Multi-color Properties of Silver Glaze Images Photo-engraved on Glass Plates

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Abstract

Recent progresses in nanotechnologies enabled the coloration of glass plates coated with silver and titanium dioxide by laser irradiation. The colored samples display very different colors according to whether they are obtained by reflection or transmission of light; in specular or diffuse directions; and with or without polarizing filters. This printing technology, that we call PICSLUP, enables the production of gonio-apparent color images. In this paper, we recall the physical principles that allow the appearance of these multi-coloration effects, show the color variations under various illumination and observation configurations, and present the first color images that we could print. We also analyze the possibility of extending the color gamut with halftoning and show some preliminary spectral reflectance and transmittance predictions done with the Yule-Nielsen modified Spectral Neugebauer model.

Introduction

In ancient history, glassworkers were already capable of producing colored glasses with dramatic color changes depending on the position of the light source with respect to the observer. It is the case, for example, of the Lycurgus cup exhibited at the British Museum of London, which looks green by reflection of light and red by transmission of light [1]. It was discovered that this color change is due to the presence of gold and silver nanoparticles within the glass substrate [2], which cause a wavelength dependent light absorption by a physical phenomenon called surface plasmon resonance [3]. Metal nanoparticles are also responsible for the colored gloss effects displayed by lusterwares [4, 5], ceramics coated by a metallic glaze, characteristic of the ancient Islamic art and of the Art Nouveau. The progresses in photonics, and more recently in nanotechnologies, did not only permit to discover the reason of these surprising color effects, but also to reproduce them with modern technologies, especially lasers. The printing technique presented in this paper, the Photo-Induced Colored Silver LUster Printing system (PICSLUP) is based on these physical principles, since it is now possible to control the growth under laser irradiation of metal nanoparticles in an inorganic substrate containing the necessary metallic ions [6, 7].

This paper aims at presenting the technology and the type of colors that can be achieved in different illumination-observation geometries, according to the command parameters of the printing system. We will also address the possibility of extending the color gamut by halftoning and show the first color images that we could print. The interest of these images is that their colors completely change from one viewing angle to another one, which gives high potential for secured imaging and decorative arts.

Physical principles of the PICSLUP technology

Before printing, the glass support is coated with a mesoporous film of amorphous titanium dioxide elaborated by a sol-gel process and loaded with silver salt. This film is transparent and colorless, but it contains many small silver nanoparticles of about 1−3 nm in diameter [8]. Due to the localized surface plasmon resonance of these nanoparticles, the film slightly absorbs light. When the film is irradiated by a laser beam (an Ar-Kr CW laser is used at different wavelength in the visible range: 488 nm, 514 nm, 530 nm and 647 nm) with enough power, the small absorbance of the film is sufficient to induce a high increase of temperature, which favors the nanoparticle growth. An interesting interference effect, which sets up within the film itself between the incident field and guided modes excited by scattering on the growing nanoparticles [9], then occurs and promotes the organized growth of nanoparticles along lines periodically spaced parallel to the incident laser polarization. This anisotropy at the nanometer scale, shown in Figure 1, gives to the sample a dichroic spectral behavior, i.e. polarization sensitive colors [6, 7]. The arrangement of nanoparticles within the films also influences the color sensitivity to the illumination/observation angles. The final color of the samples is determined by several physical parameters: the nanoparticle shape, size and spatial organization, as well as the film thickness and refractive index that evolve during the laser treatment.

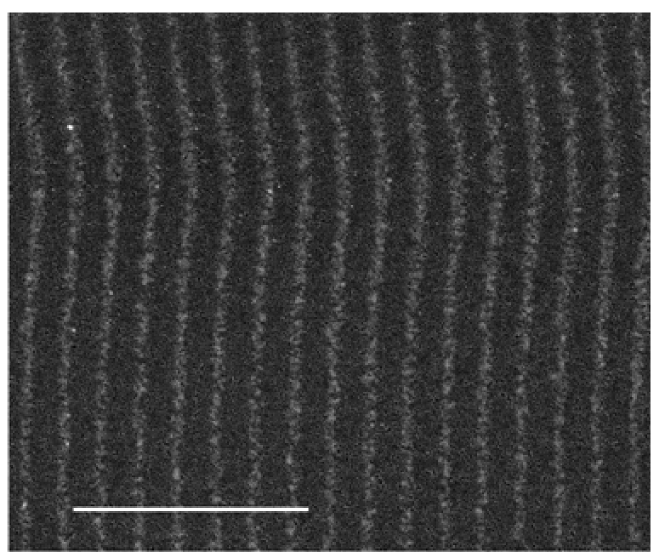

***Figure 1**. Image made by scanning electron microscopy of a printed area where the nanoparticles are well aligned (Scale bar: 2 µm)*

