Statistical Optics and Effective Medium Theories of Color

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Abstract

We discuss the relation between the color of a Xerographic image and the color of the individual toners (or pigments and binder) making up the image. We analyze the dielectric constant of the composite image in terms of those of the constituent colored toners via the use of static effective medium theories (EMTs). One application of EMT is to predict the color of toner as a function of varying pigment loading. Another application is to predict the color of an image as a function of amount of cyan, magenta, yellow, and black toner, i.e., color mixing laws. We show that different color mixing laws result for different pigment microgeometries in the color image. Variational bounds are able to limit the range of average image color obtainable for fixed amounts of color toners.

Introduction

In color Xerography an image may be composed of up to four types of color toner: cyan, magenta, yellow, and black. Each color toner is a composite, consisting of colored pigment suspended in a transparent binder. These four color toners are applied sequentially to surfaces, the photoreceptor, intermediate transfer belt, and ultimately paper. If the development, transfer, and fusing steps are sufficiently gentle the resulting multilayered image on paper may consist of segregated layers of fused monocolor toner. If, on the other hand, these process steps are disruptive to the colored toner layers, a randomized color image will result. The degree of randomization may vary continuously, from almost none, resulting in a layered image, to almost complete, resulting in a random composite image. The degree of mixing may depend not only on the nature of the machine process steps, but also on the type of paper on which the final image is formed. Coated papers are found to result in more lammelar color images than uncoated papers.

Both extremes in color images, randomly mixed and lammelar, can be obtained with Xerographic color machines currently commercially available or in development. In the present report we concentrate on the color of randomly disordered color images. (i.e., images in which the color toners at any point are randomly disordered spatially).

In such randomly disordered images, the overall image color will be determined by the percent of each toner present, and by the optical constants of those toners. Optics does not tell us how to relate the composition of a composite image layer and the dielectric constants of the constituent toners (or equivalently, the optical constants of pigments and binder) to average values which describe the overall optical properties of the image layer. These parameters must be obtained from other theories. We use effective medium theory to evaluate average optical parameters for use in calculating color.

The goal of effective medium theory (EMT) is to predict the average of a materials parameter (in this case, the complex dielectric constant) of a composite system in terms of the values of that parameter for each of the components of the composite. The basic approximation in EMT is to replace the composite image composed of particles (unfused toners) or domains (fused toner remnants) of different absorptive and refractive properties by a single medium whose average refractive and absorptive parameters are determined in a predictable way by those of the components of the composite system. Thus, EMT is not a theory of optical scattering, rather it is a theory which indicates how the parameters in optics calculations (or other calculations) for composite systems are related to those of the component parts.

The EMTs used to provide color mixing models were derived for static (infinite wavelength or zero frequency) properties via arguments involving spatially averaging electric fields. However, in color science we are interested in the frequency dependent complex dielectric constant $\varepsilon(\omega)$, where ω is 2n times the frequency of the light, or equivalently in the wavelength dependent $\varepsilon(\lambda)$. The static arguments used in deriving EMTs can be applied to the dynamic dielectric properties of composites, e.g., $\varepsilon(\omega)$ or $\varepsilon(\lambda)$, as long as a *quasistatic criterion is* satisfied [Lozovik and Klyuchnik[1]] requiring that the size of inclusions or domains to be averaged is small compared to the wavelength, λ, of light. In Xerographic toners pigment diameters range from approximately 20nm to 800nm, with volume-averaged diameters falling at approximately 80-150nm [Paine, Stone, Hooper, Gerroir[2]]. The visible light band covers the range from 380nm to 700 nm. Thus, the quasistatic approximation is approximately satisfied, and the predictions of static EMTs should be good approximations.

In this paper we analyze color as a function of the relevant material parameters of pigment and binder and the microgeometry of pigment in the image. We first discuss the reflectivity of a single-layer color image within the context of the Williams-Clapper[3] reflectivity model. We then show how parameters in the Williams-Clapper model can be obtained by effective medium theory. Applications to both toner color as a function of pigment loading, and color mixing laws for varying amounts of colored toners in color images are discussed.

