nmmm "nano-micro-meso-macro"
Colour and appearance – a multiscale approach

Patrick Callet; CAOR-Mines ParisTech-PSL University and Centre Français de la Couleur; Paris, France

Abstract

Among optical properties required for characterizing visual appearance in any lighting and viewing conditions, the most fundamental ones play an important role in predictive rendering. Spectroscopic ellipsometry is useful to acquire the complex indices of refraction of any homogeneous material. A multiscale approach using fundamental optical properties that are the components of the complex dielectric tensor of all the material compounds acquired separately is illustrated using automotive paints as an example.

Introduction

One can reads about hematite mineral in the dedicated webpage of "Mindat.org":
Originally named about 300-325 BCE by Theophrastus from the Greek, "aematitis lithos" for "blood stone". It is possibly the first mineral ever named ending with a "-ite" suffix. Translated in 79 by Pliny the Elder to haematites, "bloodlike", in allusion to the vivid red colour of the powder. The modern form evolved by authors frequently simplifying the spelling by excluding the "a", somewhat in parallel with other words originally utilising the root "haeme". This very spectacular changing in colour due to the grinding was, maybe, known in prehistorical cultures for engraving and painting use. The grain size impact on colour was also known by painters when they prepared their palette and decided how to adjust the lightness of their colour. Big grains are always darker than smaller[1]. This practical knowledge tends to disappear due to the industrial preparation of colours for fine arts by grinding, mainly since the 1850s. Ultrafine grinding is not easy and produces a lot of difficulties and risks for health. To avoid these problems the direct chemical synthesis of nanoparticles was prefered. This leads to a very accurate grains size distribution. We shall see, in the nexts sections, how the predictive chromatic properties are obtained using *intrinsic optical* properties. The main idea lies in two notions:

- the dielectric tensor components of all the compounds participating in a painting material;
- a homogeneization principle dealing with the scale transitions from nano to macroscopic visual properties

The first modelization we made, during the period 1992-1996, led to the rendering in spectral ray-tracing of interference colours as the scientific basis for the rendering of metallic paints[2]. The models appeared after reading the works of Franz[3] and Parker[4] describing multilayer mica pigments and natural biological structures. This kind of approach was known as physically based rendering. Today, spectral properties are considered at a more fundamental level than the macroscopic ones of reflection, transmission or emission of light. In a predictive rendering approach, this is also essential[6]. All the models briefly described hereafter use very intimate properties of materials. For several decades it was considered as pertinent the only reflection, transmission or emission spectra for scientifically defining visual appearance. Very nice pictures, while computed in trichromatic mode, were then produced, mainly for the movie industry then the video games market; these pictures are very different from our needs. We want to be able to take decisions of manufacturing any product on the basis of digital synthetic images. Colour "in ancient times" was then reduced to diffuse spectra for material characterization and the acquisition were made by spectrophotometry. Using specular properties of surfaces it is possible to reach a deeper level of knowledge on materials. To do this the required constraint is to produce a state of surface for which the Fresnel formulas are applicable (smoothness, planarity, no internal scattering).

Homogeneization principle

Predictive rendering needs to characterize all the visual properties of the materials being on design. For industrial painting materials, the good prediction of the resulting visual appearance based upon the known compounds really used, is essential. Once a complete chain of computation is defined and validated it is then possible to substitute some compounds having similar good optical data and chemical compatibilities (feasibility). The substitution, e.g. changing a pigment or a binder, must lead to a new colour or/and shininess for the new paint. In a new sense this is a WYSIWYG[1] process. The general method is based upon the use of *effective media theories*. A *unit cell* defining the most representative elementary volume[12] of the the composite material is defined. The compounds, particle and binder, are characterized by their complex dielectric tensor and more frequently by the complex refractive indices if the particles are in polyhedral shape with a lot of symmetries. Cubic or spherical inclusions are, by nature, optically isotropic. As we do not considered very asymetrical particles and no more particularly oriented the mean value of the complex index of refraction $n(\lambda)$ is used. This complex index, wavelength dependent, gather the optical index $n(\lambda)$ and the absorption index $k(\lambda)$. Effective media theories are formulated using the dielectric functions (relative permittivities) according to $n(\lambda) = \sqrt{\varepsilon(\lambda)}$ moreover than the indices. That is supposed a unit value for $\mu(\lambda)$, the magnetic permeability. That last property is pertinent for ordinary materials over the visible spectrum. The hypotheses made for the definition of the unit cell are: small characteristic dimension of the embedded particle compared to