All these final physical parameters depend on the exposure conditions i.e. the laser power, focusing and wavelength, and the scanning speed of the laser on the sample. By varying these experimental parameters, several colors can be created in each point of the surface as in continuous-tone photographic printing. Figure 2 shows microscopic images of a printed surface captured by a calibrated RGB camera. The colored areas combine the gonio-apparent properties of both lusterware and stained glass: the colors perceived by reflection or transmission of light, in or out of the specular direction, are completely different. Due to the self-alignment of nanoparticles, both reflected and transmitted colors vary with the polarization of light.

Current color capabilities

The printing process has different command parameters: exposure time (tuned by the laser scanning speed), laser power, laser wavelength, and laser focusing. This results in the appearance of a wide range of colors.

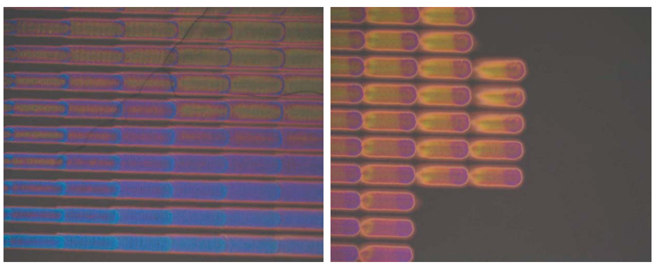

***Figure 2**. Lines printed with varying laser focuses on the horizontal direction (100 µm period), and varying translation speeds on the vertical direction (50 µm period).*

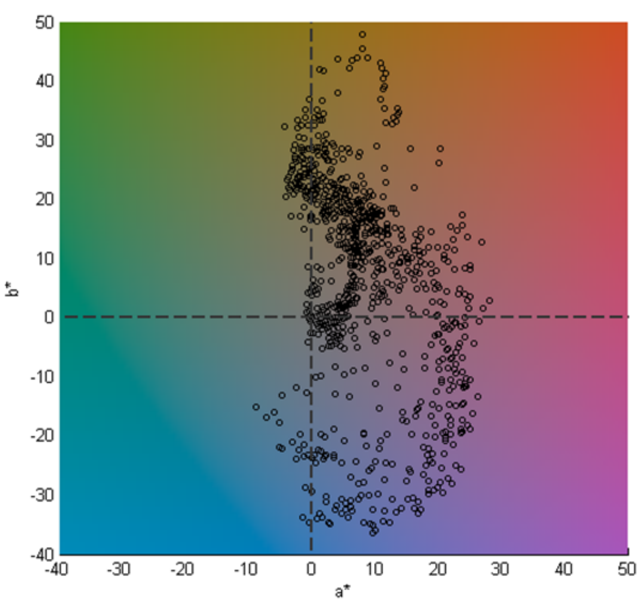

***Figure 3**. Colors obtained with a controlled combination of elaboration parameters, and measured by a color-calibrated microscope in the 0°:0° illumination/observation geometry. The colors are represented in the CIELAB color space by assuming a D65 illuminant. The reference colors in the background were calculated by fixing a lightness value L* of 50 units.*

The colors displayed in Figure 3 were obtained with a color-calibrated microscope [10] from samples printed on glass with a combination of many different elaboration parameters by measuring in the 0°:0° illumination/observation geometry.

However, these measurements are not sufficient to characterize the samples produced by the PICSLUP technology, since they exhibit different colors according to the respective positions of the viewer and the light source. Moreover, in most of the produced samples, the colors observed in transmission mode are greatly different from the colors observed in reflection mode. These properties are illustrated by the pictures shown in Figure 4 of the first image we could print with PICSLUP, where different colors can be observed in specular reflection, non-specular reflection and transmission configurations. This image was designed from a black and white portrait of Marilyn Monroe by Ben Ross, 1953, quantized in four grey level values, and then colorized using a tetrachrome harmony's principle [11] in four colors pre-selected in the specular reflectance gamut.

