Nanoporous Inkjet Photo Paper with a High Dynamic Range

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Abstract

High gloss photo-like ink-jet papers based on capillary absorption have been used in ink-jet printing for about 15 years. Their strong advantage compared to swellable media is the fast ink absorption. This allows printing at highest printer speed, very high resolution, dye and pigment compatibility and strong laminate adhesion. The main drawbacks of such papers compared to polymer papers are often the lower permanence to light and to air-borne contaminants, as well as reduced color brilliance and black density when printed with dye-based inks. While great progress has recently been made in inkjet colorant development, the design of the receiving layer is a key contributor to print stability.

This paper describes the design and properties of highly transparent nanoporous silica layers that provide a very large gamut and high maximum density with dye-based inks, high sharpness with minimum blurring. The gamut gain is particularly strong in the dark blue and red sector of the color space and in black, as areas of high ink load and strong depth penetration benefit most from layer transparency. The permanence of dyes in a high surface area nanoporous matrix depends, among others, on the chemical environment. The molecular covalent surface treatment of the silica during manufacturing of the dispersion influences the final humidity and ozone stability of dye-based inks. Photographic coatings allow deposition of precise multi-layer assemblies, which incorporate specific functions in layers to improve e.g. physical properties like gloss or scratch resistance.

Introduction

The development of improved photo-like inkjet media continues to be an active area of research. The mechanism of ink absorption within the receiving layer is based on two major principles, either governed by osmotic pressure forces (polymeric or swellable media), or by capillary forces (micro- and nanoporous media). Sometimes a combination of swellable and porous features is used to reconcile the best of each technology in the design of specific ink receiving layer.

Historically, in the late 80's and early 90's, photographic companies were well suited to design and coat polymeric swellable photo-like inkjet media [1]. The advantages of such swellable media are good light and air contaminant fading resistance, high gloss and high quality manufacturability in photographic cascade and curtain coaters. The disadvantages are poor water and finger smudge resistance, long drying time, reduced pigment performance and slow ink absorption leading, to ink coalescence with the fast modern printer generation.

In recent years and since the mid 90's, considerable efforts were devoted to the design and manufacturing of glossy porous photo-like inkjet media. With the appearance of fast piezo printers, the need for rapid absorption of the inkjet drops into the receiving layer became indispensable in order to avoid ink coalescence. The "instant dry" features, good water fastness and finger smudge behavior, as well as the compatibility with pigmented inks favored the nanoporous inkjet photo paper as the technology of choice, despite their weaker robustness to air-borne contaminants.

Possible Nanoporous Dispersions

During the time course of HDR (high dynamic range) inkjet layers development, the main options regarding the possible nanocomposite structures and compositions were evaluated for their performance and manufacturability in our laboratory and pilot coaters.

Doping modifications of Aluminium oxide/hydroxide (pseudo-bohemite) with the lattice incorporation of one or more rare-earth ions have been reported [2] [3], together with carboxylic acid organic surface modification [13]. This technology was used in our first generation of professional nanoporous inkjet photo paper, presented during Photokina 2000 [4].

Mixture of morphologically different primary particles of Aluminium oxide, pseudo-bohemite and cationic silica were shown to influence the porosity, leading to improvement in ink absorption and image quality (IQ) [5].

Multilayer assemblies of Aluminium oxide, pseudo-bohemite and cationic silica were shown to improve gamut and enhance pigment compatibility [6].

Fumed silica is an interesting inorganic oxide showing high ink uptake capacity per gram. In order to be able to act as a mordant and fix the negatively charged dye from the inks, its surface requires, imperatively, a charge reversal from anionic to cationic. The surface modification and cationisation of fumed silica can be achieved through several techniques:

- Outer sphere negative charge neutralization by cationically charged polymer additions [11].
- Inorganic treatment with Aluminium Chlorohydrate leading to cationization through octahedral polyaluminium complexes.
- Organic treatment with an aminosilane coupling agent leading to a reaction between the silanol groups of aminosilane with the silica surface silanol groups to form siloxane bridges [7].
- A combination of the above methods [8].
- Inorganic-organic complex, like the reaction product of aminosilane coupling agent with an hydrosoluble Aluminium [9] or Zirconium salt [10].

