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Inkjet Alchemy - Inkjet-printing of Thin Metal Oxide Films with Metallic Appearance

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Abstract

In this paper, we *describe a new way of producing digital prints with high reflectivity and dichroic or metallic appearance. The special visual effect is achieved using conventional office class inkjet printers and jetting inks containing metal oxide nano-particles onto surface of nano-porous substrates, such as inkjet photo papers. A thin metal oxide layer of uniform thickness in ~10-1000µm range may be produced almost instantly by ambient drying of the print. The formation of metal oxide layer of highly uniform thickness is a result of interaction of metal oxide ink with surface of inkjet media of certain pore structure and high volume porosity. Capillary forces drain liquid phase of the ink into the substrate, while retaining the nanoparticles on the surface. These forces also help to flatten jetted metal oxide particles into optically uniform and continuous layer with high optical reflectivity.*

The appearance of the films produced is highly dependent on refractive index, native coloration and printed layer thickness of the metal oxide used. Inks based on magnetite (Fe_3O_4, refractive index ~2.5) printed into layers with ~ 50-100-nm thickness produce prints with visual appearance of metallic gold. Inkjet printing may also be used for stacking high refractive index metal oxide films with layers of conventional colorants (organic pigment particles) and produce prints with metallic color appearance.

Introduction

Inkjet (IJ) technology is very well entrenched in home, office and commercial large format printing market. In recent years inkjet printing has helped to accelerate the analog to digital transformation of the huge industrial print markets. Significant portion of the *analog* industrial printing output (packaging, greeting cards, wallpaper, book covers, etc.) contains embellishments which cannot be reproduced utilizing most *digital* printing methods. Digital printing using thermal transfer technology offers limited capability for metallic appearance prints at high cost.

Here we report method to produce inkjet prints with variable and broad metallic color palette using conventional office class inkjet printers and jetting ink/s containing metal oxide nano-particles onto surface of nano-porous substrates, such as inkjet photo papers. Key ingredient of our metallic printing technology developed by us is magnetite (iron oxide, Fe_3O_4) nanoparticle inkjet ink formulation. Methods of producing variable metallic color prints also include: a) under-printing the magnetite (metallic luster ink) with dye-based color inks; b) overprinting or under-printing the magnetite ink with inks based on color pigments [1-3].

Nature of Metallic Appearance

Our "metallic" prints look metallic because of their light-reflective properties. We know the surface has metallic luster if we can see a strong directional (specular) reflection of light from it. High specular reflectivity means that an observer sees very strong (high contrast) interplay of highlights and shadows when viewing object illuminated by a directional light source (see Figure 1).

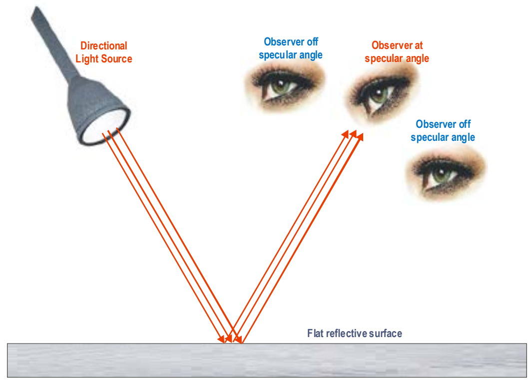


Figure 1. *Directional light reflection from metallic surfaces is perceived as a strong interplay of highlights and shadows by an observer*

An object surface begins to looks metallic if it's able to reflect at specular angle >12-15% of the incident light intensity (highly polished surface of true metals can reflect up to 85-95% of incident visible light). The higher is the intensity of the reflected light at specular angle (combined with low reflection off specular angle) the more metallic is perceived the appearance of the object surface. In order for inkjet print to "look metallic" it should also be able to reflect significant amount of incident light directionally with minimized light scattering.

Our Solution – How It works

Inkjet technology has developed several different methods to create prints with metallic appearance. Unfortunately all of them suffer from a number of disadvantages: (a) layers made of noble metals nanoparticles jetted onto smooth substrates are capable of very strong light reflectivity, but also carry a baggage due to toxicity issues and high cost (gold, silver); (b) formulations based on micron-sized metal flakes (usually aluminum) jetted onto suitable substrates can also produce metallic print, but are difficult to implement with high resolution low drop volume inkjet printheads.