***Figure 4**. Color image printed with PICSLUP (1 x 1 cm), showing the dramatic color change depending on the illumination and measurement geometries. Left: Specular reflection mode (45°:45° geometry); center: Non-specular reflection mode (45°:0° geometry): right: Transmission mode (0°:0° geometry).*

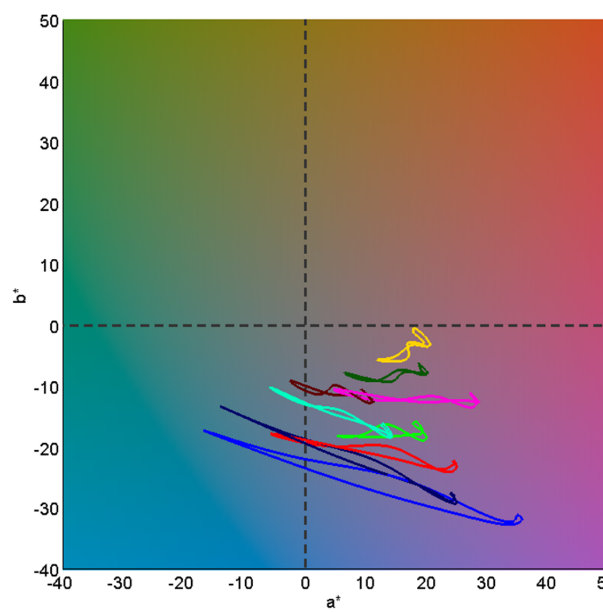

***Figure 5**. Color variation of 9 different samples when rotating a polarizer between 0° and 180°. In each curve, 0° and 90° correspond to the left and right extrema, respectively. The colors are represented in the CIELAB color space by assuming a D65 illuminant. The reference colors in the background were calculated by fixing a lightness value L* of 50 units.*

It was also demonstrated in a previous study that the colors exhibited by these samples are very sensitive to polarization [7], property that can be used to further increase the amount of colors that can be produced with the technology. Figure 5 shows the colors obtained by measuring 9 different samples with a calibrated microscope in the 0°:0° illumination/observation geometry while a polarizer placed in front of the detector is rotated between 0° and 180°. The irregularities of the lines are due to the low intensity of the light in some polarization angles.

As it can be observed, the reproducible regions of the color space (color gamut of the system) have considerably increased with the use of polarization with only a few tested samples, which suggests that an even greater coverage can be obtained with a more exhaustive evaluation.

Extended color capabilities by halftoning

Halftoning is an ancient technique used by engravers to produce the impression of grey level images from a binary printing process, by juxtaposing small areas with and without ink at a higher frequency than the human visual system's modulation transfer function. Multi-color halftoning is based on the same principle by printing several halftone images with different color inks, typically cyan, magenta, yellow and black. The PICSLUP technology being a continuous-tone printing system able to reproduce several primary colors in each pixel of the printed image, halftoning is not strictly required. However, as its color gamut is limited in some regions and concave (see Figure 3), there is an interest in seeing whether halftoning could increase the color gamut and make it more convex. The most suitable type of halftoning with the PICSLUP technology is the line halftoning, a variant of the dot-off-dot halftoning [12], where lines of different primary colors are periodically juxtaposed without overlapping.

In this study, first experiments were carried out on single color halftones, where all the printed lines have the same color. In the full-tone color patch (100% surface coverage), all printable lines are printed, and in the halftone color patch (50% surface coverage), one line over two is printed. We also printed two-color halftone patches where lines of two colors are alternated, covering each one 50% of the surface. Through these first experiments, we wanted to verify that the spectral reflectance or transmittance of the halftones patches could be predicted from the ones of the full-tone patches with such kind of surfaces which are not usual in color reproduction and optically very different from ink printing on paper. For that purpose, we used the Yule-Nielsen modified Spectral Neugebauer (YNSN) model in reflectance mode [13, 14], or accordingly in transmittance mode [15].

Let us consider the reflectance mode corresponding to a given measuring geometry, and denote as $R_1(\lambda)$ and $R_2(\lambda)$ the spectral reflectance factors (or similarly, transmittance factors) of two primary colors at a given wavelength λ. The Yule-Nielsen modified Spectral Neugebauer equation predicts the spectral reflectance factor of the halftone as

$$R(\lambda)=\left[(1-a)R_1^{1/n}(\lambda)+aR_2^{1/n}(\lambda)\right]^n \quad (1)$$

where a denotes the surface coverage of the second primary color (the first primary color filling the rest of the printed area), and n is an empirical parameter, having generally a real value higher than 1, modeling partial mixing between the fluxes interacting with each primary. The n value generally depends on the measuring geometry [15], especially with a clear printing support in which the optical dot gain due to the multiple reflection between the two interfaces of the glass plate way have different importance in reflection and transmission modes.

