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THE CORRESPONDENCE BETWEEN MACROSCOPIC APPEARANCE AND MICROSCOPIC COLORS INVESTIGATED BY LIGHT AND ELECTRON MICROSCOPY

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Keywords: effect pigments, real structure, color, SEM, TEM, FIB

ABSTRACT

Plate-like effect pigments (with diameters between 5 – 40 µm and less than 1 µm thick) are widely used to create decorative appearance in coatings, prints, plastics and cosmetics. Thereby it is well-known that the particles of one and the same ensemble do not have the same microscopic color; the colors will deviate from particle to particle and also over the surface of individual particles itself. Since the effect pigment appearance depends on the microscopic color as well as on its local lateral distribution, it is important to elucidate the reasons for these local changes for typical interference pigments.

INTRODUCTION

The continuous work to improve the pigments' coloristic behavior requires a strong control of the properties governing interference, absorption and reflection over the ensemble of effect pigments. The trend to more saturated colors on a macroscopic level can be followed by a more homogeneous distribution of the colors on a (light) microscopic level. As an example the development of interference colors from Iriodin® 9231 to Pyrisma® T40-24 SW Green via Iriodin® 9235 and Iriodin® 97235 is shown in **fig. 1a-d** (macrographs) and **fig. 2a-d** (micrographs). Although the more homogeneous microscopic color distribution is evident, the reason for having different local colors cannot be elucidated by only using light microscope images. Therefore, the recent work deals with an investigation into the real structural changes creating the local deviation from the averaged interference condition and yielding a local change in the color. For the sake of simplicity only effect pigments are tested whose layers are composed by a substrate (transparent) and a deposit (transparent or semitransparent).
From the physical description of color creation by thin film interference (and absorption) described in standard textbooks [1] the principal reasons of local color changes can be derived as follows:

- 1 local change in the optical thickness of the substrate
  - 1.1 local change in layer thickness and/or
  - 1.2 continuous change in layer thickness and/or
  - 1.3 local change in index of refraction
    - 1.3.1 by change in material (chemical reactions) and/or
    - 1.3.2 by loss or addition of material (e.g. air filled gaps)
- 2 local change in the optical thickness of the deposit; in full analogy to 1.
- 3 local bending of the flake

Thereby it is not important whether such structural deviations result from the normal crystallographic behavior of the material itself (fig. 4 – 6) or are induced by mechanical or environmental stresses (fig. 7 – 8).

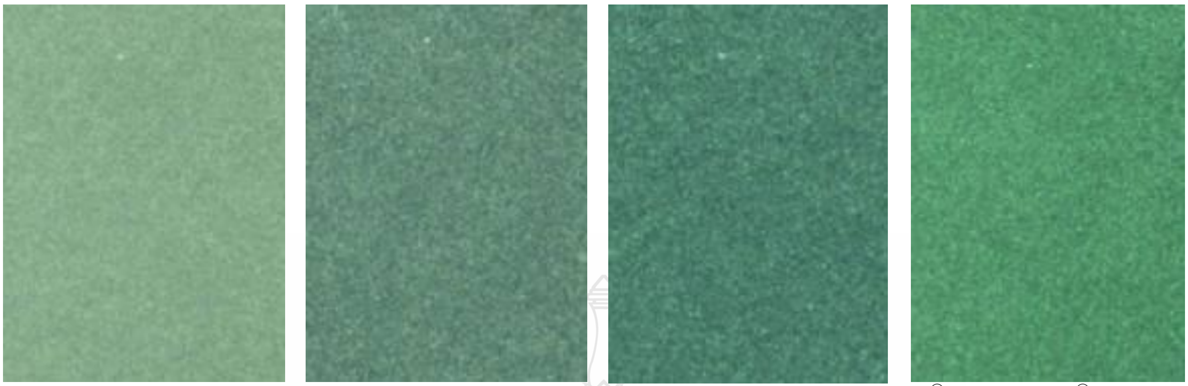


Fig. 1: Photographs of panels made of green interference pigments with rising saturation: Iriodin® 9231, Iriodin® 9235, Iriodin® 97235 and Pyrisma® T40-24 SW Green (from left to right)