We have developed a low cost, environmentally friendly alternative metallic effects printing solution based on jetting formulations containing nanoparticles metal oxides (MeOx) of high refractive index (*n*) onto optically smooth nano-porous substrates. Optical reflectivity of the MeOx layers produced by our approach is inherently lower than that of the ones made with true metals. However, by combining our optimized MeOx nanoparticle colloidal dispersion technology with recent advances in high end inkjet porous photo media, we have demonstrated wide variety of metallic effects. Most of our inkjet formulations capable of producing wide array of metallic colors were based on iron oxide (magnetite, i.e. Fe_3O_4) nano-particles.

Let's look at the optical reflectivity nature for the case thin transparent MeOx films. Reflectance (*R*) off the surface of film of MeOx with refractive index n_2 in environment with refractive index n_1 (see Figure 2) is described (in first approximation) by simplified Fresnel equation:

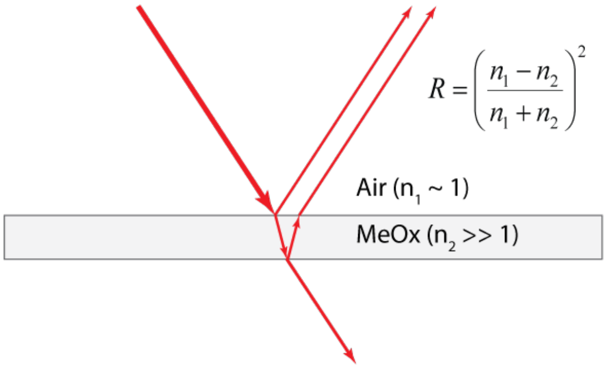


Figure 2. *Light reflectance off transparent layer with refractive index n_2 in environment with refractive index n_1.*

The higher is n of the MeOx printed layer the higher is light reflectivity off its surface. Layers of printed iron oxide films have very high n (~2.4 for Fe_3O_4) and so may be reflective enough to look metallic. In order to maximize reflectivity of the film we also need to enable specular reflection off its bottom layer surface. The key problem boils down to question – how to produce thin MeOx films which are not only microscopically smooth but also have very uniform thickness. To achieve metallic effects, something needs to force the MeOx nanoparticles in the ink to form thin polished-like surface (see Figure 3).

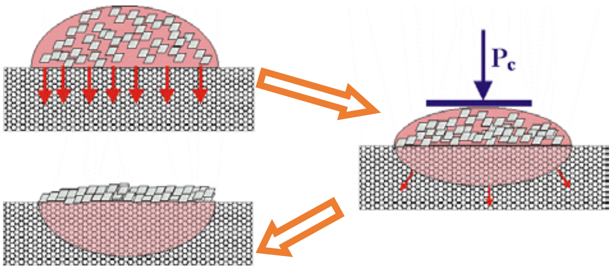


Figure 3. *Formation of optically uniform reflective layer during rapid drying of sub-100nm MeOx ink on microporous substrate. Capillary pressure developed due to "sucking" action of the substrate flattens the metal oxide particles cake into thin film.*

This planarizing factor is achieved when strong capillary force is developed during interaction of MeOx ink with media surface. Key structural component of porous high end ikjet photo paper is an ink-receiving layer composed of low *n* inorganic oxide (precipitated amorphous SiO_2) with high absorptive capacity and small pore size (typically 10-50 nm). During the printing of the ink its liquid phase is quickly absorbed into the ink receiving layer while the metal oxide particles are retained on the surface. We believe that the dimensional uniformity and reflectivity of the MeOx layer is a result of capillary pressure developed by "sucking action" of the microporous substrate.