[1]What You See Is What You Get: this old expression was important during the 80's in the computer graphics community. It means more today, dealing with visual properties and spectral simulation.

the wavelength, weak concentration p of particles to avoid any multiple scattering. That last restriction is necessary because the index of refraction of non-homogeneous particle does not make sense. We shall see further some adaptations of this hypothesis for a more dense medium. Thus an *effective* dielectric function $\varepsilon_e(\lambda)$ is evaluated *vs* $\varepsilon_i(\lambda)$, for the inclusions and $\varepsilon_m(\lambda)$ for the hosting medium (binder) ; the definitions are given, exluding the explicit wavelength dependence for more clarity, in the set of eq. (1).

$$\varepsilon_e = \varepsilon_{e1} + i\varepsilon_{e2} \quad \varepsilon_i = \varepsilon_{i1} + i\varepsilon_{i2} \quad \varepsilon_m \quad \text{(real number)}$$
$$n_e = \frac{1}{\sqrt{2}}\sqrt{\varepsilon_{e1} + \sqrt{{\varepsilon_{e1}}^2 + {\varepsilon_{e2}}^2}}$$
$$k_e = \frac{1}{\sqrt{2}}\sqrt{-\varepsilon_{e1} + \sqrt{{\varepsilon_{e1}}^2 + {\varepsilon_{e2}}^2}} \qquad (1)$$

One of the most efficient predictive model of colour properties is known as *Maxwell Garnett effective theory*. We use that model for the spectral simulation of coloured glasses[5, 14] or colloïdal solution. An example of complex index of refraction of red-purple glass containing a very small amount (0.05%) of spherical nanoparticles of gold is presented in Figure 1. It is important to understand what the influence of an absorption band on the real part of the index of refraction is. It is well known that the resulting colour of the glass depends on the shape of the nano inclusions. It is frequently found in Computer Graphics simulation, that a selective absorption is considered for the rendering of transparent materials. This is made without any modification of the optical index. That last error is found even in scientific simulation softwares. It is not possible, for physical reasons, to modify the optical index without modification of the absorption index. The two parts of the complex index of refraction are not independent but intimately linked by a causality law expressed by the Kramers-Krönig relationships[5]. The predictive model for simulating optical properties of nano particles embedded in a binder is built using mathematical and physical techniques (statistics, Fourier based computations, spectroscopic ellipsometry). We describe hereafter an example of coloured glass predictive properties. The Maxwell Garnett formulation, convenient for glasses and colloïdal solutions is then written down as:

$$\varepsilon_e = \varepsilon_m \frac{(1+2p)\varepsilon_i + 2(1-p)\varepsilon_m}{(1-p)\varepsilon_i + (2+p)\varepsilon_m} \qquad (2)$$

leading to the explicit relationships for ε_{e1} and ε_{e2} using eq. (1). The process of calculating an effective dielectric function may be repeated at several successive levels from nano to micro, micro to meso and, finally to macroscopic level. Notice that we admit the just discernable (macroscopic) visible detail is about 50μm of spatial extension. From the point of view of light, that dimension defines a huge structure, an interaction volume of about 10^6 times the mean wavelength over the visible spectrum. The laws of classical optics applied when the characteristic dimension of the particle interacting with light is greater than the wavelength. At lower observation levels and upstream from the quantum mechanics world, the scattering theories are required and combined with statistical parameters evaluation (vacuities and particles volume distribution, aggregates formation, etc.). The general process of homogeneization we used is given in Figure 2 below. The successive implemented steps for building the model are:

- Multiscale microstructure modeling from SEM images ;
- Numerical homogenization of its optical properties ;
- Comparison between numerical and measured optical properties ;
- Validation.