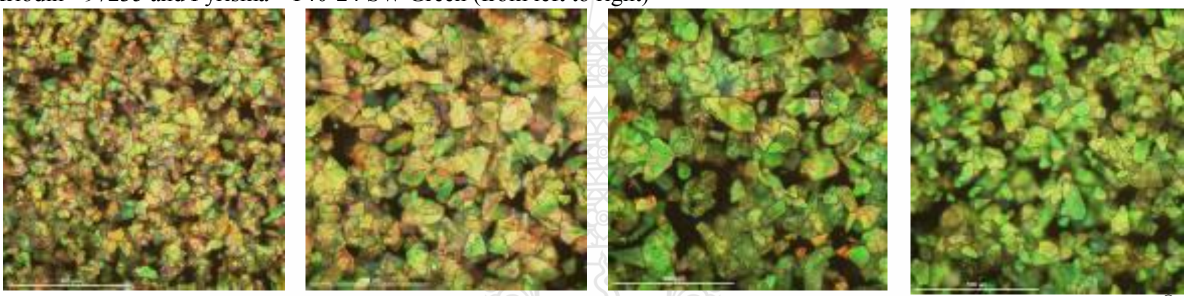
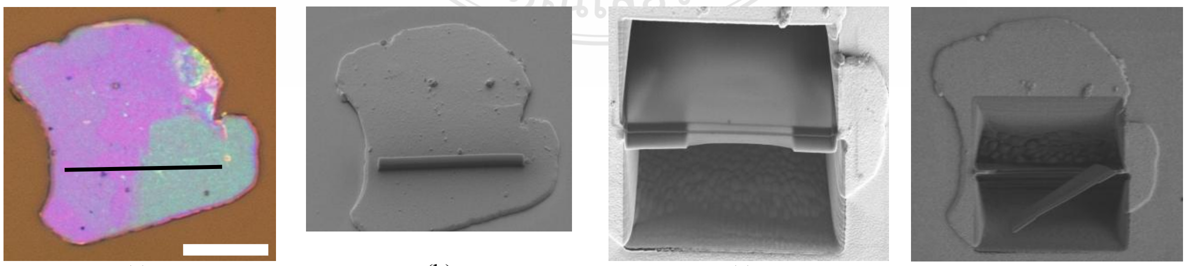


Fig. 2: Micrographs (bright field, obj. 20*, marker 100 µm) of green interference pigments with rising saturation: Iriodin® 9231, Iriodin® 9235, Iriodin® 97235 and Pyrisma® T40-24 SW Green (from left to right)

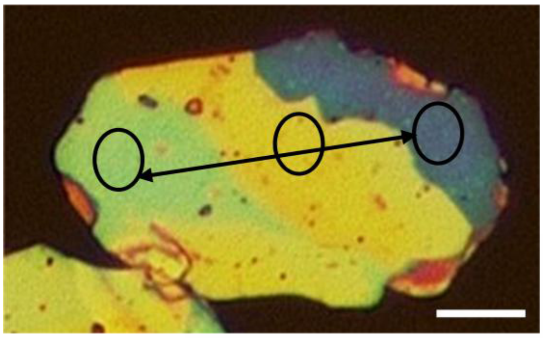
EXPERIMENTS AND RESULTS

The standard experimental procedure to analyze the real structure of effect pigments can be described as follows: **1**. Identify and mark local color deviation on selected flakes using a light microscope (**fig. 3a**), **2**. Analyze the color deviation roughly by color imaging or more accurate by micro-photo-spectrometry, **3**. Isolate and transfer this particle on a flat holder for focused ion beam (FIB) preparation, **4**. Protect the particle by depositing a metal layer (**fig. 3b**), cut the particle from both sides by an ion beam along the marked line (**fig. 3c**), lift of the lamella (**fig. 3d**), rotate and put it on a TEM grid, **5**. Analyze the geometry and the constituents by TEM imaging in diffraction contrast (**fig. 4 – 6b**) or SEM imaging in secondary electron imaging mode (**fig. 7 – 8b**) and microspot EDX. To carry out such preparations and analysis research light microscope Eclipse 90i /Nikon/Zeiss spectrometer, FIB (V600CE+/FEI), SEM (SU70 / Hitachi) and TEM (Tecnai G2 F20 STWIN/FEI) are used, respectively.