Indeed, extent of capillary pressure developing during fast drying of MeOx ink on the porous substrate may be estimated from Young-Laplace equation:

$$p_c = \frac{2\gamma \cos\theta}{r}$$, where:

$\boldsymbol{P_c}$ is capillary pressure, **γ** is surface tension of the ink (typically in 20-50 dyne/cm range), **θ** is contact angle of the liquid wetting the solid phase (contact angle between silica coating and aqueous ink is very good, so we may assume **θ** = 0) and **r** is the capillary (pore) radius (5-50 nm range for microporous silica used ink the photoglossy papers).

Assuming the above values the calculated capillary pressure value is in the range from ~100-2,000 psi. Thus, the pressure developed may act like some kind of "steamroller". It is high enough to flatten the drying layer of the metal oxide particles into dense, uniform and optically reflective layer with specular reflectance high enough to look metallic (see Figure 4).

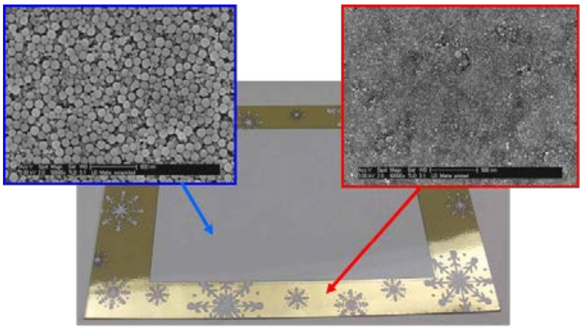


Figure 4. *The "Gold Print" produced on "HP Advanced Photopaper" demystified by SEM (magnification ~50K):*
On left: Media media surface with sub-50-nm surface pores.
On right: Very thin & compacted layer of jetted Fe_3O_4 nanoparticles forms of optically-smooth reflective surface. The produced MeOx layer has "gold" appearance without actual gold being present!

Media Matters

In order to produce "gold"-looking print with magnetite nanoparticles ink inkjet paper should be able to perform two important tasks:

1) The surface pores should be small enough to retain practically all Fe_3O_4 nanoparticles (15-50 nm) on the media surface (see Figure 5).
2) Absorbing capacity of the ink-receiving layer should be high while its average pore diameter in it should be small enough in order to develop capillary pressure capable of flattening the metal oxide cake into layer with strong specular reflectivity.

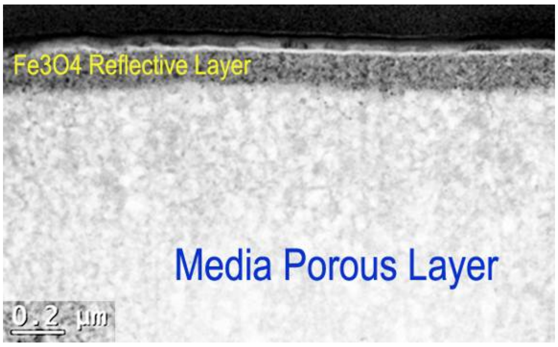


Figure 5. *TEM x-section photo of reflective Fe_3O_4 layer inkjet-printed on "HP Advanced Photopaper" (magnification -60K).*

As one can see only high end porous inkjet glossy papers, such as “HP Advanced Inkjet Photopaper”, have surface pores population with diameter small enough to retain practically all magnetite particles on the surface. These papers give us “metallic”-looking prints when printed with Fe_3O_4 nanoparticle ink. Low grade porous inkjet photo and brochure papers (average pores in 50 nm - few 100 ns range) may produce glossy prints with our magnetite ink, but they do not look convincingly “gold” (see Figure 6). Plain office grade papers have average pore diameter in micron range. Jetting on them our magnetite ink produces prints with very unappealing look. Well, it just looks like “printed rust”.

Figure 6. *Impact of media pore size on visual appearance of the MeOx print. The same Fe_3O_4 nano-particles formulation was printed on: (top) high end photopaper - complete retention of MeOx on media surface; (middle) brochure paper – partial penetration of MeOx into media pores; (bottom) plain office paper – full penetration of MeOx particles inside the media.*

Writing System Is in Charge

Having a perfectly jettable ink with Fe_3O_4 nanoparticles of the right size and printing it on the suitable inkjet media is not just enough to produce perfect-looking “metallic” prints. One needs to have a tight control over thickness of the MeOx layer deposited on media surface during the jetting. The metallic appearance of the print is highly dependent on thickness of the magnetite layer produced and, hence value of jetted ink flux per surface area of the print. “Too much of a good thing” gives us print appearance which doesn’t look metallic at all (Figure 7).