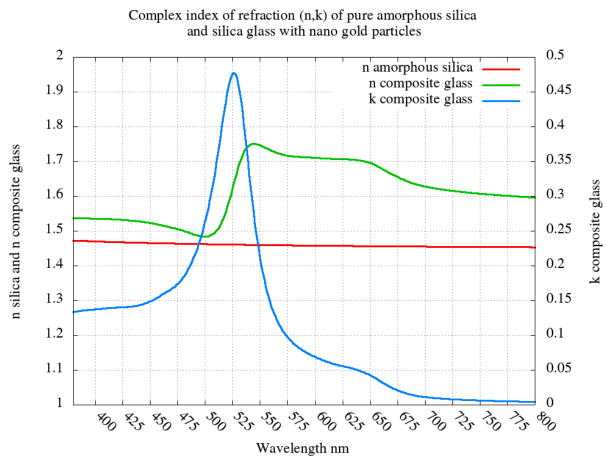

Figure 1. *Complex index of refraction of a silica glass including nano particles of gold at a volumetric concentration of 0.05% compared to pure amorphous silica. Notice the very important variation in the optical index not only in the neighbourhood of the absorption wavelength band.*

A so basic example, useful for the general comphension of the theories of effective media, permits to build a more sophisticated model validated by physical measurements and perceptual experiments.

An opaque paint and its compounds

The results presented here were acquired and produced within the LIMA[2] project. A paint is composed of, at least, two physical phases: a *continuum* generally called “binder” and a *discontinuum* generally called “pigments”. In automotive industry the binder is made of a resin (mainly epoxide) also used in the finition process as “clear-coat” so that it allows to have a varnish effect perfectly adapted to enhance the global paint gloss as it is in optical contact with the pigmented layers. Using classical pigments permits to produce “opaque paints” while nano-structured lamellar pigments (in 1D) leads to metallic lustre and goniochromatic properties. The visual effect, whatever the pigment structures, is always linked to a size parameter giving a visual appearance of *continuum* or not, depending on the viewing distance. As it was previously written we have to record the complex dielectric functions of all the compounds making the paint. Notice that these functions are intrinsic properties and, for that reason, do not depend on the size of the sample. We measured all the required dielectric functions by spectroscopic ellipsometry, a very accurate technique thanks to a small device available at the Museum of Mineralogy in Ecole des Mines de Paris. The reader is invited to learn more about this method, if necessary, with the excellent presentation made by Fujiwara[10]. A hematite pseudo-cubic crystal

[2]Light-Interaction-Material-Aspect supported by the french national agency for advanced researches ANR under grant 20284. Five academic labs and three companies were involved.

was selected in the museum (Figure 3) to match the optical properties of the nano pseudocubes produced by a controlled chemical process (reaction involving $FeCl_3$ in water with a CTAB surfactant at 180°C during 18h). The *continuum* was also characterized by spectroscopic ellipsometry. The optical constants are drawn in Figure 6.

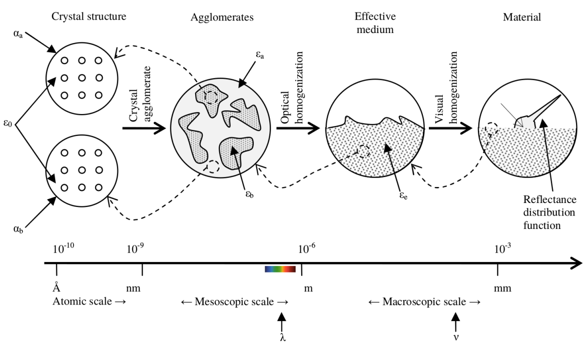

Figure 2. *The links between the successive scales of representation are presented in a schematic view from nanoscopic (crystallographic properties) to macroscopic visual properties.*

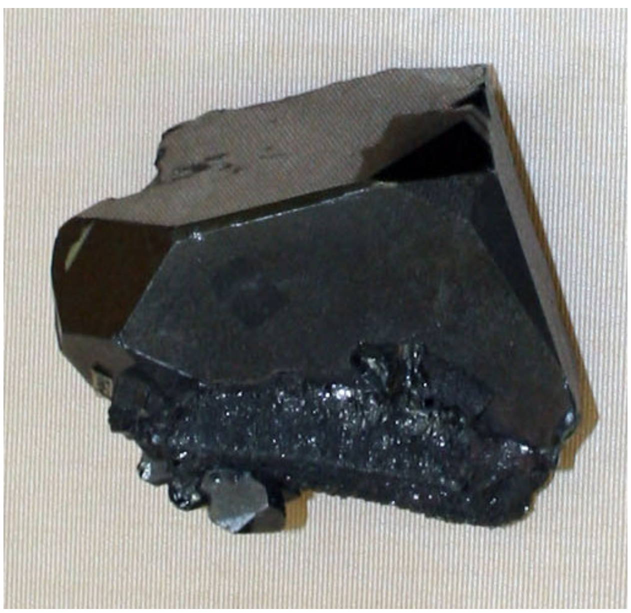

Figure 3. *A macroscopic sample of hematite having a sub-metallic lustre, displayed in the Mineralogy collection at Ecole des Mines de Paris, used for easily determine the dielectric tensor components by spectroscopic ellipsometry.*