The reflectance factors were measured by using as white references achromatic surfaces reflecting comparable radiance as the samples, either with a 20°:20° geometry in the specular reflectance mode, or a de:8° geometry in the non-specular reflectance mode. The transmittance factors were measured by using as white reference the void between the light source and the detector in the 0°:0° geometry.

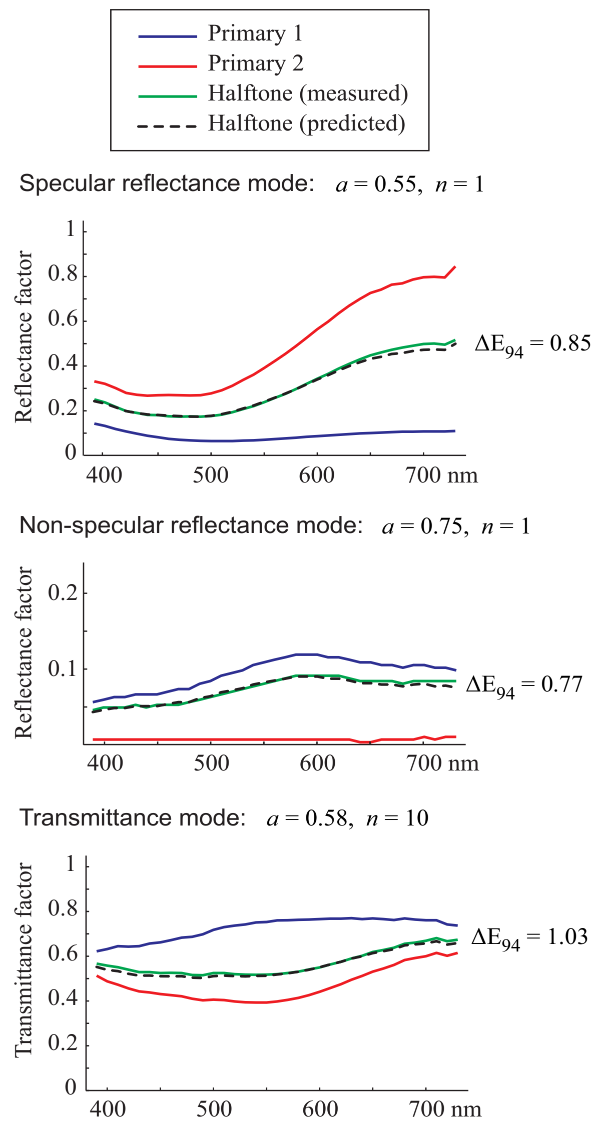

***Figure 6**. Measured spectral reflectance (specular and non-specular modes) and transmittance of fulltone primaries printed with PICSLUP and a halftone made with these primaries, and spectrum of the halftone patch predicted with the Yule-Nielsen modified Spectral Neugebauer model with the fitted parameters a and n values indicated above the plots.*

Through our experiments, we experienced the difficulty of performing accurate reflectance measurements on very specular reflectors, either in the specular direction because of a slight tilt of the sample may change considerably the captured radiance, or in a non-specular direction because the reflected flux is very low. Nevertheless, from the measurements we carried out with a home-made multi-angle bench, we obtained satisfying agreements between the measured and predicted spectra for halftones.