It’s not surprising that metallic appearance of the magnetite prints has very strong visual correlation with measured specular reflectivity of the print surface. Maximum specular reflectivity corresponds to most “metallic” appearance of the print. Through controlling ink flux of the Fe_3O_4 ink by means of printer writing systems we can optimize the “metallic” luster effect (see Figure 8).

a)

b)

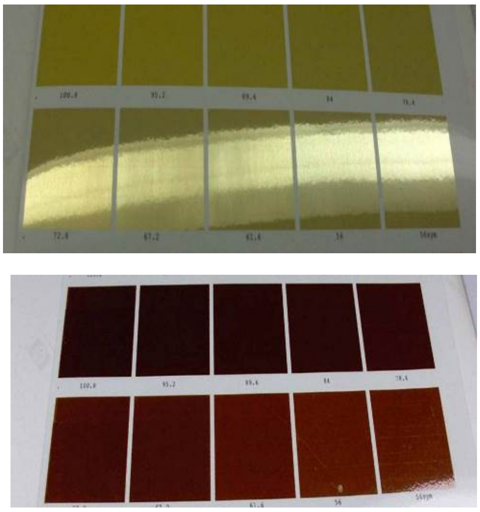


Figure 7. *a) Visually appealing gold luster demonstrated with the prints having calculated Fe_3O_4 layer thickness of ~100 nm;*
b) higher magnetite nano-particles concentration and higher ink flux produces Fe_3O_4 layer thickness of ~1000 nm and results in dark brown prints totally lacking metallic appearance.

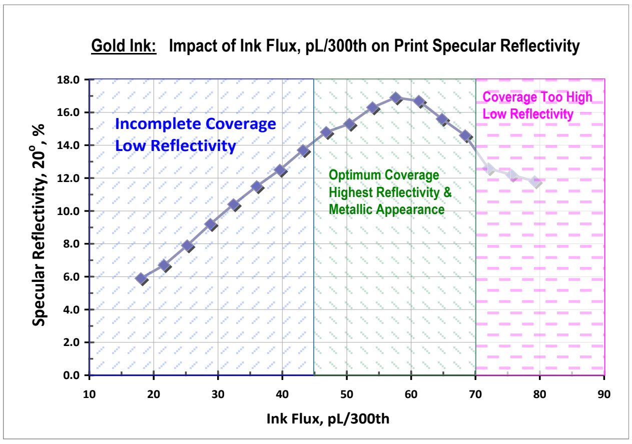


Figure 8. *Reflectivity and metallic luster of the magnetite prints are very ink flux-dependent. The maximum reflectivity is reached at specific ink flux (printed Fe_3O_4 layer thickness) range. (Case of ink containing 2 wt.% of Fe_3O_4 particles)*

Figure 9 tries to explain why magnetite print metallic luster and appearance is so dependent on magnetite layer thickness and coverage. Indeed gold sheen of the magnetite prints is a product of interaction of “physical” and “chemical” colors of the Fe_3O_4 layers. By “chemical color” we mean the layer coloration caused by preferential blue and green part of the spectra absorption by bulk of the material. “Physical color” in turn is related to light reflection from top and bottom of the Fe_3O_4 layer (it’s semi-transparent at optimum thickness) as well as to chromatic interference between light beam reflected from the top and bottom interfaces. When the magnetite layer is too thick, most of the incident light is absorbed by bulk thickness of the material. Thus “chemical color” of the layer overpowers its “physical color” and print acquires dark-brown non-metallic appearance like shown in Figure 7b.