Influence of the crystallographic structure

We were concerned by optical anisotropy of hematite crystals. Depending on the grinding process, the lamellar pigments can deposit similarly to aluminum platelets inside a paint film[13]. The scattering by the platelets edges could be negligible so that the useful optical properties lie within the petal plane of the rose-like crystals. Though it was not possible to measure the 3 dielectric permittivities of the sample presented in Figure 4 without modification of the state of surface (these crystals are museum's treasures) this situation is not critical. The results of such ellipsometric measurements, converted into complex indices are given in Figure 5. Though the difference in optical indices may appear important, it does not have a noticeable chromatic influence. A general evaluation could be made to estimate what are the just noticeable increase in n or/and k producing a visible change on the chroma. The embedded nano pseudocubes pigments inside a hosting medium made of epoxide resin and for a 7% volumetric concentration and a mean large diagonal of 250 nm are shown in Figure 7. These pigments give the sample a rusty-red appearance. When embedded in the epoxide resin, the hematite pigments give the same look as their own to the curves but have a less amplitude in n and k. This is not so surprising as the resin is very transparent while slightly absorbing in the red part of the spectrum. With a moderate pigment volumetric concentration, while very high in comparison to that of metallic pigments in a vitreous medium producing a more intense colour effect with a very few particles, we obtain that rusty-red coloration. The metallic appearance has been studied by McCamy, considering two scales of optical properties ; the interested reader may look at[18, 19].

Figure 4. *Anisotropic lamellar hematite crystals in rose-like shape having a high metallic lustre. Ellipsometric spectroscopic measurements were made in two independent directions taken in the petal plane, except in the third dimension (thickness) where no measurements were possible. The difference in optical properties is not very significant when used at nano or microcospic level. Museum of Mineralogy of Ecole des Mines de Paris.*

Combined with a SEM image analysis of real paints a statistical model[8, 9] was derived accounting for aggregates formation of platelets, emptiness distribution due to rheological and electrostatic properties of the mixture during the application process (platelets sedimentation, surface tension, cooling inhomogeneity, etc.). That model was built after the segmentation and binarization steps of the SEM images specifically produced. We also, in the same way, determine the optical properties of ethylcellulose as binder for several nano pigments concentrations and crystallographic shapes. All these measurements led to compute physically based images for some given environments with normalized lighting and viewing conditions. A visual comparison was made between a spectral and computed image of a metallic paint and the corresponding picture of the painted plate displayed in the same conditions of visualization on the same calibrated screen. Thus we could made comparisons between the elaborated model and the observed real paints, modifying the pigment volumetric concentration and the size of the exclusion zones (Figure 8). Different powders of synthetized crystals of hematite were pro-

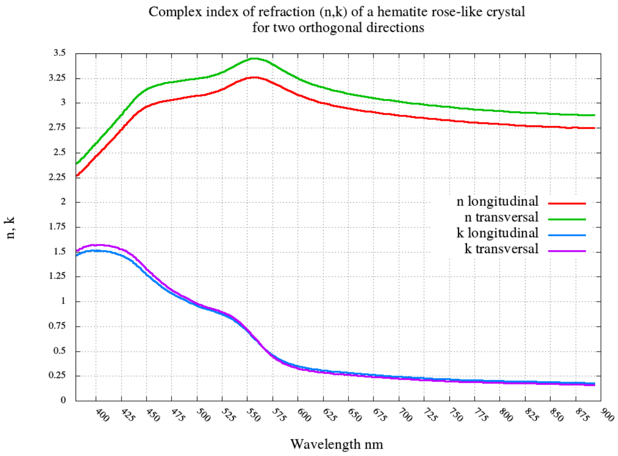

Figure 5. *Comparison of the complex indices of refraction of a rose-like hematite crystal measured for two orthogonal directions. The difference in absorption (curves "k") is very weak while it is not so negligible for the optical index. We nevertheless use a mean optical index.*

