorbing strongly at 830 nm, the wavelength of the systems IR diode lasers, will exhibit some visible coloration. Melt transfer materials typically employ an architecture where the absorber is incorporated within a non-transferable layer underlying the pigment layer to be transferred. These materials, however, generally work best at a donor to receiver spacing around 3 μm . At 8 μm , the exposure difference between complete transfer and ablative breakdown of the absorber layer narrows appreciably. Single-layer ablative materials work acceptably at an 8 μm spacing as do propulsive materials. Depending on power density, single-layer ablative materials tend toward incomplete transfer, with higher power densities being better. Incorporating an underlying assisting layer, such as a dynamic release layer or 'shutter' layer (one whose optical

density falls precipitously during exposure) eliminates this concern. Both types of ablative materials incorporate the IR absorber within the pigment transfer layer and, as a result, the transfers exhibit the color of the absorber. Bleaching technologies are available, however, they are risky where the other image colorants are dyes. In propulsive transfer materials, as in melt transfer materials, the absorber is incorporated in a separate layer underlying the colorant transfer layer. Unlike melt transfer materials, pressure generated by exposure of the propellant layer makes for more robust transfer at higher donor to receiver spacing. In the simplest case, the propellant layer is at least partially transferred and so, therefore, is some of the IR absorber. Heterogeneous propellant layers have been studied,⁷ wherein the absorber is microstructurally separated from the gas generating propellant. Ideally, only the propellant and/or its decomposition products are transferred. As will be discussed in more detail later, the high opacity of the metal flake layer and the fact that the absorber ends up, finally, between the opaque final substrate and the metal flake allows the simpler solution to be pursued.

Propellant Layer Formulation

The critical variables in formulating a simple propellant layer are the selection of propellant material and radiation absorber and the amounts of each. To begin, only polymeric propellants were considered, as a film forming binder is generally needed to provide layer integrity. The initial consideration was whether the polymer needed to be exothermic in its decomposition to give reasonable exposure, i.e., 200-400 mJ/cm². Figure 1 shows the final print density versus exposure curves comparing cellulose nitrate, which undergoes exothermic decomposition, to poly(methyl 2-cyanoacrylate-co-ethyl 2-cyanoacrylate) (75:25), hereinafter called polycyanoacrylate, which undergoes mildly endothermic depolymerization and to cellulose acetate propionate (CAP), which undergoes endothermic decomposition. The materials were coated from solvent solution via common laboratory techniques, such as wire wound rod. The pigment transfer layer during propellant layer development featured a cyan pigment (copper phthalocyanine (PB15:4), 50% size of 0.2 μm), as it was thought that the relatively large particle size and non-uniform distribution of the aluminum flake pigment would confound the evaluation of propellant layer factors. Test materials were imaged to Kodak Approval digital color proofing film I01/Intermediate/1834 on an external drum test fixture having a printhead similar to that in a Kodak Approval system. Specifically, The printhead delivered 30, 25 μm wide ($1/e^2$) spots on 10 μm centers at a nominal wavelength of 830 nm. Exposure was varied by changing mean laser power at a constant surface velocity of 1550 cm/s. The imaged intermediate was laminated to Champion Textweb via a two-roll laminator at a nominal temperature of 120°C. The data shows no advantage for the exothermic decomposition of cellulose nitrate over the endothermic depolymerization of a low ceiling temperature polymer such

as polycyanoacrylate; however, the endothermic decomposition of cellulose acetate propionate results in a speed loss of around 20 mJ/cm². Variations in maximum density primarily reflect differences in pigment dispersion quality. The lack of advantage for cellulose nitrate is not surprising as the chemical energy released by the decomposition of 200 mg/m² of cellulose nitrate is, at best, an order of magnitude less than the energy being delivered by the laser beam. All of the materials gave speeds within acceptable bounds. Ultimately, polycyanoacrylate became the preferred propellant not because of the ease with which it depolymerizes, but rather because of the ease with which it polymerizes. After imaging, the gasified monomer and oligomers condense and repolymerize, eliminating any issues with debris build-up and/or process emissions.

