Professional paper

Possibility of exact realization of silver tones in electrophotographic printing

ABSTRACT

Except for standard CMYK colors in high-quality printed products, designers often choose metallic silver tones. With this method, designers underline important segments and parts of printed publications. Silver applications today are mostly performed with expensive foil printing techniques or lithographic offset printing. However, the development of new Xerox electrophotographic machines has enabled the application of an additional silver toner that achieves a metallic effect of silver tones. In this paper, the possibility of successful realization of silver PANTONE 877C printed with the conventional offset printing (HUBER printing ink series Alchemy) and with silver Xerox emulsion aggregation (EA) toner was investigated. The test used 170 g/m² gloss art printing paper printed on printing press Heidelberg GTO ZP 52 (offset printing conditions) and Xerox Versant 180 (electrophotographic printing conditions). Due to the easier modification of the electrophotographic press conditions (RIP Fiery FS 200), the printing was performed with two screenings (AM and FM distribution of printing elements in a halftone image). Due to the use of different silver pigments, two colorimetric measurement methods (M0 and M3 mode) were also analyzed. Colorimetric analysis (CIE LAB measurements and ΔE2000 color difference) showed that the silver halftones of Xerox EA toner also achieve large color changes ΔE_{mean}>5. However, the PANTONE 877C tone will be better reproduced in full tone (ΔE_{OFF_Xerox} = 4,2) while the rasterization process will achieve higher average tone deviations. By varying the Fiery RIP settings (FM-AM screening), a better imprint will be obtained with FM screening (average difference ΔE_{FM_AM} = 0,64).

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Introduction

Printed products to achieve added value, need to be additionally printed with special inks and varnishes. By current representation, the silver print is at the very top option, which, together with gold and white inks, makes up the majority of such effects.

Thus, silver ink use achieves highly reflective imprints (metallic effect) which also has a high coverage (good brightness on darker printing substrates) (Hanisch, 2021).

Traditional printing techniques for creating silver tones are the application of metal foil (cold foil printing process or hot stamping process) and the printing of silver inks using the lithographic offset printing machines. The foil printing techniques achieve an accurate and completely uniform layer of real metalized foil on the print, with a final thickness of 1 to 2 µm.

Thus, a layer of top-quality aluminum (simulates the effect of silver) due to its high reflection creates a high metallic luster (L. Co, 2011).

In offset printing, the silver inks will have to be adapted to the inking and damping unit of a printing press. Thus, pasty lithographic offset inks will have precisely adjusted ink tack and viscosity (40-100 Pa·s) to achieve ink film thickness in a range between 0.5 and 1.5 µm. Although such a silver print is acceptable, it is also characterized by its unevenness (especially on larger printing surfaces) where the effect of reflection is reduced due to the use of small pigment particles (Kipphan, 2001; Majnarić, 2004).

An alternative to lithographic printing is Inkjet digital printing techniques and electrophotography (EP). Thus, in the Inkjet technique, we can be found machines with standard CMYK inks and additional white or silver inks. Thus, ROLAND DGA company in your Inkjet machines integrate fifth channels (5. Inkjet solvent ink) which has the possibility of applying silver ink with metalized pigment particles (L. Co., 2010).

In the electrophotography printing technique, the silver print effect is developed by Xerox company. It is possible with the construction of the Xerox® Iridesse machine, which along with standard CMYK toners, it is possible to use additional toners such as White, Clear, Silver, Gold, and Fluorescent Inks. Silver electrophotographic tones (jobs) can thus be achieved within a few minutes without any waste of pape (L. Co., 2021b).

Theoretical part

Silver inks for offset printing

When we define offset inks, it is important to note that these are inks must have an exactly dynamic viscosity (η). Therefore, depending on the method of preparation of silver and gold offset metallic inks can be distinguished in two forms: one-component inks and two-component inks. In highly productive lithographic offset, one-component inks are generally preferred. They are created by factory mixing: 50% paste (which contains aluminum laminar pigment in a concentration of 90%), 40% one-component varnish (hydrocarbon resin, soy dehydrated oil, aromatic distillate with a low sulfur content), 7,5% polyethylene wax, 2% manganese dryer, and 0.5% antioxidant. Since the gloss effect decreases over time, such inks need to be kept in the original (vacuumed) packaging. The inks must contain resinous binders based on organic hydrocarbons that will achieve the desired viscosity and maintain pH neutrality. Metallic one-component inks must contain dryers (cobalt or manganese salts). Their addition achieves better drying of the print, especially on paper and cardboard printing substrates. Due to the drying of silver offset printing inks, the pH of the damping solution must not be less than 5.5.