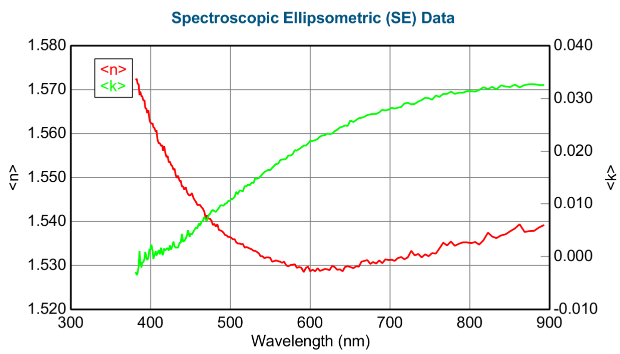

Figure 6. *The binder optical characteristics. Measured by spectroscopic ellipsometry, the optical data n and k exhibit a greater transparency in the blue region of the spectrum.*

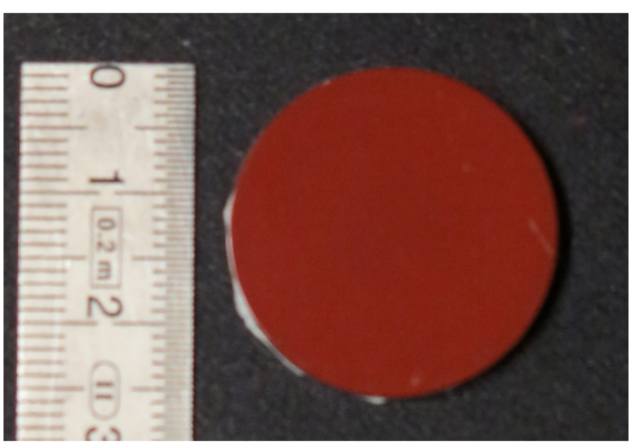

Figure 7. *We prepared several samples of embedded hematite pigments in several crystallographic shapes at the nanoscale and several concentrations (5 - 7 and 10%). Here is a nano pseudocubes powder inside an epoxide resin for a 7% volumetric pigments concentration.*

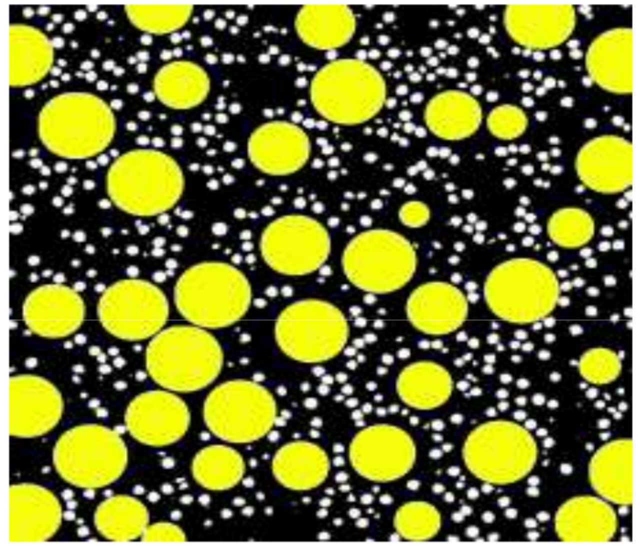

Figure 8. *From a statistical analysis of a SEM image of a real paint made of nano pseudocubes are extracted several parameters useful for a mathematical modeling: exclusion zones (yellow disks), concentration, contacts and alignments, etc. Image size: 20μm x 20μm.*

duced within the LIMA project framework. Three SEM images of synthetized rods, rhombohedral and pseudocubes shaped nano crystals are given in Figure 9. The corresponding dry nano pseudocubes powder is also shown in this Figure. The same method of measurements/computations was used for a slightly more complicated composite material, a grey metallic paint. In the previous case the Representative Elementary Volume[12, 11] or Unit cell was cubic due to the pigments properties and then, according to their specific properties, it will now be very flat: 450μm x 450μm x 20μm.