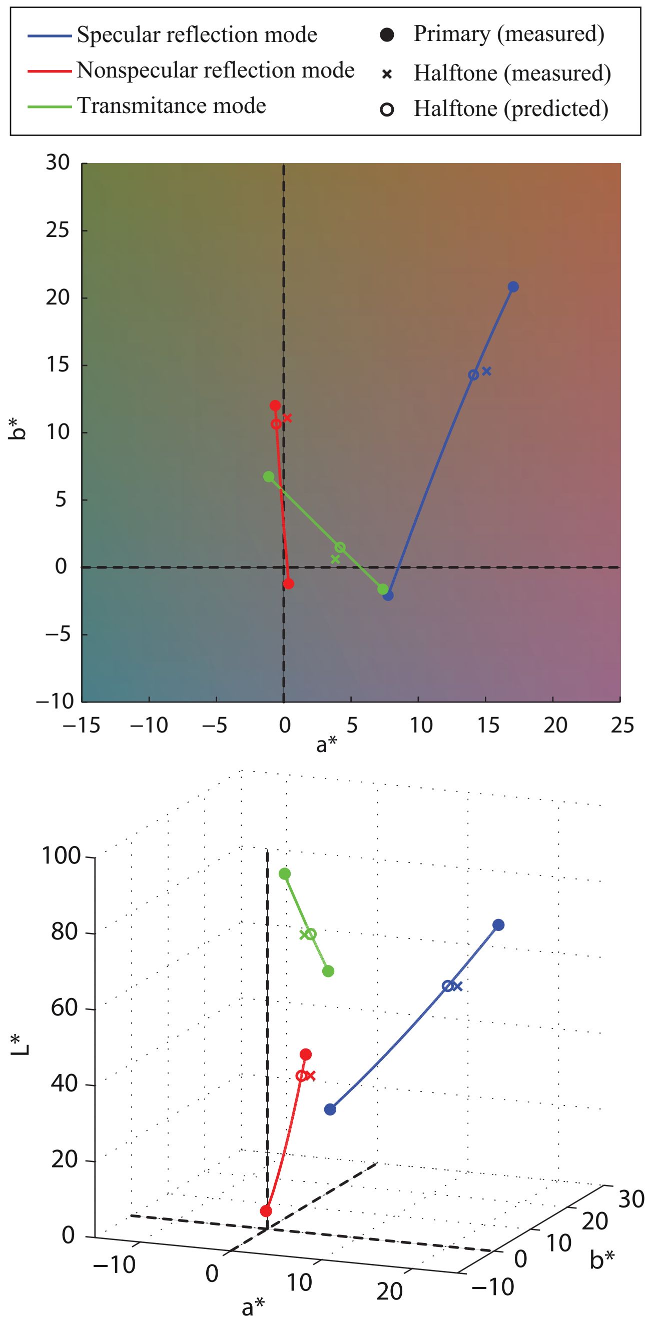

Figure 7. 2D and 3D representations of the measured colors in the specular and non-specular reflectance modes and the transmittance mode of fulltone primaries printed with PICSLUP and a halftone made with these primaries. The reference colors in the background of the 2D view were calculated by fixing a lightness value L of 50 units.*

By way of illustration, we reproduce in Figure 5 the measured and predicted spectra for one 50% halftone in the three modes: specular reflectance, non-specular reflectance and transmittance. The CIE ΔE94 [16] color-difference values computed between the predicted and measured spectra in these three modes, indicated in the figure, are rather good. The surprising results comes from the very high value of surface coverage fitted in diffuse reflectance mode, which indicates that this value might incorporate optical phenomena not taken into account in the Yule-Nielsen model, especially slight scattering by the engraved areas whose impact in comparison to the low reflected radiance may be significant. Similar differences in the fitted surface coverage values according to the measuring mode were already noticed with transparencies printed by inkjet, but this did not prevent good reflectance and transmittance predictions [17].

From the measured and predicted spectra, colors where computed in the CIELAB color space by assuming a D65 illuminant. By varying the surface coverage a of the second primary in the Yule-Nielsen modified Spectral Neugebauer equation, we can predict the set of colors achievable with a pair of primaries. The ones achievable with the primaries used for the sample presented in Figure 6 are displayed in Figure 7 in 2D and 3D views of the CIELAB color space. As we can see, the set of colors obtainable by halftoning with two primaries draws an almost straight line. Hence, we might expect that the color gamut displayed in Figure 3 for the specular reflectance mode could become convex, more appropriate for gamut mapping, but this still needs to be verified from a comprehensive set of halftone color patches.

Conclusions

The PICSLUP technology is a contactless printing system on functionalized glass plates which enables printing color images with similar multi-color properties as stained glasses and lusterwares, reproducing their transparency and specularity, and their ability to display different colors according to the respective positions of the observer and the light source. Additionally, the colors depend on the polarization of light. All these properties give this technology a high potential for graphical arts and anti-counterfeiting applications since multiple images can be displayed in one printed area without need of any instrument. Thanks to the gamut extension by line-halftoning, the number of achievable colors in the different illumination-observation geometries can be considerably increased. We can for example imagine two identical colors in specular reflection mode being different in transmission mode. Our first tests to check whether the spectral reflectances and transmittances of halftones could be predicted from the ones of primary colors are promising and open the possibility to develop advanced gamut mapping in order to select the fulltone or halftone colors to be printed in each pixel for a targeted multiple image design.

Acknowledgments

This work was supported by the French National Research Agency (ANR) within the program “Investissements d’Avenir” (ANR-11-IDEX-0007), in the framework of project PHOTOFLEX n°ANR-12-NANO-0006 and the LABEX MANUTECH-SISE (ANR-10-LABX-0075) of Université de Lyon.

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