Image Reflectivity

Color is determined by the wavelength dependence of reflectivity [Billmeyer and Saltzman[4]] of the image. The wavelength dependence of the reflection coefficient, and hence the color, in the present model is due to the wavelength dependencies of the complex index of refraction of the pigments, binder, and to the wavelength dependence of paper reflectivity. The reflectivity of single-layer color images on a paper substrate has been calculated by Williams and Clapper[3] as

$$R(\lambda)=\frac{T_{air-image}(\theta_1,\theta_2)t_{image}^{1+sec(\theta_2)}R_{paper}(\lambda)\,T_{image-air}(0,0)}{1+R_{paper}(\lambda)\quad\int d\Omega_3\, t_{image}^{2sec(\theta_3)}R_{image-air}(\theta_3,\theta_3)} \tag{1}$$

where θ_1 is the angle of incidence of light on the color image, θ_2 is the angle of light after specular transmission through the surface layer (which is assumed to be smooth). Light is assumed to exit the image normal to the surface. $R_{image\text{-}air}$ is the specular reflection coefficient of the image-air interface for light inside the color image. $T_{air\text{-}image}$ is the specular transmission coefficient of the image surface. These optical coefficients are given in terms of image dielectric constants or indices of refraction by standard optics texts [Born and Wolf[5]]. R_{paper} is the diffuse reflection coefficient of the paper surface, which is assumed to be a Lambertian reflector. The image layer transmission at normal incidence, t_{image}, is given by [Born and Wolf[5]]

$$t_{image}=\exp(-\frac{4\pi v_2 h}{\lambda}), \tag{2}$$

where λ is the wavelength of the light, and h is the thickness of the toner layer.

The parameter v_2 is related to the complex dielectric constant ε_2 in the absorbing toner layer by

$$v_2^4+v_2^2(\varepsilon_{2R}-\sin^2\theta_1)\frac{1}{4}\varepsilon_{21}^2=0, \tag{3}$$

where ε_{2R} is the real part of the complex dielectric constant of the imageε_2 and ε_{21} is the imaginary part of the complex dielectric constant. The complex index of refraction, n_2, of the image is related to the complex dielectric constant by

$$n_2=\sqrt{(\mu_2\varepsilon_2)}, \tag{4}$$

where $\mu2$ is the average magnetic permitivity of the image.

All of the color information within this single layer model is contained in the parameter v_2 through the effective complex dielectric constant $\varepsilon_2(\lambda)$ of the image layer, and through $R_{paper}(\lambda)$

Effective Medium Theory

EMT is a continuum theory; it replaces a complex multi-component medium which fills all of space with a single averaged material which also fills all of space. Edge effects are not considered. Thus, in the strictest sense, the use of EMT is limited to the analysis of solid area calculations.

There are several EMTs available in the literature, each of which predicts a different value for the average properties of a composite material in terms of those of the constituents [see Barrera, et al.;[6] for citations of recent literature]. Thus, there is no *a priori* prediction of the average optical properties of a colored image. These theories differ in their assumptions regarding the microgeometry of the composite.

Two of these models can be applied in a natural manner to Xerographic color images. The first of these effective medium theories is due to Maxwell Garnett.[7,8] Maxwell Garnett (MG) theory assumes a structure with separate particles embedded in a continuous matrix or binder. This microgeometry (for a single type of particulate inclusion) is appropriately applied in color Xerography to modeling toner as a composite composed of pigment particles suspended randomly in a polymer binder. For single colored pigment particles in a binder, this results in a continuum model for the optical properties of colored toner.

The single inclusion MG analysis results in the following expression for the average complex dielectric constant for the composite [Garnett,[7,8]]

$$\varepsilon_{MG}=\varepsilon_m\frac{3f_1\varepsilon_1+(1-f_1)(2\varepsilon_m+\varepsilon_1)}{3f_1\varepsilon_m+(1-f_1)(2\varepsilon_m+\varepsilon_1)}, \tag{5}$$

where ε_m and ε_1 are the frequency-dependant complex dielectric functions of the matrix (or host or binder) and inclusions (e.g., pigment), respectively, and f_i is the *volume* fraction of inclusion i. This theory is not symmetrical with interchange of inclusion and matrix material.