A real and virtual metallic paint

In situ measurements of the complex dielectric functions at a nano-micro level was also obtained by EELS (Electron Energy Loss Spectroscopy) on a metallic paint sample. The local measurement thanks to the SEM device permits to compare in several places of the sample preparation the local dielectric function to the macroscopic one obtained by spectroscopic ellipsometry on the separate phases[16]. The comparison for the same compounds was remarkable. The computer generated plates coated by virtual metallic paints differ according to the flakes density, diameters distribution, height repartition for the same chemical compounds. A photographic image of a real sample of paint and a computed image in spectral mode by simulation based upon the the previous analyses for determining the physical and statistical parameters were compared (Figure 10). These visual comparisons were made with a specific methodology (the viewer does not know which image among the two simultaneously displayed is computed). Thus we could made several variations in the spatial distribution of the metallic platelets, their orientation, the number of aggregates, etc. and proposed these images for comparison with pictures of real prepared samples on the same display device. To do that, the emission spectrum of the real light sources used were measured and the display device accurately calibrated. Another

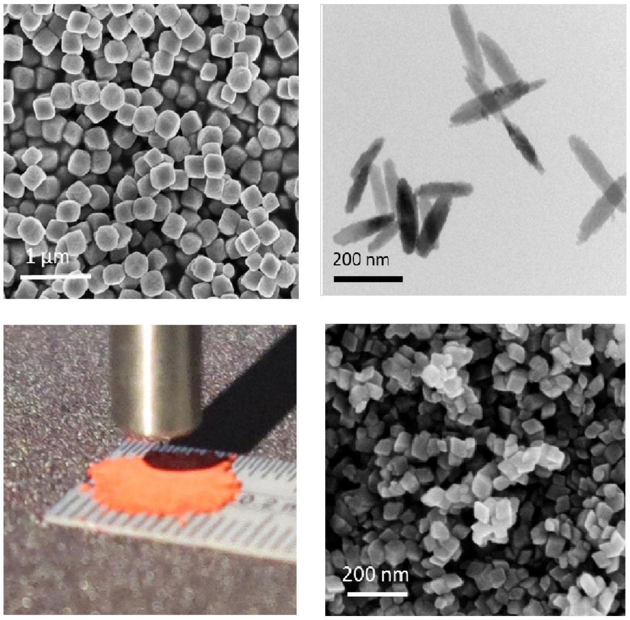

Figure 9. *Top left: nano-pseudocubes. Top right: nano rods. Bottom left: spectrophotometric measurement of the nano pseudo-cubes powder produced for making a red-orange paint. Bottom right: rhombohedral crystals.*

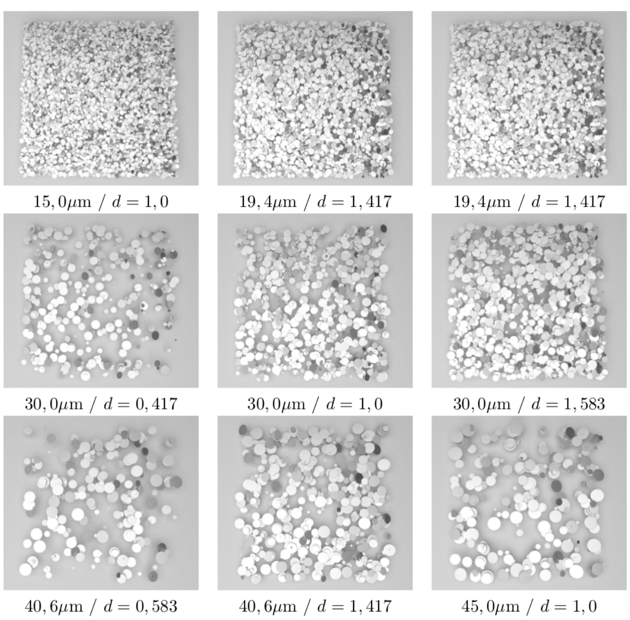

Figure 10. *A set of generated density maps containing several metallic flakes with various diameters and radii. The simulated sample of painted plates were obtained in the size of 15cm x 10cm including 332 x 240 microstructures.*

aspect of the validation process was the determination of the role of binocular vision of metallic paints. As, at a reading distance, the platelets appearing in specular mode are different for each eye this could influence the perception and identification of the material. A set of visual experiments were then proposed to about 40 volunteers where they had to discriminate between two images. The rendering in physically based mode of the appearance of such sophisticated materials was obtained thanks to the "LIMA Engine", a free CPU-GPU software elaborated within the LIMA project. It is centered on the use of measured BRDF, effective media computations, spectroscopic ellipsometric measurements always defined over a spectral range densely sampled. Charly Collin[20] proposed a BRDF approach based upon the radiative transfer equation solving in vectorial mode, while not spectrally computed. This model is derived from an atmospheric stratified description used in meteorology. It is not very convenient and no more pertinently applied to metallic paints as it ignores the interfaces separating the layers and the corresponding change in indices.

