Low-frequency correlations $(1/f^{\alpha}$ type) in paint application of metallic colors

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Abstract: We examine trial-to-trial variability of color coordinates in automotive coatings containing effect pigments, which are considered a reference paradigm for engineering angle-dependent color effects. We report the existence of correlations that show 1/f - Fourier spectra at low frequencies in all color coordinates. The scaling exponent was lower at near-specular conditions for lightness variations, suggesting a contribution from the deposition of metal flakes in metallic colors. However, the exponent was lower near the specular for blue-yellow variations, suggesting a contribution from chemical pigments in solid colors. These results were independent of the illuminant spectra. The methods employed are useful in the evaluation of industrial color matching among assembly parts.

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OCIS codes: (310.3915) Metallic, opaque, and absorbing coatings; (310.1620) Interference coatings; (310.1860) Deposition and fabrication; (290.1483) BSDF, BRDF, and BTDF; (330.1730) Colorimetry; (000.5490) Probability theory, stochastic processes, and statistics.

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1. Introduction

Automotive coatings are functional multi-layer thin films that can provide protection against corrosion, weather resistance and improved color appearance over time [1, 3]. The physical mechanisms of color appearance are a central issue and depend on the pigments deposited in the basecoat [1-3]. Two main categories of pigments can be considered: conventional

chemical pigments and effect pigments [1-3]. Chemical pigments can be organic and inorganic and have typical particle sizes less than microns. They can absorb light and produce diffuse scattering [1-3]. However, effect pigments are manufactured with particle sizes of several microns and they modulate the flow of light by specular reflection (e.g., metal flakes), multi-layer interference (e.g., mica-based pigments), and diffraction [1, 2], by producing angle-dependent color effects or "goniochromism" [2-4]. Those colored coatings containing only conventional chemical pigments are often called "solid colors" whereas those coatings containing metal pigments, "metallic colors" [2, 3]. Figure 1(a) shows an optical microscopy image of a metallic-green paint. Yellow squares labeled as "1" and "2" indicate an example of an aluminum flake and a mica-based interference pigment, respectively.

Fig. 1. (a) Optical microscopy image of a metallic-green paint (50x, dark field illumination). Yellow squares labeled as "1" and "2" indicate an example of an aluminum flake and a mica-based interference pigment, respectively. (b) Schematic representation of the illumination and detection positions for metallic colors at the aspecular angle γ of 15°, 25°, 45°, 75° and 110°.

The Bidirectional Reflectance Distribution Function (BRDF) is usually determined from a finite number of detection positions [2, 3]. For a fixed illumination angle (usually 45° from the surface normal), a set of detection or viewing angles is defined from the specular reflection (usually labeled as the aspecular angle, γ) [2, 3]. DIN (The Deutsches Institut für Normung) recommends the use of 25°, 45°, 75°, and optionally 110° angles from the specular [5], whereas the ASTM (American Society for Testing Materials), prescribes 15°, 45°, and 110° angles [6, 7]. Figure 1(b) shows a schematic representation of the aspecular angles recommended by the DIN and the ASTM [5-7].

Color matching among assembly parts is a complex issue that depends on a considerable number of errors from different paint application processes, manufacturing parameters, measurement errors as well as human factors. A classic example in the automobile industry is the final color appearance of the vehicle body that must be the same for add-on parts such as bumpers, fenders, spoilers, etc. (usually called "color harmony") [3]. For each color design, color tolerances are a set of thresholds that aid for the visual acceptance of car parts and they are usually defined relative to a reference or "master" panel at each viewing angle [2, 3]. However, the use of color tolerances ignores texture effects [2, 3] and does not relate the intrinsic trial-to-trial color variations with the deposition of different effect pigments. In the present study, we describe a novel method of examining color harmony in metallic colors. We measured the reflectance spectra of car pieces painted in the production line in serial order following the current standards of gonioappearance [5-7]. Reflectance spectra were transformed to color coordinates [2-4] and color coordinate variations were referred to the corresponding master panel. Each painted sample is therefore represented by its color variation and the entire batch production is mapped as color fluctuations in the time domain. These temporal color series are treated as stochastic time signals that can be transformed to the Fourier domain and the power spectral density can be estimated using a low-variance method [8]. A common type of correlations in many stochastic signals follows $1/f^{\alpha}$ Fourier power spectrum, where f is the frequency and α is the scaling exponent [9-11]. When there is no correlation in the color coordinate variations at different time scales, $\alpha = 0$, the Fourier power spectrum will be flat and all the frequencies have equal probability, i.e., the power spectrum will resemble "white noise". If $\alpha = 2$, there exits strong long-term correlations and the Fourier power spectrum resembles "Brown noise", i.e., similar to a random walker that follows a traditional one-dimensional Brownian motion over time [10, 11]. However, a wide range of phenomena and many mathematical models can obey to a scaling exponent α close to unity known as "flicker noise", "pink noise", "1/f noise" or "1/f scaling" [9-11]. Here, we ascertain whether the trial-to-trial variability of color coordinates in metallic colors are correlated over time and follows $1/f^{a}$ Fourier spectra. We also investigate the suitability of the exponent α to discern the contribution among different types of pigments by examining the