In this paper we will focus on the results obtained by the latter technique and by specific photographic multilayer arrangement with the aim of achieving a nanoporous inkjet photo paper showing high dynamic range with dye inks and improved features with pigments ink as well.

Photographic Multilayers Concept

A schematic view of a photorealistic inkjet paper (Fig. 1) shows the plurality of layers used in the construction of the "optically controlled" more transparent ink receiving layer of our new generation photo paper ("Galerie new"). The ultra-thin layer (8) reconciles the pre-print features of gloss enhancement and scratch resistance with the improvement of post-print properties like smudge and gloss control with pigmented inks. The sub-surface layer (7) enhances the dye fixation and reduces light scattering. The bulk layers (6) and (5) quickly absorb the ink vehicle and fix the humefactant.

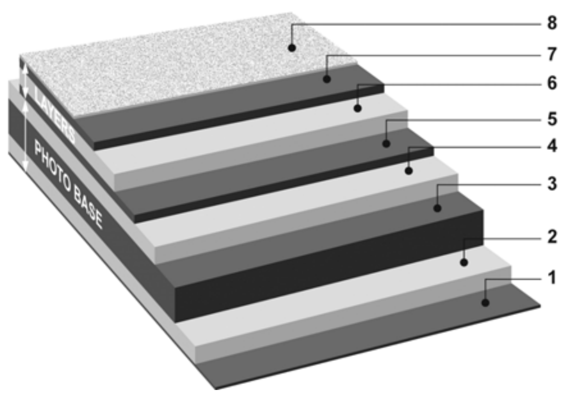

Figure 1. *Schematic view of a photographic-like multilayered inket media*

An innovative new base with more compacted raw paper fibers (3) was also designed for optimizing weight, flexibility increased opacity (4) and improved feeding (1). As compared to the previous generation of product [4], a warmer, less greenish shade was evaluated by professional photographers. This study, supported by a worldwide analysis of commercial photo media (Fig. 2) resulted in a cleaner, more natural white tint (a* = +0.8 and b*= -4.5).

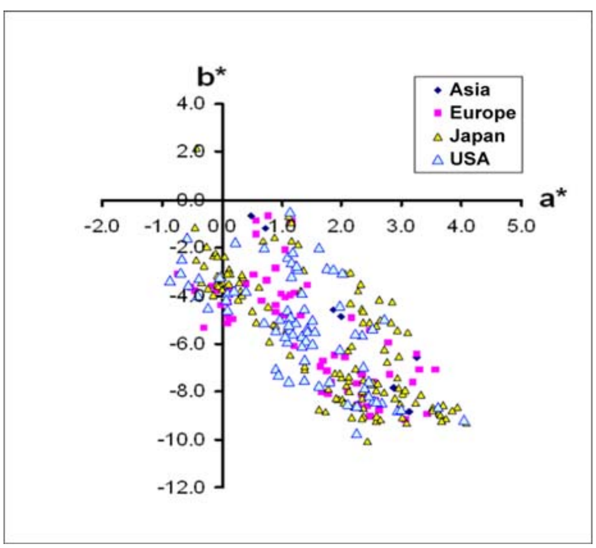

Figure 2. *a* vs. b* tint survey of competitive photo inkjet products, by region*

Experimental

The surface of fumed silica was cationically converted and dispersed as taught in [9] or [10]. The stable composite coating formulation was comprised of cationic dispersion, binder(s), additives, plasticizer, crosslinker and surfactants. The coating solution was applied to an RC-photobase with a curtain or cascade multilayer photographic technique. The thickness is adjusted so that the dried layers present an ink uptake capacity of 28 ml/m^2.

The high gamut property requires layers exhibiting low light scattering that remain transparent when printed and after partial drying of the ink humefactant. The handling of high surface area fumed silica, the choice of aminosilane with appropriate HLB and dispersing properties, together with the minimum surface treatment to keep high porosity, are key elements for the manufacturability. The molecular structure of the aminosilane also plays a important role for the permanence behavior of the layer [10].