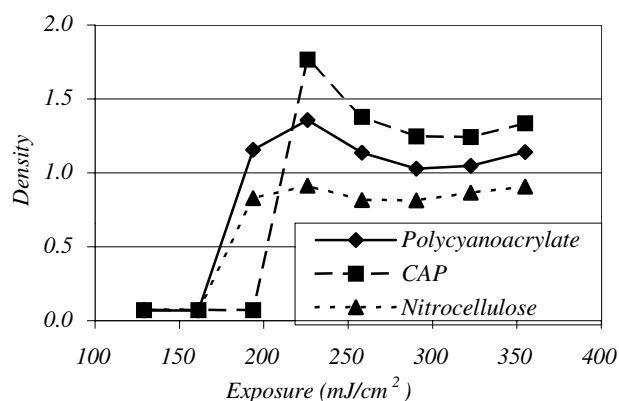


Figure 1. Reflection density of cyan transfer on final receiver versus exposure for different propellant types.

The other major component of the propellant layer formulation is the IR radiation absorbing material. Although IR absorbing pigments are well known, only dyes were considered as they can have very high extinction coefficients and it is generally easier to work with soluble materials. Various classes of dyes were evaluated including cyanine, oxonol, telluro-, seleno- and thiopyrillium, and tetraaryl polymethine. Unsurprisingly, given acceptable stability to exposure, dye class had little effect on imaging speed when normalized for absorbance. A speed index is plotted versus optical density at 830 nm for a number of IR dyes at various levels in Figure 2. Interestingly, additional absorbance above about 0.85 OD does not increase the speed even though, at that level, almost 25% of the laser energy is lost. The explanation comes from an understanding of the temperature profile within the propellant layer during imaging. Although the optical density is uniform throughout the layer, the temperature decreases exponentially from the exposed side because the temperature varies not by the absorbance but rather by $1/\text{transmittance}$. Therefore, although more photons are absorbed at higher density, disproportionately more of them heat and gasify the propellant layer nearest the exposing beam and less are absorbed toward the pigment layer

interface. The net effect is that the pressure builds faster at higher density, but the depthwise progression of gasification proceeds slower. The ungasified propellant resists the motive force of the pressure build-up and the effects balance out. For an IR dye with an extinction coefficient of about 2.5×10^5 , a density of 0.85 results from a level of about 35 mg/m^2 . Similarly, increasing propellant coverage beyond a sufficient amount does not yield increased speed and eventually leads to a loss in speed.

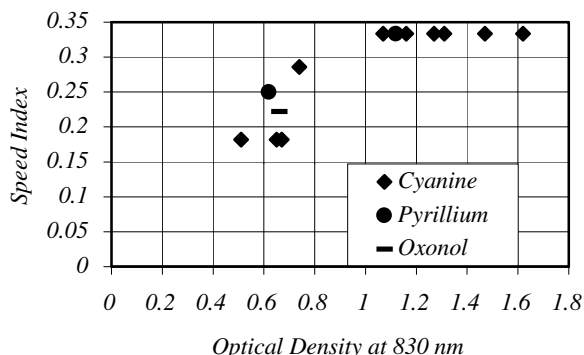


Figure 2. Speed Index ($1/mW/100$ at constant time) versus optical density at 830 nm for various IR dyes in 225 mg/m^2 polycyanoacrylate.

Transfer Layer Formulation

In a propelled transfer architecture, the colorant transfer layer is not affected by the laser radiation. This means that the binder molecular weight is not degraded by the imaging exposure as in single-layer ablation. Nor does the binder go through a change in state that dramatically reduces the strength of the layer as in melt transfer. Because the transfer layer integrity is unchanged by exposure, the material properties crucial for quality imaging must derive from material selection. For high-quality halftone imaging, the critical challenge is to balance the toughness of the transfer layer against the motive force from the propellant layer in imaged areas and against the adhesion of the transfer layer to the propellant layer in unimaged areas. If the transfer layer is substantially too tough no transfer will occur because the motive force is insufficient to overcome the strength of the transfer layer. If the layer is slightly too tough a loss of small dots will be seen, since small dots have a high ratio of perimeter (cohesive strength) to area (motive force). Similarly, if the toughness is about right but the adhesion is too low the small holes will be lost. Finally, if the toughness is too low the transfer layer will disintegrate during transfer and the small dots will be diffuse and unstructured, the small holes will fill in, and the D-max will drop due to loss of covering ability. This last effect can be seen at higher exposure levels in Fig. 1. Key factors determining layer toughness, i.e., cohesive strength, are layer thickness, layer composition, binder molecular weight, and binder morphology. The key factors determining