power spectra at different aspecular angles [see Fig. 1(b)]. Finally, the color series of metallic colors are compared to those of solid colors as a control condition.

2. Methods

2.1 Dataset and instrumentation

Two different color batch productions were examined. All panels were solvent-borne coatings and they were representative of original equipment manufacturer (OEM) paints of automobile suppliers in Europe. The outermost layer of typical solvent-borne coatings is a transparent lacquer that provides protection and a glossy finish. After that, the pigments are dispersed in a transparent basecoat providing the desired color appearance and opacity or hiding power [1-3]. The first color batch comprised of 159 plastic planar pieces. These were plastic pieces coated in serial order using a metallic-green paint. The color recipe contains lenticular aluminum flakes, mica-based interference pigments, conventional absorbing green and blue pigments and carbon black pigments [see Fig. 1(a)]. It corresponds to a typical metallic color that exhibits goniochromatic effects from a mixture of effect and chemical pigments [1-3]. Metal flakes are responsible for lightness changes and the interference flakes for chromaticity changes as a function of the aspecular angle γ . Flakes were oriented, on average, parallel to the substrate [1-3]. Color effects from aluminum and interference flakes dominate nearspecular reflection whereas those color effects from absorption pigments are predominant far from the specular [see also Fig. 1(b)] [1-3]. The second color batch comprised of 181 plastic planar pieces coated with a white-red paint. The color recipe contains only titanium dioxide [1] and opaque red pigments and corresponds to a typical solid color that shows poor goniochromatic effects. Both paints were uniformly spread using a painting robot [3] in a production line following the automotive standards for plastic parts [3].

Reflectance spectra were measured using an X-Rite MA68 II multi-angle spectrophotometer. This spectrophotometer is in agreement with the industry standards for metallic colors [2, 3, 5-7] [see Fig. 1(b)]. A calibration procedure was done periodically to perform white and zero reflectance reference measurements by using a certified white ceramic tile and a black trap, respectively. For each painted sample, its reflectance at each aspecular angle was averaged from a minimum of 4 consecutive recordings. The spectral reflectance factor was measured in the visible range from 400 to 700 nm in 10-nm steps within the range of 0- 400% in accordance with the operator's manual. The total number of reflectance measurements was 759 and 905 for the metallic-green and the white-red solid color, respectively.

2.2 Data analysis

2.2.1 Colorimetric analysis

The colorimetric methods employed are standard for the representation of pigmented coatings and they are described elsewhere [2, 3, 12]. The CIE (Commission Internationale de l'Éclairage, International Commission on Illumination) XYZ tristimulus values were calculated from reflectance spectra using the CIE 1964 10-deg color matching functions [12]. The XYZ tristimulus values were converted to the CIE 1976 $L^*a^*b^*$ color space (CIELAB) [2, 12]. Color variations are defined as the difference between the test and the master panel and they have both positive and negative values. They are denoted by the lightness difference ΔL^* , red-green, Δa^* and the blue-yellow difference, Δb^* or alternatively, in terms of ΔL^* , chroma difference, ΔC^*_{ab} (related with the saturation or the reciprocal of white), and the hue difference, ΔH^*_{ab} [2, 12]. Color differences were examined under four different illuminants. These were the CIE standard illuminants D65 and A as well as the spectral power distributions of the fluorescent lamps FL2 and FL11. The illuminant spectra selected reproduce most of the common illumination sources used in industrial color testing [2, 3, 12].