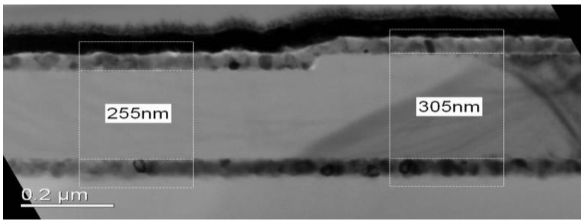


(a) (b) (c) (d)

Fig. 3: Light microscope imaging and marking of a local color deviation on a single particle (a), deposition of a metal protection stripe (b), both sided ion beam thinning of the lamella along the marked line (c) and lift of procedure of the lamella (d) [Pyrisma® T40-27 SW Indigo, marker 10 µm]

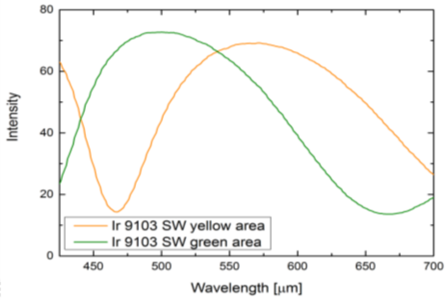


(a)

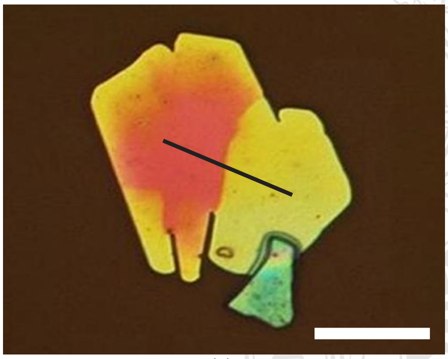


(b)

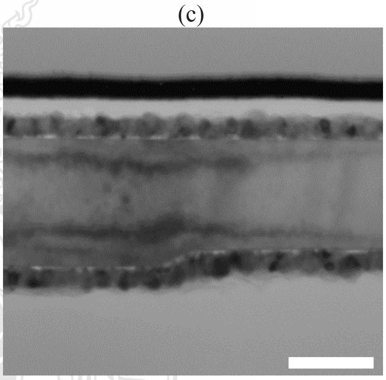
Fig. 4: Color variation on the surface of a (dielectric) silver-white particle composed of TiO_2 on mica [Iriodin® 9103 Sterling Silver SW, marker 10 µm] imaged with light microscope **(a)**. The colored patches are analyzed by their reflection spectra **(c)** and the change in the interference condition by TEM: steps on the mica surface yield different thickness of the mica layer for all color patches **(b)**. Fitting the spectral data on both sides of the step and the measured thickness of the layers with the interference formulae the local index of refraction of the deposit can be calculated.



(c)

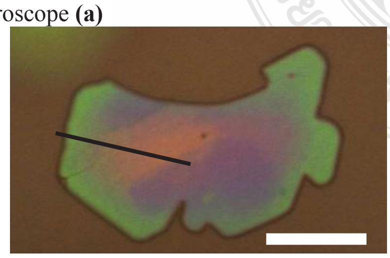


(a)

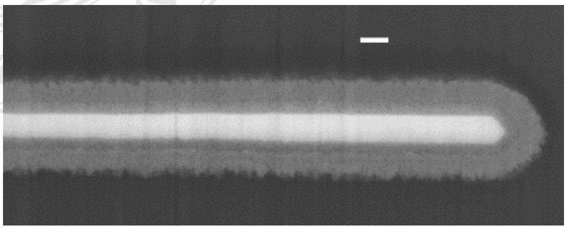


(b)

Fig.5: Color variation on the surface of a (dielectric) silver-white particle composed of TiO_2 on alumina [Xirallic® T60-10 SW Crystal Silver, marker 10 µm] imaged with light microscope **(a)** and analyzed by cross-sectioning the particle along the marked line: stepwise variation in the alumina thickness (marker 200 nm) **(b).**



(a)



(b)

Fig.6: Continuous color variation on the surface of a (dielectric) silver particle composed of TiO_2 on alumina [Xirallic® T60-25 SW Cosmic Turquoise, marker 10 µm] imaged with light microscope (a) and analyzed by cross-sectioning the particle along the marked line: continuous variation in the alumina and titania thickness from the center to the border area **(b),** marker 200 nm.