In absence of fumed silica, the formation of an Al-O-Si covalent bridge between N-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane ("DAMO") and Aluminium Chlorohydrate is demonstrated (Fig. 3) with ^{27}Al NMR peak appearance at 63.5 ppm [12]. At a given stoichiometry the Al-O-Si organic-inorganic complex is stable for days, and can only be destroyed at low pH by addition of HCl 1N.

Locron + DAMO, ^{27}Al NMR

c(Al(III) [mmole/kg]	c(DAMO [mmole/kg]	pH	Int (Al) [%]
80	0	4.66	100%
84	10	6.30	87%
82	22	6.96	53%
88	25	7.10	40%
84	33	7.67	27%
80	40	7.94	28%
86	41	7.95	28%
86	54	8.61	32%
80	81	9.65	43%
88	156	10.28	56%
88	156	10.18	67%
~88	~156	4.41	96%

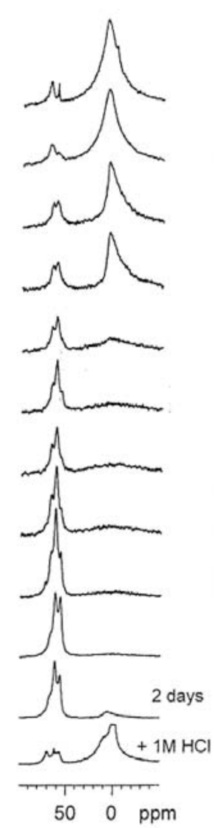

Figure 3. *^{27}Al NMR peaks formation at 63.5 ppm showing the formation of the Al-O-Si Aluminium-Aminosilane organic-inorganic complex under certain stoichiometry [12]*

Results

Dynamic Range and Optical Density with Dye Inks

The more transparent layers of our new generation of photo paper ("Galerie New") reduces light scattering giving cleaner highlights, deeper shadows, more open mid-tones and improved sharpness. The increase in optical density (OD) range is very visible in the Black 4K, and is independent of the dye printer manufacturer (Fig. 4, 5, 6). A lower OD contrast around densities of 0.5 is beneficial for skin and mid-tone rendition. The improved dynamic range is also visible over the full color sectors YMCBGR showing between 9 to 19% saturation gain (Table 1).

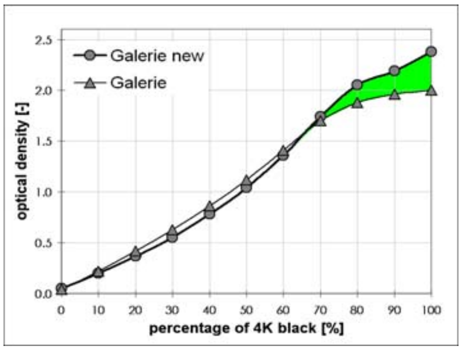

***Figure 4**. Densitometric curves optical density vs. inkload 4K, printed with CANON Pixma iP5200, compared for Galerie, previous and new generation*

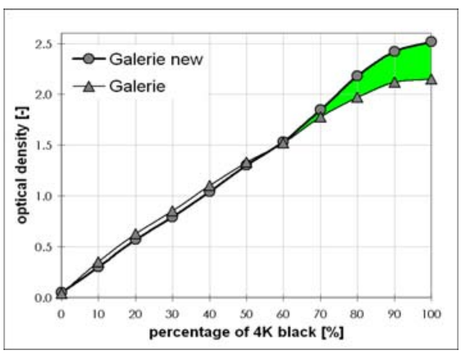

***Figure 5**. Densitometric curves optical density vs. inkload 4K, printed with EPSON R360, compared for Galerie, previous and new generation*