adhesion are the composition of the materials in contact, which devolves to the transfer layer binder composition with the prior selection of propellant layer composition. In the cyan model system described above, the typical transfer layer thickness was $0.3\text{-}0.5 \mu\text{m}$ and the binder to pigment ratio was between 1 and 2 to 1. With this system, binder polymers having molecular weights around 100,000 daltons or greater showed little or no transfer. At molecular weights broadly around 30,000 daltons good mid-scale transfers could be obtained. However, the quality of the highlight and shadow dots varied greatly, depending on other material properties (such as solubility and T_g), exposure, layer thickness uniformity, and pigment to binder compatibility. At very low molecular weights, as in oligomeric or molecular glasses, disintegrated transfers were seen. Another approach was adopted rather than identify a polymeric material with the needed adhesive properties and compatibilities and adjust and readjust the molecular over the course of development. That approach was to start with a low molecular weight material with the needed compatibilities and tune the cohesive strength with the addition of a suitable amount of a medium molecular weight polymer.

Initial screening experiments identified a number of promising systems including: an acrylic 'oligomer' (AO) reinforced with polyethyl methacrylate (PEM); partially or fully hydrogenated wood rosin esters (WRE) reinforced with various polymers such as polyvinyl butyral (PVB), polyethyl methacrylate (PEM) or a linear polyester (LPE); and, an oligomeric polyester diol (PED) reinforced with a linear polyester (LPE). Full system evaluation of efficacy and compatibility led, ultimately, to the adoption of a wood rosin ester based formulation.

The unmentioned factor in the above discussion of transfer layer toughness is the aluminum flake pigment. Unlike commonly used process color pigments, which are roughly spherical, evenly dispersed and small, relative to the imaging spot size, aluminum flake pigments are true flakes, oriented within the layer and a significant fraction of the imaging spot size. Aluminum pigments are almost exclusively made by one of two processes: the more common Hall process⁷ and the more specialized Levine⁸ process. Common lithographic inks predominately feature Hall process pigments and, therefore, that direction was taken. The flakes come as one of two broad types: leafing and non-leafing. Leafing pigments are coated during manufacture with a fatty acid, typically stearic acid, which renders the flakes surface active. This causes the flakes to align with the vehicle surface during application thereby giving the laminar structure necessary for specular reflectivity. Non-leafing pigments are not surface active and, generally rely on larger size and/or lateral shear during application to generate a laminar structure. The desire for a relatively small particle size coupled with the choice of a low molecular weight material as the primary binder and, therefore, the expectation of low viscosity during application, led to the selection of a leafing pigment. Even with leafing pigments the typical minimum weight average

particle size is around 8 μm . A side effect of selecting a leafing pigment is that the formulation cannot employ a solvent that solubilizes stearic acid. Generally, this limits the choice to either polar, protic solvents such as alcohols or apolar, aprotic solvents such as aliphatic or aromatic hydrocarbons. Several commercially available aluminum flake pigment pastes were evaluated with little difference seen in performance seen among equivalent grades.

Having selected the materials, the next stage in formulation was the determination of amounts. Sufficient pigment is needed to produce the roughly continuous laminar structure needed to produce the desired specular reflectance. That amount was determined to be around 180 mg/m^2 . As alluded to in the section on propellant layer formulation, metal flake pigments offer a unique way to address the IR dye stain issue. As the flakes are totally opaque to visible light, any light passing through the layer does so through the inevitable gaps between the flakes as they align in a monolayer. With a relatively small particle size the gaps tend to be small but numerous. The surface activity that leads to the formation of a monolayer also leads additional flakes to align with the first layer. As more material is added to the formula the formation of additional layers statistically eliminates the gaps and the metal flake layer(s) become opaque enough to effectively mask the color of the IR absorber transferred in the process. Effective masking occurs at aluminum flake levels of 300-350 mg/m^2 . However, the benefits of adding more pigment are not without cost. Increasing the number of metal flake layers and, generally, the overall thickness of the transfer layer both increase the cohesive strength and, therefore, decreases the resolution. Table 1 illustrates the effects of increasing pigment amount in the transfer layer formula. The color bleed through ($\bullet\text{H}$) was determined against an aim press sheet that measured $-1, -2$ for a^* and b^* , respectively.