Each individual type of colored toner (C, M, Y, K) is a composite material, consisting of a mixture of the bind-er polymer, pigment, magnetite, carbon black, charge control agents, lubricants, etc. Given the pigment and binder complex dielectric constants, the optical properties of each colored toner (C, M, Y, K) be modeled using MG EMT in terms of the pigment loading and dispersion.

For a fused multicolor image, the multicomponent (n > 2) version of MG EMT [Wang and Wu[9]] can be used to predict the average complex dielectric constant of the composite image, assuming that pigments have been randomly distributed throughout the image in the fusing process. In the later application, this gives a color mixing model. This analysis gives where ε_m is

$$\varepsilon_{MG}=\frac{(1-\sum_i f_i)\varepsilon_m+\sum_i[3f_i\varepsilon_i\varepsilon_m/(\varepsilon_i+2\varepsilon_m)]}{(1-\sum_i f_i)+\sum_i[3f_i\varepsilon_m/(\varepsilon_i+2\varepsilon_m)]}, \tag{6}$$

the dielectric constant of the matrix material, and the ε_i are the dielectric constants of the n types of inclusions. The f_i are volume fractions of the i-th type of inclusion. All sums in Eq. (6) are from i = 1 to 4, the number of colored pigments in the image.

The use of multicomponent MG EMT, Eq. (6), for the effective image complex dielectric constant is equivalent to choosing a color mixing model. The MG color mixing model is only appropriate for microgeometries consistent with randomly distributed pigments in a percolating binder. The color mixing model which results from Eq. (6) is *pigment-based,* because it is assumed that each color pigment is randomly distributed throughout the image. The identity of individual toner particles in the fused image is assumed to be lost. This microgeometry does not appear to be appropriate for present Xerographic color fusers. However, the effects of building fusers with this property can be predicted by the model.

The second EMT of Xerographic interest is due to Bruggeman.[10] Bruggeman (BR) EMT is designed to model an aggregate structure in which domains of geometrically similar components form the aggregate. There is no distinguishable host and inclusion. The best application of the Bruggeman EMT in xerography is to the case of fused color solid area images. All of the different color toner remnant domains are treated on the same footing, there is not a need to view one color or component (e.g. binder) as a percolating matrix, as in MG theory.

The Bruggeman effective dielectric function for a two component system is obtained by solving the quadratic equation for ε_{Br}, which is obtained from

$$\frac{3f_1}{2+\frac{\varepsilon_1}{\varepsilon_{Br}}}+\frac{3(1-f_1)}{2+\frac{\varepsilon_2}{\varepsilon_{Br}}}=1. \quad (7)$$

where ε_2 and ε_1 are the frequency-dependant complex dielectric functions of the host (or matrix or binder) and inclusions, respectively, and f_i is the volume fraction of material i.

The Bruggeman model treats the host and inclusions on an equal basis (which the MG theory does not), as can be seen by noting that the effective dielectric constant expression [Eq. (7)] is symmetrical with respect to interchange of indices 1 and 2. This symmetric expression corresponds to a topology of spheres of both types of inclusions embedded self-consistently in the effective medium.

Eq. (7) reduces to [Landauer[11]]

$$\varepsilon_{Br}=\frac{1}{4}[\gamma+(\gamma^2+8\varepsilon_1\varepsilon_2)^{1/2}] \quad (8)$$

where

$$\gamma=(3f_2-1)\varepsilon_2+(3f_1-1)\varepsilon_1. \quad (9)$$

The Bruggeman model can also be used to predict the complex dielectric constant of toner as a function of pigment loading, just as the MG model. For low loading, as is usually the case in Xerographic color toners, the Bruggeman result reduces to the MG result.