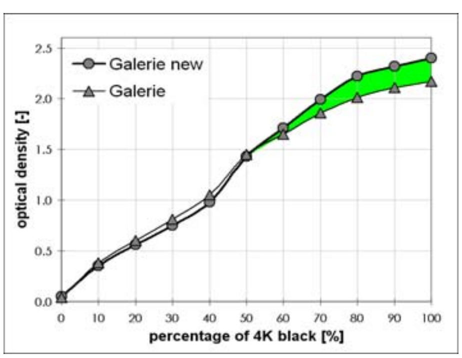

***Figure 6**. Densitometric curves optical density vs. inkload 4K, printed with HP 8250, compared for Galerie, previous and new generation*

Table 1: Maximum optical density gain per color sector, for Galerie and Galerie New printed with Canon Pixma iP5200

Color sector	Galerie	Galerie new	density gain
C	2.11	2.49	+18%
M	1.74	1.93	+11%
Y	1.84	2.04	+11%
R	1.63	1.78	+9%
G	1.81	1.97	+9%
B	2.07	2.39	+15%
1K / 4K	2.00	2.38	+19%

Gamut Volume and blackness

A significant gain in total gamut volume is observed for typical dye printers from Canon, Epson and HP (Table 2). Much lower L*min values (deeper blacks) are measured. This resulted from improved layer transparency and better control of unfavorable haze occurring upon interaction between the ink additives and the layer components such as binder(s), surfactants and surface treating agents. Example of Gamut gain / loss for different color sector and density is shown in Fig. 7.

Table 2: Gamut volume and L*min compared for Galerie and Galerie New, for several dye and pigment printers

Printer / ink type	Galerie		Galerie new	
	L*min	Gamut	L*min	Gamut
Canon iP5200 /dye	9.4	580 k	3.9	641 k
Epson R360 / dye	6.6	643 k	3.0	720 k
HP 8250 / dye	7.1	477 k	4.1	489 k
Epson R2880 pigm.	4.0	816 k	3.2	793 k
HP Z3200 pigment	4.0	755 k	4.1	759 k
HP B9180 pigment	5.5	633 k	3.9	658 k

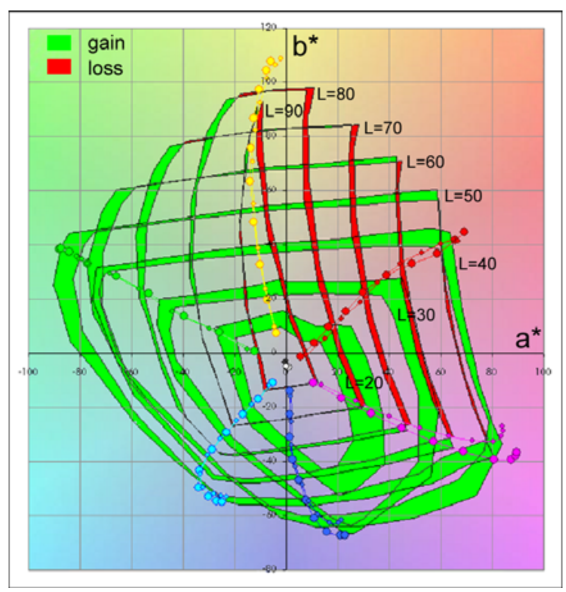

***Figure 7**. Comparative gamut volume gain / loss of previous and new generation Galerie, printed with CANON Pixma iP5200*

Dye Diffusion

Improvement of the image blurring under high humidity storage conditions is an important feature for image permanence. Careful selection of layers components and surface treating agents greatly improves this property. For example a print on HP 8250 dye printer, when subjected to accelerated test of 7 days, 40°C at 80% rH, showed a 5-fold improvement of the average dye diffusion (20% bleed for Galerie vs. 4% for Galerie New).

Pigment Compatibility

Due to their excellent resistance towards light and air contaminants, pigmented inks are the preferred choice of professional photographers. Matting and bronzing are common issues found on images when printed with pigmented inks on glossy photo paper. A gloss profile measured as a function of the 3K Black ink loading shows the progress achieved between "Galerie" and "Galerie New" (Fig. 8). Looking, for instance, at the ratio of differential gloss between magenta and green colors for these two papers, the IQ improvement with pigmented inks of HP B9180 is very remarkable (Fig. 9). A carefully engineered ultra thin top layer (Fig. 1, layer 8) together with a better match of the media surface pH is essential to prevent the encapsulated pigment ink from flocculation at the photo paper surface during printing and drying.