2.2.2 Power spectra

Different approaches exist to analyze the presence of correlations in short-time series [13]. Here, the Fourier power spectra is proposed because of its calculation simplicity based on a fast Fourier transform algorithm [8] and the widespread availability of Fourier analysis in engineering applications. Instead of using the discrete Fourier transform or periodogram, the Welch's method was adapted to the study of temporal color series. The Welch's method is an extension of the periodogram where the window segments are overlapped half their length and the variance per data point is reduced by a factor 9k/11, where k refers to the number of window segments [8]. The Bartlett window was used for data windowing [8] and the power spectrum was generated at different window sizes [8]. The lowest frequency that can be resolved depends on the window size and thus small and large windows are usually assigned to high and low frequencies, respectively. The power spectrum was generated using the first 128 painted samples of each color series at the window sizes of 4, 8, 16, 32 and 64. The lowest frequency available was 2/N and not 1/N, where N is the number of data points. This is because the power estimated at 1/N contains the largest variance and it can be affected by trends that mask the presence of 1/f noise [11]. The final power spectrum was the result of the lowest five frequencies that can be resolved at the different window sizes and it was normalized to the window sizes in order to preserve the frequency order. A similar procedure has been used successfully in time series analysis of different stochastic data [11]. In all color variations, the power spectrum was fitted to a power function in a linear plot using a nonlinear least square fitting procedure based on the minimization of the Chi-square statistics [8]. The regression coefficient R-square, R^2 , provided the goodness-of-fit [8].

3. Results and discussion

Figure 2(a) represents the color coordinate variations of the entire batch production associated with the metallic-green color in a linear plot. Color series are ordered in the time axis as a function of the trial number. Variations are expressed by ΔL^* , ΔC^*_{ab} and ΔH^*_{ab} because this particular color design has high chroma values and they correlate better with visual perception [2, 12], as indicated by the paint supplier. The temporal color series are represented at 15°, 45° and 110° , separately. Those color variations at 25° and 75° are at intermediate CIELAB variations and are not represented for the sake of clarity. The illuminant D65 was used. Color fluctuations are higher near-specular reflection than far from the specular and they are higher for lightness variations, ΔL^* . For instance, the range of values (maximum – minimum) for ΔL^* , ΔC^*_{ab} and ΔH^*_{ab} was 32.1, 16.4 and 14.3 CIELAB units, respectively at 15° and 4.8, 1.7 and 3.4 CIELAB units, respectively at 110°. Figure 2(b) represents the color coordinate variations of the batch production associated with the white-red solid color in a linear plot. Color variations are expressed by ΔL^* , Δa^* and Δb^* at 15°, 45° and 110°, separately, as recommended by the paint supplier. As expected, goniochromatic effects are residual except for the blue-yellow difference, Δb^* . For instance, the range of values for ΔL^* , Δa^* and Δb^* was 6.4, 2.9 and 11.36 CIELAB units, respectively at 15° and 7.3, 2.8 and 9.3 CIELAB units, respectively at 110°. Figures 3(a) and 3(b) represent the power spectra of the color series in Fig. 2 for the metallic-green and the white-red solid color, respectively, in a double logarithmic plot. Note that here frequency is not in Hz but in cycles per trial.

Fig. 2. Linear plot of CIELAB color coordinate variations as a function of the trial number. The illuminant D65 was used (a) Lightness ΔL^* , chroma, ΔC^*_{ab} and hue difference, ΔH^*_{ab} of the metallic-green color. (b) Lightness ΔL^* , red-green, Δa^* and blue-yellow difference, Δb^* of the white-red solid color. Data are presented at the aspecular angle γ of 15° (solid lines), 45° (dashed lines), and 110° (dash-dotted lines), separately.