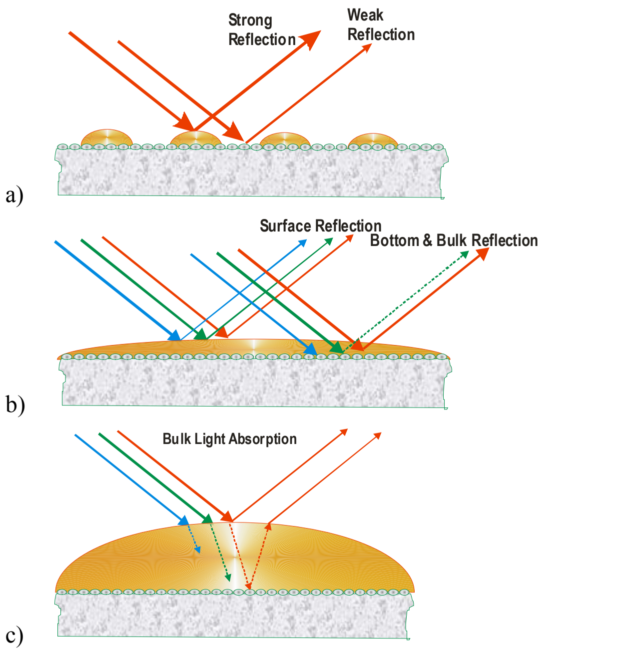


Figure 9. *Effect of magnetite layer coverage and thickness on print surface light reflectivity and metallic appearance: a) incomplete Fe_3O_4 coverage gives weaker specular reflectivity and "dilutes" metallic luster of the print; b) interplay of light directionally reflected off the top and bottom interfaces of the magnetite layer of optimum thickness produces "gold" appearance effect; c) magnetite layer is too thick. Its bulk absorbs most of the incident light. No metallic luster effect.*

Chromatic interference can contribute noticeably to visual coloration of the printed magnetite layer. By adjusting ink flux and Fe_3O_4 layer thickness within roughly 100-300 nm range one can produce "gold" prints with bluish, purplish, greenish or reddish sheen. Thus careful control of ink writing systems knobs may produce reflected metallic colors of different hues by using the same ink (Figure 10).

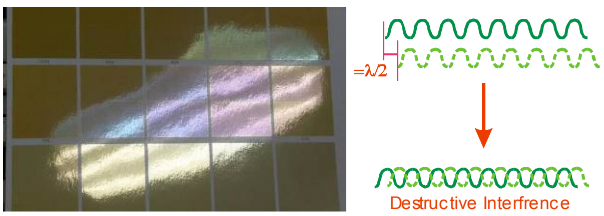


Figure 10. *Chromatic interference of light in semi-transparent magnetite layers (thickness in the range of $\lambda/4$- $\lambda/2$ of the visible wavelength range) can produces "gold" prints with variable hues.*

Metallic Color Effects

We already have mentioned that thin magnetite layers printed according do our technology are not only highly reflective but also remain *partially transparent*. Semi-transparency of the MeOx layer can be utilized to produce an array of printed metallic colors of variable hues. Native color hue of the optimized Fe3O4 metallic print is that of gold. This limitation can be overrun by stacking MeOx layer with conventional colorants (dyes and pigments) during the printing process. Below we have described couple the example cases.

MeOx + Dye -"Metallic" Spot-Color Inks

Soluble colorant (dye) is directly added to the metal oxide ink & printed on nano-porous inkjet photo paper. In this approach, magnetite particles form a reflective layer on the surface, while the dye (with liquid phase of the ink) is absorbed into media porosity. Thus dye ends up in the media surface layer and under the reflective magnetite layer. The specular reflected light has different metallic hue depending on the color of the dye added to the "metallic" ink (see Figure 11).