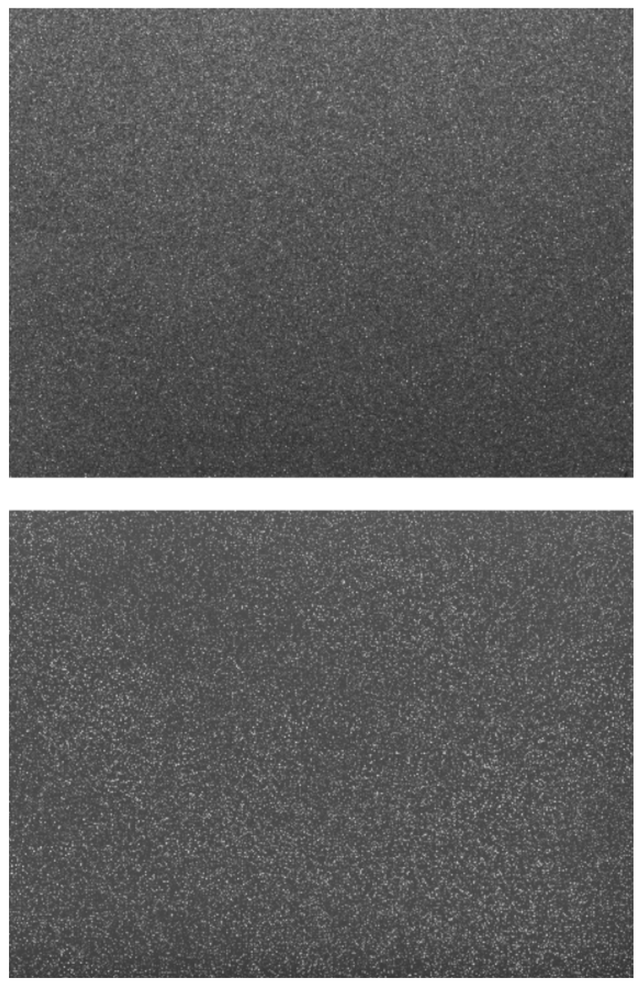

Figure 11. *One of the sets of images of the metallic paint plates displayed simultaneously for visual comparison. Top: picture of the "real" reference plate. Bottom: the computed image to be visually evaluated. The viewer has to choose what image is, according to him, the photograph of the real plate.*

An interesting model of visual properties depending on the viewing distance was proposed by Pattanaik and al. [17] ; we, nevertheless, prefered to make visual experiments by ourselves and manipulate the physical parameters for generating images, reproducing real ligthing conditions.

Conclusion

Within the LIMA project framework we got opportunities to work at a very low level of optical properties for preparing composite materials having an industrial interest. We studied in detail real materials used in automotive industry for making painted surfaces. It progressively appeared that fundamental and intrinsic properties of materials were involved in the restitution of the visual appearance for defined ligthting and viewing conditions. A specific spectral rendering software was also elaborated. A validation process took place based upon visual experiments involving unexperimented volunteer viewers. Predictive rendering of materials is very useful for taking manufacturing decisions within an industrial context. It is quite obvious that all functions must be used in a spectral representation even for the description of the environment (used as "environment maps") for a realistic and convincing result. As there were no spectral and polarized light sensor available to record such images and for combining with the other spectral data involved in the simulation, we decided to create such a missing tool. It is always under construction and validation[6].

References

[1] Patrick Callet, Pertinent Data for Modelling Pigmented Materials in Realistic Rendering, Computer Graphics Forum, 15, 2, pg. 119-128. (1996).

[2] Patrick Callet, Physically based rendering of metallic paints and coated pigments, Visualization and Modelling, Academic Press Ltd., pg. 287-301. (1997).