The results demonstrate the existence of 1/f scaling in all color coordinate variations. In some cases there is a low-frequency white noise plateau suggesting that the color series shows no correlation at very long time scales i.e., a short-range process. These data points were

discarded from power law fits. In all cases, the coefficient R^2 was between 0.89 and 0.99 and the standard error of the resulting exponent α varied between 0.01 and 0.2. In the metallicgreen color, the power spectrum was higher at 15° in all color coordinates. Interestingly, the exponent α was close to zero at 15° (-0.25) for lightness variations, ΔL^* , but it increases near to unity (-0.9) at 110°. This suggests low correlations in the deposition of aluminum flakes. Regarding hue variations, ΔH^*_{ab} , the exponent α varies slightly from -0.7 at 15° to -0.79 at 110° suggesting a possible contribution from interference pigments. In contrast, the magnitude of the power spectrum for the white-red solid color was very similar at different aspecular angles except for blue-yellow variations Δb^* . The scaling exponent α remains invariant for lightness variations, ΔL^* , but it does not neither for red-green, Δa^* nor blue-yellow variations, Δb^* . In the latter, the exponent varies from -0.7 at 15° to unity at 110° suggesting a possible origin from the deposition of chemical pigments, measurement errors as well as corrections of the final color recipe in the line. Table 1 summarizes the values of the exponent α for different illuminants. Although there is some dependency with the illuminant spectra especially for ΔH^*_{ab} at 15°, ΔC^*_{ab} at 45° and for Δa^* , the analysis in Fig. 3 is corroborated.

4. Conclusion

We have demonstrated that trial-to-trial variability of metallic and solid colors show 1/f-Fourier spectra at low frequencies and reflects anomalous diffusion in comparison to the classic Brownian motion (α = 2). Although we cannot exclude a potential source of variability from instrument noise, the evaluation of the exponent α at different aspecular angles suggests that power law correlations may be derived in part from the deposition of pigments. Those car plants and supplier painted parts having the same exponent α in the same color design will share the same type of correlations over time. This is interesting in order to select the right painted pieces and thus to control better color harmony. Although noise analysis has been restricted to automotive coatings, the methods employed based on the Fourier transform are general may be useful in different industrial paint processes.

Fig. 3. Double logarithmic plot of the power spectrum generated from color series. The illuminant D65 was used. (a) Lightness ΔL^* , chroma, ΔC^*_{ab} and hue difference, ΔH^*_{ab} of the metallic-green color. (b) Lightness ΔL^* , red-green, Δa^* and blue-yellow difference, Δb^* of the white-red solid color. Data are presented at the aspecular angle γ of P5(circles), 45° (triangles), and 110° (squares), separately. Straight lines indicate power law fits. Numbers indicate the resulting exponent α at different aspecular angles.

		15°			45°			110°	
Metallic	ΔL^*	ΔC^*_{ab}	ΔH^*_{ab}	ΔL^*	$\Delta C^*{}_{ab}$	ΔH^*_{ab}	ΔL^*	$\Delta C^*{}_{\mathrm{ab}}$	ΔH^*_{ab}
D65	-0.25	-0.91	-0.70	-0.89	-0.76	-0.83	-0.90	-0.96	-0.79
А	-0.26	-0.92	-0.56	-0.89	-0.84	-0.83	-0.91	-0.92	-0.74
FL2	-0.26	-0.91	-0.69	-0.89	-0.69	-0.84	-0.90	-0.93	-0.73
FL11	-0.26	-0.91	-0.57	-0.89	-0.82	-0.85	-0.92	-0.94	-0.79
Solid	ΔL^*	Δa^*	Δb^*	ΔL^*	Δa^*	Δb^*	ΔL^*	Δa^*	Δb^*
D65	-0.73	-0.70	-0.72	-0.88	-0.70	-0.76	-0.75	-0.61	-1.10
А	-0.75	-0.74	-0.72	-0.89	-0.79	-0.73	-0.76	-0.86	-1.01
FL2	-0.73	-0.82	-0.76	-0.88	-0.80	-0.77	-0.75	-0.76	-1.02
FL11	-0.74	-0.88	-0.77	-0.89	-0.91	-0.77	-0.75	-0.89	-1.02

Table 1. The exponent α of the Fourier power law spectra at different illuminants and aspecular angles

Acknowledgments

Supported by the European Regional Development Fund – ERDF through Programa Operacional Factores de Competitividade – COMPETE (FCOMP-01-0124-FEDER-014588), by the National Portuguese funds through the Fundação para a Ciência e Tecnologia – FCT (PTDC/CTM-MET/113352/2009), and by the Center for Physics, University of Minho, Portugal.