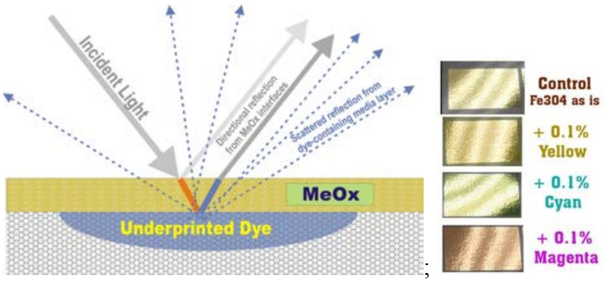


Figure 11. *Left - separation of reflective metal oxide pigment and soluble dye on the media surface; Right - impact of dye addition on metallic colors of the prints produced with inks based on 2.0 wt.% dispersion of Fe_3O_4 (Mv~30 nm).*

Instead of direct addition of the soluble colorant to the "metallic" ink, dyes are introduced into print "*in vivo*" during the printing. It is done by under-printing (or overprinting) of magnetite ink over regular inkjet dye-based ink. The resulting metallic color print structure is essentially the same as is produced according to single ink containing dye colorants and MeOx nanoparticles. The major advantage of this approach is that the ink flux of dye-based ink and "metallic" ink can be modulated independently. It results in large & flexible metallic colors palette which can be produced utilizing magnetite ink plus conventional dye-based (Cyan, Magenta, Yellow) thermal inkjet inks (TIJ) inks. Since dye-based colorants prefer to stay in liquid phase of the ink, the dye-based ink always ends up in the media ink-absorbing layer i.e. under the reflective magnetite layer (see Figure 12). Hence, resulting metallic color is not significantly affected by order of the inks being jetted down.

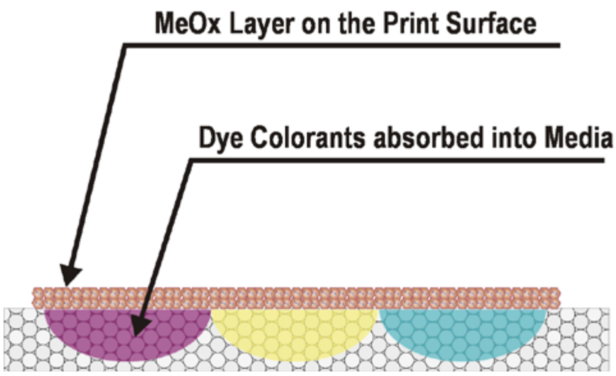
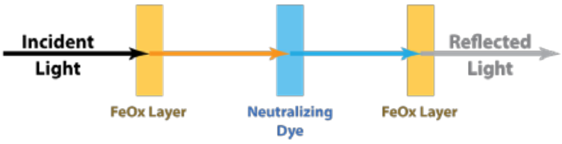


Figure 12. *Under-printing or over-printing of "metallic" magnetite with conventional dye-based ink results in prints with the same or very similar metallic colors. The reason for it is the same final print structure – dye colorants tend to absorb into media porosity and always end up under reflective metal oxide layer.*

"Gold" to "Silver" Transformation

Fine-tuning of added or under-printed dye hue may be used for "neutralization" of Fe_3O_4 layer native coloration. The final outcome of such "optical neutralization" is printed layer with neutral metallic look. For example gold-looking magnetite print can converted into neutral silver-looking by cancelling MeOx yellow coloration through addition to ink formulation carefully tuned dye mix of bluish hue. In such print the neutralizing dye mix would reside just under semi-transparent reflective layer of the iron oxide. Neutral white light passing through iron oxide layer would acquire yellow coloration. Then its color would be altered (tinted blue) by interaction with neutralizing dyes below (see Figure 13a for the graphic explanation). Finally after passing back through Fe_3O_4 layer color of this bluish-tinted light would be corrected back to neutral one. Example of such color-neutral MeOx print is presented on Figure 13b

a)



b)

Figure 13. *a) Color transformations of incident white light passed through semi-transparent Fe_3O_4 layer and reflected off iron oxide/media interface; b) Visual comparison of the print made with original Fe_3O_4 ink (as is), the one created with ink containing neutralizing Cyan & Magenta dye mix and the one printed with C&M dye-neutralized "Silver" Fe_3O_4 ink.*

MeOx Inks and TIJ Pigmented Inks

Pigment-based color inkjet inks contain colorants in the form of discrete solid phase particles. Like magnetite particles these particles are also retained on the media surface and form a distinct layer. Thus printing with both reflective metal oxide ink and color pigment inks tends to produce prints with two-layer structure. Positioning and structure of the layers is affected by the order in which both inks are jetted onto the media. When magnetite ink is jetted first color pigment forms transparent colored layer on top of the reflective oxide layer as shown in Figure 14. Jetting color pigment first leads to formation of semi-transparent metal oxide layer on top of the colored background produced by color pigment as shown in Figure 15. The stacking order of layers dramatically affects the way light interacts with the print surface. Both jetting sequences produce prints with unique & vibrant metallic color appearance.