[3] Klaus-Dieter Franz, High Luster Mica Pigments for Automotive Coatings, Mondial Couleur 85, proc. AIC, Monte-Carlo. (1985).

[4] Andrew Richard Parker, 515 Million Years of Structural Colour, Journal of Optics A – Pure and Applied Optics, 2, 6. (2000).

[5] Max Born and Emile Wolf, Principles of OpticsElectromagnetic Theory of Propagation, Interference and Diffraction of Light. Pergamon Press, Oxford, 1975.

[6] Thomas Muller, Patrick Callet, Fernando da Graça, Alexis Paljic, Philippe Porral, Romain Hoarau, Predictive rendering of composite materials, A multi-scale approach , proc. SPIE, San Francisco, (2015).

[7] Sylvain Dumazet, Patrick Callet, Simulation of pearls, physically based rendering, the virtuelium approach, proc. AIC Congress, Sydney, (2009).

[8] Enguerrand Couka, François Willot, Patrick Callet, Dominique Jeulin, Optical response of a hematite coating: ellipsometry data versus Fourier-based computations, Advanced Science, Engineering and Medicine, American Scientific Publishers, 7, 11, pg. 925-931. (2015).

[9] Enguerrand Couka, François Willot, Dominique Jeulin, Mona Ben Achour, Anthony Chesnaud, et al., Modeling of the multiscale dispersion of nanoparticles in a hematite coating, Journal of Nanoscience and Nanotechnology, American Scientific Publishers, 15, 5, pg. 3515-3521(7). (2015).

[10] H. Fujiwara, Spectroscopic ellipsometry. Principles and applications, Wiley, Tokyo, 2007.

[11] D. Azzimonti, F. Willot, D. Jeulin, Optical properties of deposit models for paints: full-fields FFT computations and representative volume element, Journal of Modern Optics., 60(7), pg. 1-10. (2013).

[12] T. Kanit, S. Forest, I. Galliet, V. Mounoury, D. Jeulin, Determination of the size of the representative volume element for random composites: statistical and numerical approach, International Journal of Solids and Structures, 13-14, 40, pg. 3647-3679. (2003).

[13] S. Manickavasagam, C. Saltiel, H. Giesche, Characterization of colloidal hematite particle shape and dispersion behavior, Journal of Colloid and Interface Science, 280, 2, pg. 417-430. (2004).

[14] Maxwell Garnett, Effective medium models for the optical properties of inhomogeneous media, Philosophical Transactions of the Royal Society of London, B 203, pg. 385. (1904).

[15] S. Paciornik, O.d.F.M. Gomes, A. Delarue, S. Schamm, D. Jeulin, A. Thorel, Multi-scale analysis of the dielectric properties and structure of resin/carbon-black nanocomposites. The European Physical Journal of Applied Physics, 21, 01, pg. 17-26. (2003).

[16] Enguerrand Couka, Franois Willot, Dominique Jeulin. A mixed boolean and deposit model for modeling of metal flakes in paint layers. Image Anal Stereol, 32(2):813. pg. 97-100. (2012).

[17] Sumanta N. Pattanaik, James A. Ferwerda, Mark D. Fairchild, Donald P. Greenberg, A Multiscale Model of Adaptation and Spatial Vision for Realistic Image Display, Computer Graphics, 32, Annual Conference Series, pg. 287-298. (1998).

[18] C.S. McCamy, Observation and measurement of the appearance of metallic materials. Part I. Macro appearance, Color Research and Application, 21, pg. 292-304. (1996).

[19] C.S. McCamy, Observation and measurement of the appearance of metallic materials. Part II. Micro appearance, Color Research and Application, 23, pg. 362-373. (1998).

[20] Charly Collin, Sumanta Pattanaik, Patrick Likamwa, Kadi Bouatouch, Computation of Polarized Subsurface BRDF for Rendering proc. Graphics Interface, (2014).

Author Biography

Graduate from the university P. and M. Curie, PhD in Building Sciences, Habilitation to lead Researches in Computer Graphics (1998). Patrick Callet was scientific head of several projects concerning: 1. photonics and predicitve rendering 2. cultural heritage and colour retrieval He collaborates with great institutions in France such as prestigious museums (Louvre, National Museum of Asian Arts, Saint-Denis Basilica, Bibliothque Nationale de France. AIC delegate he is also President of the Centre Français de la Couleur.