In the preparation of the offset printing machine, it is recommended to use buffers that are pH neutral (Hubergroup print solutions, 2020).

In the case of two-component metallic inks, the silver laminar pigments are supplied in the form of a pre-treated paste that is bonded to the binder before the printing process. The pigmented paste is mixed with the binder (carrier component) taking care not to increase ink temperature and change the viscosity (mixing in mixers device maximum of 2-3 minutes to a temperature of 60° C). (Gavran et al., 2015). This avoids the problem of darkening metallic pigments, which allows a higher gloss effect. Although the proportion of pigments in the ink does not change, the main change compared to one-component inks was made in mass share.

Thus, it will contain 50% paste (which contains aluminum pigment laminar in a concentration of 90%), 39.3% two-component varnish (soluble resin in modified phenyl resin, low-viscosity linseed oil, an aromatic distillate with a low sulfur content), 7,5% polyethylene wax, 1,5% manganese dryer, 1% cobalt dryer and 0,7% antioxidants. Thus, a higher content of pigment paste will give a higher metallic luster effect with lower abrasion resistance. Binders in metallic inks (a mixture of resins and oils) are crucial for bonding pigments to the printing substrate and maintaining rheological properties (especially in inks with an extremely high content of metal pigment particles). Rheological stability and prevention of darkening are especially analyzed during the interaction of pigments and binders (Walenski, 1999).

The main characteristic of silver metallic offset printing inks is that they have pigments with a pronounced metallic luster (reflection from the printed surface). Due to their price, silver-tone shades do not contain expensive silver (original elements), but cheaper aluminum and aluminum alloys are added to them as metals for imitation silver. The color tone base is thus made up of pigment particles which are adapted in shape to a laminar sequence (extremely flat particles). Flat aluminum metal particles thus have an average dimensional width ranging from 5 µm to 50 µm, while their height varies from 100 nm to 1 µm. However, in extreme cases, such particles can have up to 10 times larger dimensions. The ratio of thickness and diameter is also known as the shape factor, and it usually ranges in metallic colors in a ratio of 1:50 to 1: 500. The reflection from the printed pigment particles on the paper depends on the detail and morphology of the aluminum pigments. In other words, it depends on surface roughness, particle width and particle length, particle size distribution, and orientation of pigments in the application medium (binders). Important factors include parameters such as the type of aluminum (pure metal or alloys), the method of production, the final treatment of pigment particles, and the viscosity of the binder used.

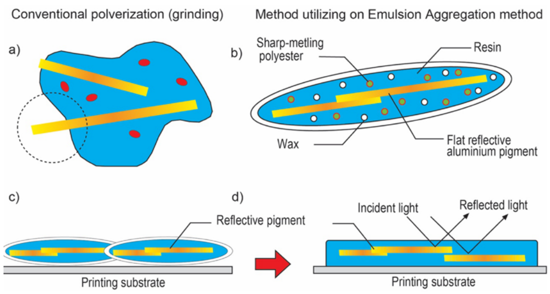
The aluminum used on the ink market can be found in the version: CI Pigment Metal 1, CI No. 77000, and CAS NO. 7429-90-5. In addition to the plate structure, it is characterized by non-resistance in acidic and alkaline media. In other words, exposure to hydrogen ions H^+ and the hydroxyl group OH^- will result in surface degradation and darkening of the imprints. Therefore, it is often found in combination with inert hydrocarbon solvents. The less flat (laminar) structure can be used in the production of all classic types of pasty printing inks, and thus realize the possibility of printing on different printing substrates. Appropriate hardeners must also be added. (Wissling, 2007; Becker et al., 2018).