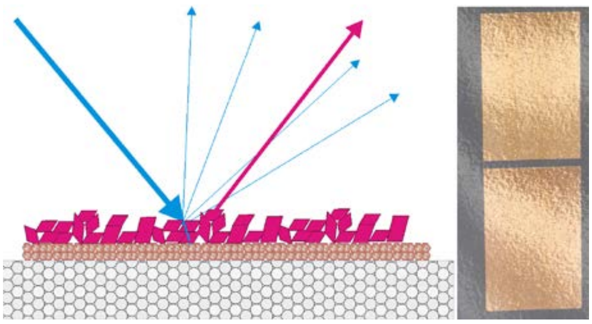


Figure 14. *Color pigment on top of the Magnetite layer. Dominant specular reflection from magnetite surface that is filtered through the colorant layer.*

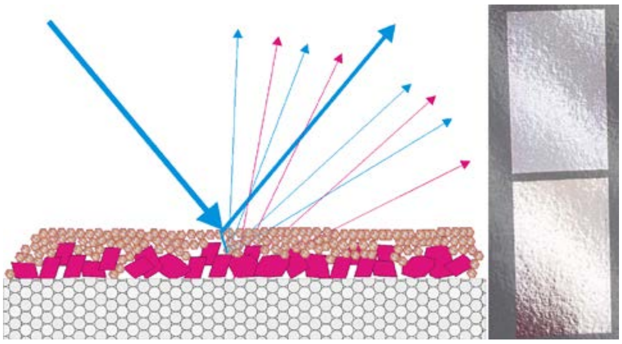


Figure 15 *Magnetite layer on top of color pigment layer. Dominant specular reflection from the Magnetite print surface is combined with diffuse light reflected from/through the pigment layer.*

Conclusion

Addition of high refractive index MeOx nano-particle formulations to the inkjet printing toolbox enables creation of "physical color" effects where visual appearance may be dramatically altered by thickness and structure of the MeOx layer produced by the jetting. The MeOx ink technology described here is backward compatible with existing inkjet hardware. Combination of "physical color" MeOx inks can bring to table with "chemical color" of conventional colorants may further expand possibilities of inkjet printing.

References

[1] US Patent US20130065031
[2] US Patent US20130084440
[3] US Patent US20130183500

Authors Biography

Vladek Kasperchik – received his Ph.D. in Physical Chemistry from the National Academy of Sciences of Belarus (Minsk, Belarus) in 1985. He joined Hewlett-Packard in 1995 as a material scientist/chemist and since then was involved in development of several printing technologies (LightScribe photothermocromic labelling technology, 3-D printing, various applications of thermal inkjet printing, etc.). He is an author of >70 US patents and patent applications.

Vladimir Jakubek received his Ph.D. in Inorganic Photochemistry from the Chemistry Department at State University of New York in Binghamton, NY in 2000. Later, he worked at IBM, Material Science and Engineering Department at Cornell University and PharmAssist Analytical Laboratory. He joined Hewlett-Packard in 2007 as a material scientist/ink chemist in the field of printing inks specializing on thermal inkjet technology with focus on ink innovation with respect to ink formulation development, print performance evaluation, ink-media interactions and ink reliability.

Jayprakash Bhatt received his Ph.D. in Organic Materials Chemistry from the University of Oklahoma in 1991. He joined HP in 2002 and since then has worked in development of Laser imaging CD/DVD disks, security inks, dye and pigment based thermal IJ inks and UV inks. Most recently he has contributed in the development of color inks for HP's Large Format Page-Wide printer systems. Prior to HP, Dr. Bhatt was involved in development of Liquid crystalline material, non-linear optical materials and different analog and digital printing technologies including direct thermal, thermal transfer and 3-D printing.