Table 1. Output Quality Metrics vs. Pigment Coverage

Aluminum Pigment Coverage (mg/m^2)	$\bullet\text{H}$	% Dot Range @ 150 lpi
180	6.2	2-98
215	5.6	2-98
270	4.1	2-97
320	2.7	3-97
430	1.4	3-97
540	1.0	5-95

The final phase involved the co-optimization of the reinforcing binder, the wood rosin ester to reinforcing binder ratio, and the binder-to-pigment volume ratio. Earlier work had shown that a binder-to-pigment ratio of between 3 and 4 to 1 gives greater stability of transferred density over exposure, i.e., greater resistance to layer disintegration with overexposure. Disintegration of the layer disrupts the laminar nature of the metal flakes thereby reducing the

specular reflectance. With the contribution to cohesive strength from the aluminum flake this ratio was reduced to 2.5 to 3:1. The final decision on the reinforcing binder was driven by small dot resolution. Figure 3 shows percent dot out versus percent dot written in the highlight region for several binder candidates. The best results were seen with the linear polyester. The low-to-high molecular weight ratio was, lastly, increased somewhat from the 3:1 above.

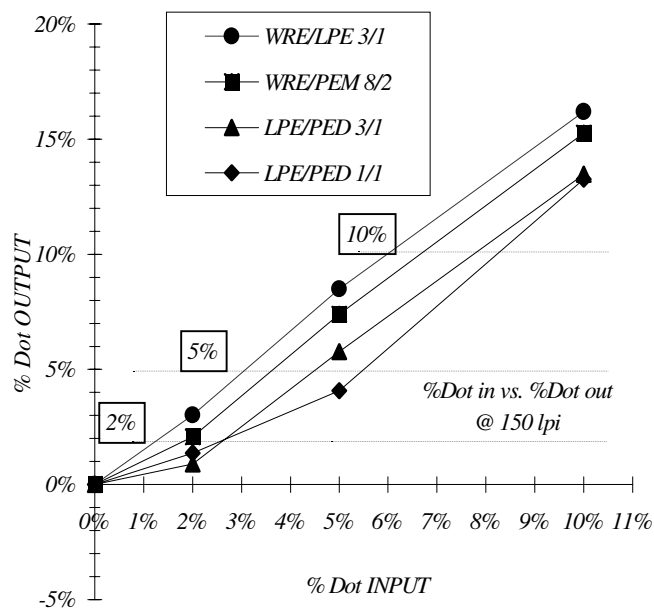


Figure 3. % Dot out vs % dot in for various transfer layer binders

Conclusion

A metallic donor was developed for direct digital halftone color proofing. A two-layer propulsive architecture featuring a propellant layer comprised of a simple combination of a low ceiling temperature polymer and an IR dye and a transfer layer utilizing aluminum flake pigments. The transfer layer also features a combination of low and medium molecular weight binders designed to optimize the cohesive strength of the layer for high quality imaging.

References

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2. US Patent 5,171,650.
3. US Patent 5,278,023.
4. US Patent 5,501,937.
5. US Patent 5,534,383.
6. US Patent 5,766,819.
7. US Patent 1,501,499.
8. US Patent 4,321,087.

Biography

David Niemeyer received BS degrees in Biology and Chemistry in 1973 and an MS in Chemistry in 1975, all from Michigan Technological University. He joined Eastman Kodak in 1976 as a bench chemist and then, in

1978, moved to the product development and research staff. Since then, he has worked, roughly sequentially, in the fields of regenerative photoconductors, electrostatic and electrophotographic recording materials and processes, photopolymer based analog color proofing systems and, most recently, laser thermal digital color proofing materials.