Due to the characteristic reflection and absorption of aluminum pigments, we achieve a typical silvery metallic luster. The reason for this is the release of bound electrons from aluminum atoms. Such electrons from one ionizing gas which is distributed within the remaining ions and fixed at exact positions within the crystal grid. Due to the interaction with electrons, the external energy (wave of white light) will penetrate the ionizing gas, and thus achieve partial light reflection and partial absorption. Changes in the density of ionizing gases on the aluminum surface will result in a specific dispersion of light in the visible range. Parameters such as refractive indices n, absorption $n\kappa$, reflections r (n, κ), and melting temperature Tm has an important role. In the case of aluminum pigments for printing inks, they are reflection 0.888; refractive index 0,280; absorption 2,91; melting point 1,336 °C (Klain, 2010). Except for the metallic pigments (make up uncoated metal shells), particles of crushed PVD (Physical Vapor Deposition) films can also be found in printing inks and substrates. Such particles are coated with absorption pigments and particles of pigments that are partially or completely oxidized (oxide coating). It is a process used to produce a metal vapor that can be deposited on electrically conductive materials as a thin, highly adhered pure metal or alloy coating. The process is carried out in a vacuum chamber at high vacuum (10–6 torr) using a cathodic arc source after which the foils are crushed at a temperature below the transition temperature to the glassy phase of the polymeric material. The most commonly used polymers are polyethylene terephthalate, polystyrene, and polypropylene The PVD method is now most commonly used to achieve particles with particularly uniform surfaces (Carneiro et al., 2011).

Silver toners for electrophotographic printing

A complete novelty in the printing industry is the generation of metallic tones in the electrophotography (EP) printing technique. During the electrophotographic printing process, each print is made in 6 independent phases: the creation of a layer of charged air (ions) on the surface of the photoreceptor by the action of the corona (phase 1), selective illumination of the photoreceptor to neutralize the previously charged surface of the photoreceptor (phase 2), applying colored and electrostatically charged toner particles to the photoreceptor (phase 3), transferring the toner powder particles to paper due to the action of the transfer corona (phase 4), fix the toner particles by heating and pressing on paper (phase 5) and final cleaning and preparation of the photoreceptor surface for new printing circle (phase 6) (Majnarić, 2015).

To achieve a silver color tone with an expressed shine, in the EP with the possibility of using fast xerographic machines with a new type of toner emulsion aggregation toner. Unlike a standard toner, it will contain: less than 90% polyester resin, 10-20% ceramic powder, 10-20%, aluminum (CAS 7429-90-5), less than 10% waxes (CAS 8002-74-2), less than 10% amorphous silicon (CAS 7631-86-9), and less than 1% titanium dioxide (CAS 13463-67-7). Thus, the final particles of aluminum pigments in the toner must be coated with silicon dioxide or acrylate. The development of such a toner (Figure 1a) was achieved progressively where the problem of the size of the metal laminar pigments (pulverization method of production) was solved by making an emulsion aggregation toner. (Kmiecik-Lowrynowicz, 2003; Diamond, 2001). Thus, with the new silver EA toner, the laminar pigment will be coated with a single fast-melting polyester resin and wax (resin) thus forming a specific oval ellipsoidal shape (Figure 1b). The result is a directed impingement of toner particles on the printing substrate (Figure 1c) which will melt after fusion and form a final imprint of a shell structure with a more visible gloss (Figure 1d). Figure 1 is a schematic representation of the structure of silver toner and its bonding to the printing substrate (L. Co., 2020).



» **Figure 1:** *Structure of Xerox silver toner: a) pulverized type of silver toner; b) emulsion aggregation silver toner; b) silver toner on the printing substrate, d) final silver print (FujiFilm, n.d.)*

Experimental part

The main goal of this paper is to test the variable silver toner cartridge created for the Xerox Versant 180 Press printing machine.

This means that now generation xerographic printing machines can use standard CMYK toner set, fluorescent CMY toner set, and special toners set which include gold toner, silver toner, white toner, and clear (varnish toner) (L. Co., 2021a).