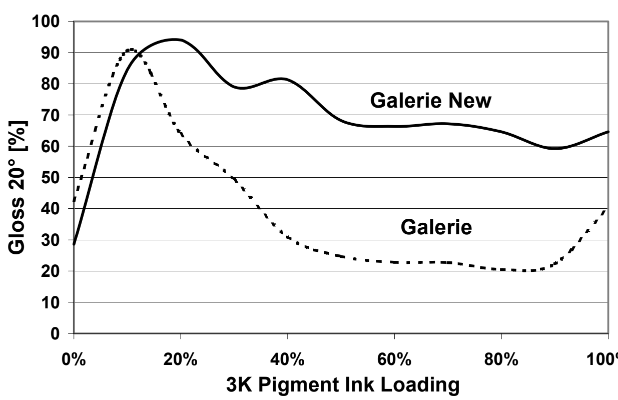

***Figure 8**. Gloss profile for the pigmented ink HP B9180 as a function of 3K ink load, compared for Galerie previous and new generation,*

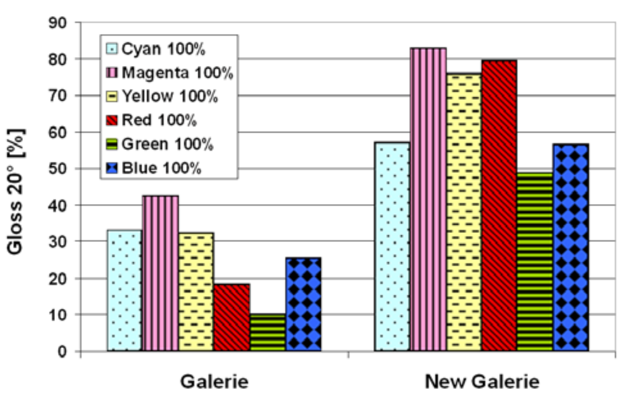

***Figure 9**. Gloss of 100% colors for pigment ink HP B9180, compared for Galerie, previous and new generation*

Conclusions

We have described the approaches used for the design of a new generation of professional inkjet photo paper with a high dynamic range. The molecular structure of the aminosilane coupling agent, used in the formation of an organic-inorganic pre-complex, plays a crucial role for the imaging and permanence properties. Highly transparent nanoporous layers, with reduced light scattering, were studied from both a performance and a manufacturing perspective. Very similar to a silver halide (AgX) media approach, thin and accurate functional layers have been introduced to allow optimal performance with both dye and pigmented inks.

With commercial dye based inks, the new generation of Galerie media exhibits a significant gain of OD ^{max}. This resulted in more vivid colors and dense blacks. Cleaner highlights, deeper shadows, more open mid-tone and softer skin tone rendition have all been welcomed by the professional photographers. Better sharpness and improved humid storage were achieved.

With state-of-the-art pigmented inks, improved differential gloss is obtained that results in much better image perception.

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Author Biography

Vincent Ruffieux received his Ph.D. in Inorganic Chemistry from the University of Fribourg (1994). He then entered the group of Prof. G. Schmid in Essen (Germany) as Pos-doctoral fellow till 1996. In 1997 he joined Ciba Specialty Chemicals in Basle (Switzerland) and worked in the Pigment Technology and Physics group. He joined Ilford in 2003. His work has focused on the surface treatment of organic pigments and the development of nanoporous receiving layers for ink-jet printing.

Pierre-A. Brugger received his Ph.D. in Physical Chemistry from the Swiss Federal Institute of Technology in Lausanne (1982). He joined the IBM Research San José, California, as a Postdoctoral fellow, working on optical memory. In 1984 he collaborated at the Lab of Ceramic Powder Laboratory of EPF-Lausanne, in the field of sol-gel mixed oxide. He joined Ilford in 1985 as a silver halide chemist. Since 1996, he has been leading the inkjet material development section, working on polymeric, micro- and nanoporous multilayer assemblies.