There are multicomponent (n>2) versions of the Bruggeman result for the complex dielectric constant, just as there are for the Maxwell Garnett theory [Wang and Wu[9]]. The effective dielectric constant, ε_{Br}, satisfies the equation

$$\Sigma_i \frac{f_i(\varepsilon_{Br}-\varepsilon_i)}{2\varepsilon_{Br}+\varepsilon_i}=0, \quad (10)$$

where f_i is the volume fraction of material i, where the sum extends from i=1 to n for a ncomponent composite. Typically n=4 for a four color image, although residual air in an image may be included as a fifth component. Eq. (10) must be solved for each different n-case. The solutions diverges if one of the f_i's is zero.

The solution to Eq. (10) for ε_{Br} provides another color mixing model which will be different from the multicomponent MG EMT. The Br result, the solution to Eq. (10), assumes randomly distributed toner particles within the color image. Hence, the ε_i 's in Eq. (10) are toner dielectric constants. The MG EMT result, Eq. (6) assumes randomly distributed pigments within the color image. Thus, the microgeometry of the image dictates the color mixing law through the appropriate EMT.

The color mixing model which results from the Bruggeman model through solution of Eq. (10) is *toner-based*, in that the image is composed of different colored domains resulting from fused individual toner particles. If the properties of pigments and binder are known, the properties of toners can be calculated via the single-inclusion Maxwell Garnett model, Eq. (5). The dielectric constants of these colored toners can then be used in the Bruggeman model to predict the composite image color.

There are several similar EMT theories available in the literature, each of which predicts a different value for the average properties of a composite material in terms of those of the same constituents [see Barrera, et al.;[6] for citations of recent literature]. Thus, there is no *a priori* prediction of the average optical properties of a colored image. These theories differ in their assumptions regarding the microgeometry of the composite, in the size of the particles relative to that of the light being transmitted, or in the degree of randomness in the inclusion dispersion. A range of values for average optical properties can be obtained, depending on the geometrical assumptions made.

However, even though a range of values for the average complex dielectric constant can be obtained from those of the constituents depending on the microgeometry assumed, these average values are restricted. It is shown by a number of authors [see 1 for references)] that *variational bounds* can be formulated which enclose these EMT complex dielectric constant values. The Wiener[12] bounds do not make assumptions with regards to the optical isotropy of the image, and so are the most general. These bounds are given by

$$\varepsilon_{Reuss=}\ \Sigma_i \frac{f_i}{\varepsilon_i} \le \varepsilon_{eff} \le \Sigma_i f_i \varepsilon_i = \varepsilon_{Viogt}. \quad (11)$$

The lower Wiener bound is called the *Reuss limit*, and corresponds to the effective dielectric constant for fields perpendicular to a series of layers of optically isotropic material. The upper Wiener bound is called the *Voigt limit*, and corresponds to the effective dielectric constant perpendicular to a set of random side-by-side patches of optically isotropic material. These are rigorous bounds on the differences between the complex dielectric constants produced by different microgeometries, and hence by different EMTs. Thus, only colors over a restricted range can be produced in a disordered multicolor image.

We now have two expressions for the dielectric constants of toner as a function of pigment loading, Eq. (5) from MG theory, and Eq. (8) from Bruggeman theory. In the talk we compare the predictions of these models for color as a function of pigment loading for some commercially available color pigments.

We also have four expressions for the effective dielectric constant of a multicolor mixture, which can act as color mixing laws when used in conjunction with the Williams-Clapper reflectivity equation, Eq. (1) and the v_2 expression, Eq. (3). These color mixing laws are the Maxwell Garnett expression, Eq. (6), the Bruggeman expression, which is the solution to Eq. (10), and the Reuss and Voigt limits, given by Eq. (11). In the talk we compare the colors predicted by the use of these different EMTs or color mixing models for images formed from commercial color toners. We find that the Voigt limit on EMT dielectric constants gives the best agreement with color data. However, the difference between the colors predicted by the four EMTs is not great, indicating that color is not very sensitive to the microgeometry of pigment in the color image.

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