The realization of the test began with the definition of a special printing form dimension 320 x 450 mm. The silver print patch was created with the vector graphics program Adobe Creative Suite Illustrator 2021. In the procedure for the Xerox Versant 180 Press (to recognize the printing form with silver tones) each printing element had to be defined as a spot color called SSilver (PMS PANTONE 877C). The finally printing form contained a halftone wedge from 0 to 100% TV with a step of 5% TV (multiplied by 3 times and positioned in a different position). The used printing machine is connected to an external RIP Fiery FS 200 with which the screen type is varied, ie linear amplitude modulated screening (AM 300 lpi) and frequency-modulated screening (FM 25 µm). The printing was done on matte-coated fine art paper, Maxi Gloss 170 g/m^2. (L. Co., 2021a).

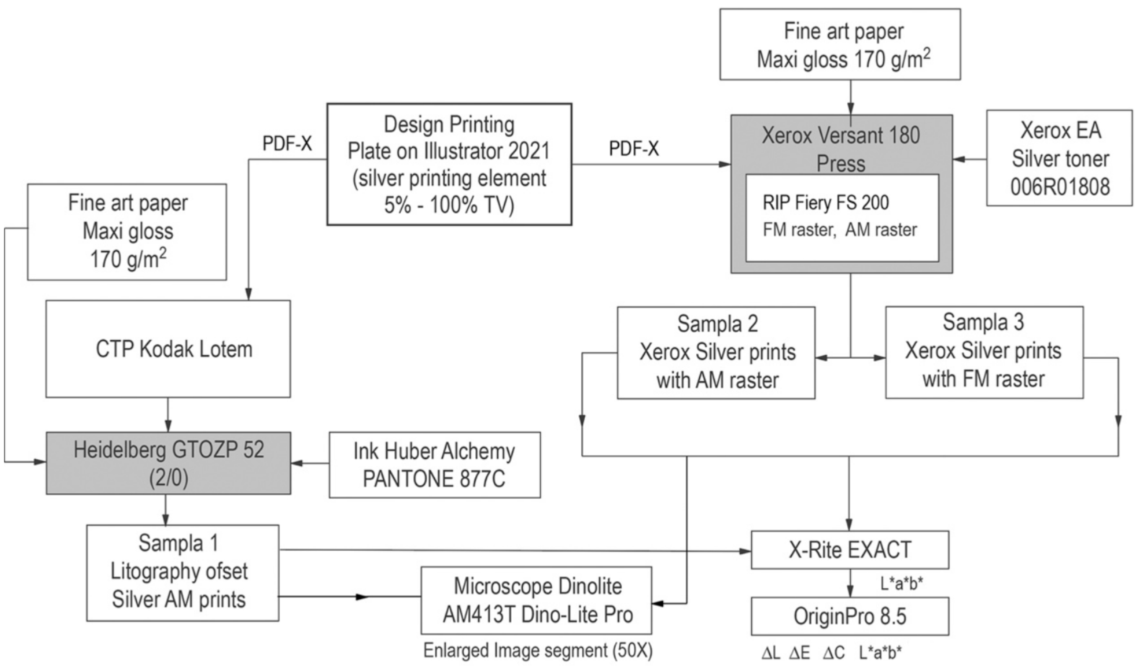
To determine the condition of the electrophotographic printing unit, SCTV reproduction curves were constructed. With SCTV reproduction curves is possible to perform compensation curves (adjust the tone values to the desired curve of the silver lithographic offset print).

For comparison of the achieved effects, the conventional lithographic offset printing was applied (two-color Heidelberg GTOZP 52 printing press). For identical design, a printing plate was created with a Kodak Lotem 400 thermal CTP device.