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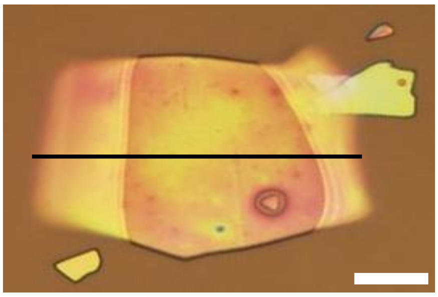
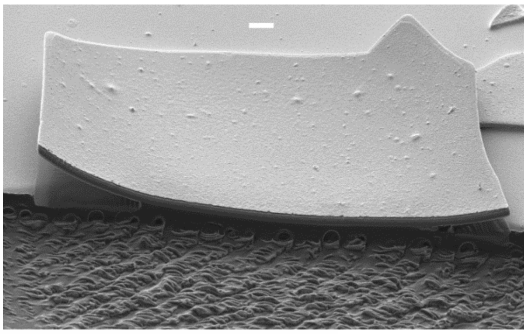
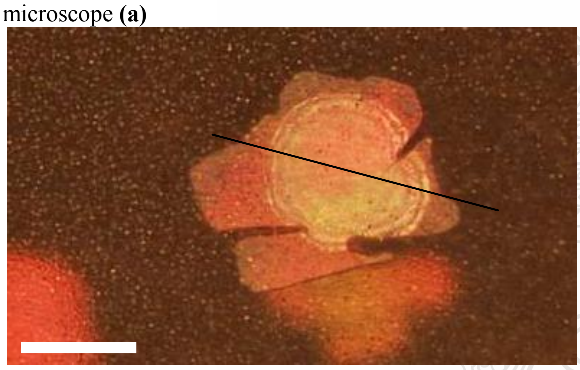


(a)

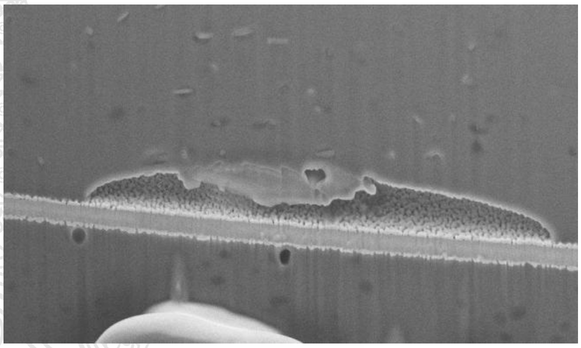


(b)

Fig.7: Continuous color variation on the surface of a particle composed of TiO_2 on silica [Colorstream® T20-01WNT Viola Fantasy, marker 10 µm] imaged with light microscope **(a)** and analyzed by cross-sectioning the particle along the marked line: continuous variation in the light incidence angle due to particle bending (marker 2 µm) **(b).**



(a)



(b)

Fig.8: Distinct color patches on the surface of a particle composed of Fe_2O_3 on alumina [Xirallic® F60-51 SW Radiant Red, marker 10µm] imaged with light microscope **(a)** and analyzed by cross-sectioning the particle along the marked line: delamination course an air filled gap between the particle surface and the binder. This air filled gap acts as additional interference layer with variable thickness creating interference lines and a local change in color **(b).**

DISCUSSION

For mica based neutral or tinted silver effect pigments, the step height distribution over the particle surface control the local color distribution which cause the desired macroscopic color by additive color mixture. For chromatic interference pigments step structures and the corresponding color deviations result in a reduction of the saturation in comparison to non-stepped structures. Sometimes the change in the height between adjacent steps and their distance is so small, that even with light microscope only a continuous color change over the particle surface can be observed. For amorphous materials as silica and glass flakes continuous changes in the thickness (wedged shaped geometries) lead also to continuous color changes over the particle surface. Since for gonio-apparent pigments the light incidence on the flake surface change the spectral composition of the reflected light bended flakes show a multicolor behavior. Additional layers (having constant or variable thickness) always influence the local colors. Such cases are found as delamination cracks between the interference layers and the substrate or the polymeric media and as foreign phases produced by chemical reactions or dissolution/removal of layers previously created.