In the second experiment, an identical printing substrate was used, and a one-component silver offset ink PANTONE 877C was manufactured by germany producer Huber group (series Alchemy). From a printed pile were a choice of 10 imprints, on which a detailed colorimetric and microscopic analysis was performed. For colorimetric analysis, an X-rite eXact spectrophotometer was used to measure the characteristic silver halftone patch (10%, 20%, 40%, 70% TV) and solid silver tone (100% TV) (Gundlach, 2020). When determining the accurate reproduction curve (SCTV compensation curve), the measurement was performed without activating the polarizing filter (standard M0 measuring mode). However, during colorimetric measurements, a polarizing filter was activated, which eliminated the reflection from the printed silver surface (Habekost & Andino, 2016; Mannig &Verderber, 2002). A CIE 3D LAB diagram was constructed from the obtained CIE LAB data, and the differences between light (ΔL), color (ΔE), and chroma (ΔC) were determined. All data is graphically displayed using the Origin 8.5 application. Dino-Lite pro microscope AM413T was used for the visual evaluation of prints. For visual analysis of silver prints elements, we used enlarged images with a magnification of 160 times. Figure 3 shows a schematic diagram of executed experiment (Kipphan, 2001).

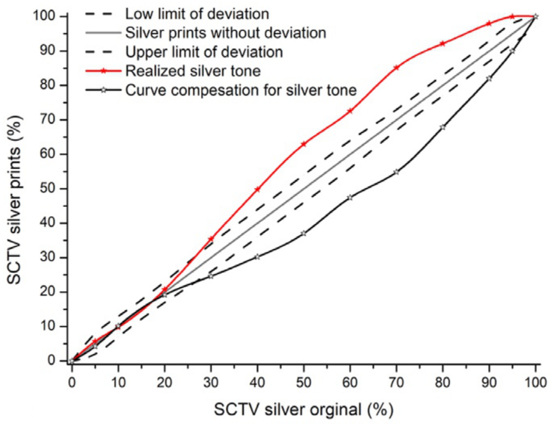
Results and discussion

For the creation of silver printing tones, two printing technologies were used: conventional lithographic offset and electrophotography with powder toner. To determine the initial surface coverage (realized with silver dot elements), preliminary densitometric methods were

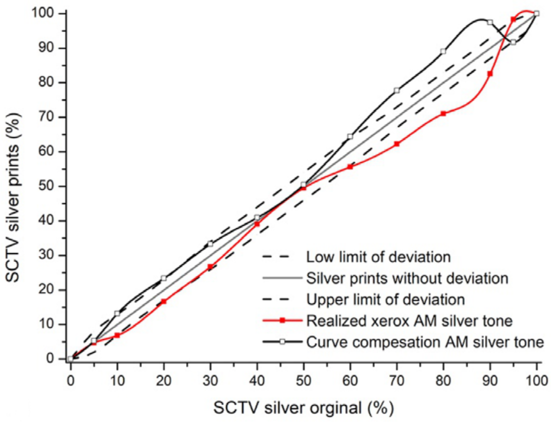


» **Figure 2:** *Schematic diagram of the performed experiment* used to determination of the tone values (SCTV curve) and comparison from the linear curve was performed.

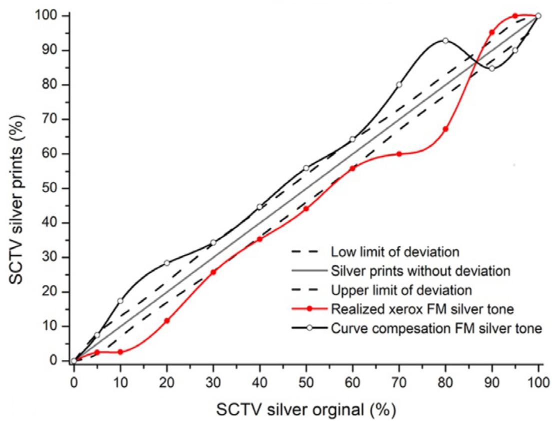
The densitometric settings used during the measurement (eXact spectrophotometer and densitometer) were: filter E, light source D50, standard observer 2°, measuring mode M0. Suggestion for the correction of all tested silver prints and compensation curves is shown in figure 3.



(a)



(b)



(c)

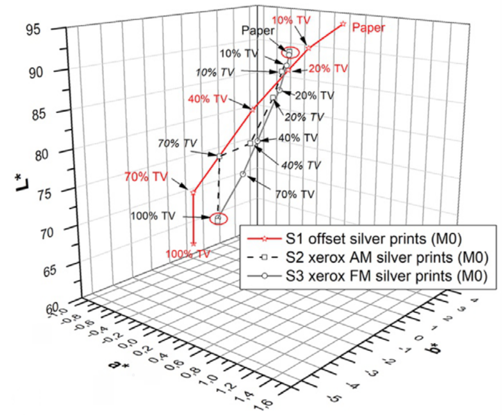
» **Figure 3:** *Realized SCTV curves of reproduction of silver prints: a) Heidelberg GTO; b) Xerox Versant 180 AM screening; c) Xerox Versant 180 FM screening*

The SCTV offset reproduction curve follows the ideal linear curve up to a surface coverage of 20% TV. After that, a higher dot gain was registered in all measured middle and dark tonal areas (exceeding the allowed tolerance limits ± 4% of SCTV). Xerox AM silver prints have a characteristic curve that is accurately reproduced in the central tonal range (40-50% of SCTV). Low tonal areas have a pronounced dot gain that follows the upper limit of standard tolerance. However, this does not apply to higher tonal areas (70-90% of SCTV). In this segment are reproduced with excessive dot gain. Particularly problematic is the patch of 95% of SCTV that has a negative dot gain and it is necessary to co-correct it. Changing the xerox silver imprint to an FM screening will have the desired effect of achieving an unwanted dot gain.

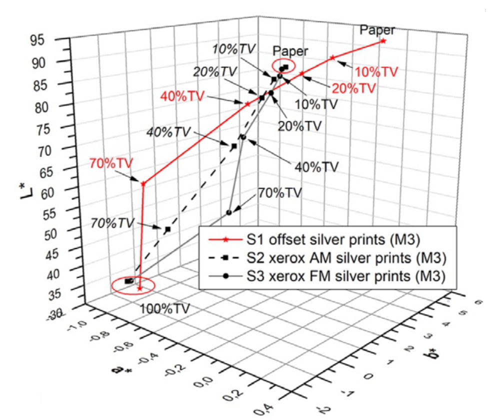
Thus, the stable part of the reproduction curve will be lost unchanged and will follow the upper tolerance limit (30-60% of SCTV). Low and high coverage of fine dot screen elements will achieve too high dot gain (20%, 30%, 70%, and 80% of SCTV), while the darkest silver screen area (90 and 95% SCTV) will have negative dot gain.

A much more important characteristic of silver prints is the colorimetric value of halftones. An important parameter that affects the realization of silver color images is also a method of screening. For colorimetric analysis of silver toner, two types of screening were used. To eliminate shine from the printed metallic surface, measurement with a polarizing filter (M3 measurement method) is recommended. However, as xerox prints contain very small particles of aluminum pigment, a measurement without the use of a polarizer was also tested (measurement with method M0) (Habekost & Andino, 2016; Mannig & Verderber, 2002). In figure 4. are shown color deviations amplitude modulated (AM) and frequency-modulated (FM) screening in relation to the reference lithographic offset print.

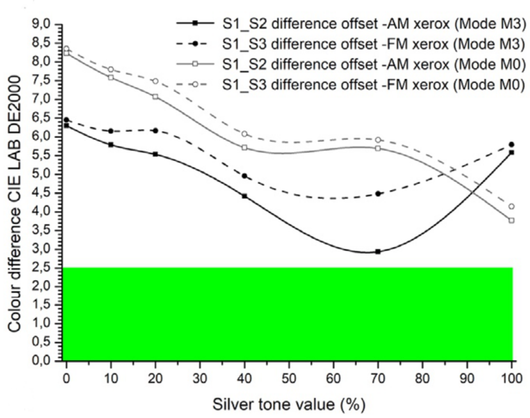
Significant differences in colorimetric measurements were observed from the CIE LAB 3D curves (Figures 4a and 4b). With the activation of the polarizing filter, longer curves along the z-axis (brightness) are achieved. This is especially confirmed by silver tones with higher surface coverage (70% TV and solid tone) where the M3 measurement method better describes the achieved color difference. Chroma of the prints did not experience major changes and the chroma deviation between xerox- offset patch is within the allowed validation tolerances ΔC <2,5. With the M0 measuring mode, light silver tones are somewhat saturated, while activation the polarizer (M3 metering mode) will reduce saturation. After printing in lithographic offset and electrophotography, a slight change in the value of the paper was detected. The reason for this change is the technological process of printing in which the dumping solution is absorbed into the printing medium (lithographic offset), while in electrophotography the print is exposed to high heat fuse rollers and required application of ICC profile (color management). With the activation of the polarizing filter (M3 measurement mode) the ΔE2000 color changes of the raster fields of the offset and xerography prints will decrease drastically (Figure 4c).



(a)



(b)



(c)

» **Figure 4:** *Color differences of offset prints and EA silver prints after screening modulation; a) 3D LAB print curvemeasured with M0; b 3D LAB print curvemeasured with M3; c) color change ΔE2000.*

Thus, for xerox prints from the FM screening, the average difference ΔE_{M3_M0} = 1.4 will be achieved; while the application of AM screening will achieve an average difference of ΔE_{M3_M0} = 1.8. The exception is full tones. They will display lower color deviations with M0 measurement mode ($\Delta E_{FM100\%\ TV}$ = 3.8; DEAM100% TV = 4.5). Experiments show that slightly better prints will be achieved by AM screening (mean DE_{AM_FM} = 0.64). There was a trend of decreasing color changes of silver screening fields due to the increase in the surface coverage of the print.

Realized color differences exceed the maximum of ΔE > 6, and the realized imprints do not match the boundaries of the potential contract proof and validation proof (Kraushaar, 2022). Because of that EP silver tones must be corrected. The reason for this is the need to use a dampening solution (emulsification of the silver ink is performed) which reduces the rheological properties of the offset ink and the silver solid tone of the imprint (Kirchner et al., 2007).

Raster imaging processor (screening device) also affects the achieved results (Figure 5). By image of print sample (enlarging and visually comparing the segment of dimension 2,10 x 1,60 mm), a large difference in the structure of the generated print elements within the silver prints was noticed. Thus, the conventional amplitude raster for offset printing is regular with visible round dot elements (average diameter (d) and circularity (c) of the printed dot in the range of 40% TV is d=195 μm and c=0,97.) This regularity continues in all silver tonal areas (patch) only increased the diameter of the dot elements. Used Fiery amplitude raster has a characteristic linear shape of the print element and is visually noticeable (reproduced) up to 60% of the TV. After that (darker silver tones) are realized as one frequency-modulated screening with different surface coverage in which the structure of the linear print element is lost. Thus, the dark silver tone areas of the AM Fiery raster look identical to the applied FM Fiery raster (small raster elements are the same size but with a different stochastic distribution). This fact confirmed the reason for the small color deviations in the Xerox silver imprints and the impossibility of achieving major color changes by applying different raster settings in the Fiery RIP.

Conclusion

When the machine operator measures a print with a larger number of silver tones (screened patch), it is necessary to activate the polarizing filter (M3 measuring mode) to reduce the color oscillation caused by excessive light reflection. The M3 measurement method has proven to be more suitable for measuring silver prints and allows precise comparison and creation of silver reproduction curves.

» **Figure 5:** *Images of segment silver imprints enlarged 160 times (after experimental printing)*

The initial setup of machines does not give satisfactory values and needs to be corrected. In lithographic offset, it is in the middle tonal areas while in electrophotography with powder toner in the low and high tonal areas. A particularly large correction needs to be made in the 95% TV area. In this case, the EA toner supply should be significantly increased.

In performed testing, the silver tones achieved in digital electrophotographic and offset printing technics have a significant difference. Silver tones generated in the solid patch (PANTONE 877C) will achieve a large color change of ΔEOF_Xerox = 4,2 (mode M0) ΔEOF_Xerox = 5,5 (mode M3). All xerox prints will look darker and with a noticed lower brightness.

Screening process (formation of a halftone silver image) will achieve additional and much higher color oscillations between offset and xerographic prints (ΔEFM_average = 5,70; ΔEAM_average = 5,05). By the variation of the Fairy RIP settings (AM and FM screening), a slight color deviation of the Xerox silver was achieved (ΔEFM_AM = 0,65). Slightly better results (closer silver-tone to offset) will be achieved by using the AM Fiery screening procedure.

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