



Hygrochromic Materials Generated by Multilayer of Elytron of the *Necrobia rufipes*

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Authors' contributions

This work was carried out in collaboration between all authors. Author IO designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors AO and BZ managed literature searches and analyses of the study performed. Author MT managed the identification of the specimen. All authors read and approved the final manuscript.

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ABSTRACT

This paper focuses on to the study of the origins of Blue spectrum reflections of the elytron of *Necrobia rufipes*, of large family of *Cleridae*. We combine experimental and numerical method, to explain the structure responsible of the elytron blue color. The experimental results have shown a main peak at 450 nm for dry structure and 548 nm for the impregnated structure, under specular angle incidence 15°. This band reflecting correspond blue and green color. The numerical reproduction of the reflectance spectrum gives 447 nm and 506 nm. These results confirm that the

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multilayer is responsible for the blue color. We notice that the angle of incidence increases, the main reflection peak moves to smaller waves length. The impregnated structure shows a very interesting property that change color depending on the relative humidity rate. This property can be used in the food industry to control the temperature.

Keywords: Blue spectrum reflectance; angle of incidence; relative humidity rate; multilayer.

1. INTRODUCTION

It has long been known that coloration of birds and insects was often due to structural frequency selection, a fact which was already questioned in 1911 in a paper by Michelson [1]. The whole concept was revisited by Lord Rayleigh a few years later [2]. The structural colors are found in bird feathers, in butterfly wing scales and many other biological surfaces, and organs [3-7]. The specific examination of beetles again dates back to Lord Rayleigh and these studies already concluded in the structural origin of the iridescence for these insects. The case has been further studied in more recent years, with better microscopic tools and on a much wider variety of species.

Thus, the specimen studied in this paper is the *Necrobia rufipes* (Coleoptera), belongs to the large family of *Cleridae*. The *Necrobia rufipes* can often be encountered from June to August, for instance, in the green vegetation bordering rivers and streams in Burkina Faso, West Africa. A dozen were captured and preserved in alcohol 90° for three weeks before the stocking at museum. This doesn't fundamentally alter the color of the elytra of *Necrobia rufipes*. Further, indication that the origin of blue reflections is in multilayer.

The male displays a spectacular iridescent blue color to violet. The phenomenon of but iridescence is not our investigation because Ouedraogo .l and al explained in a recent work. The female is seldom seen, because of predators and especially the female is less colorful [8-10]. The Fig. 1 showed the *Necrobia rufipes*. This paper deals with the origin of the blue colored reflectance from the male beetle's and structure that is responsible.

We use an experimental approach, the spectrophotometer, scanning electron microscope (SEM), and numerical method. Also, we study the behavior of the structure when it is impregnated with water.



Fig. 1. The *Necrobia rufipes* specimen

2. REFLECTANCE SPECTRUM MEASUREMENTS

The dorsal reflection spectrum has first been investigated using an Avaspec 2048/2 fiber optic spectrometer. Measurements were performed, under a 15° and 60° incidence, in the specular direction. The reflected intensity is expressed in units of the corresponding diffuse reflection obtained on a standard white diffusor.

We have two pieces of size 0.5 cm x 0.5 cm elytron *Necrobia rufipes* of which, one dry and other in water impregnated. The results are shown on Fig. 2. For the dry piece at $\theta=15^\circ$, we notice a strong reflection band extending between 400 nm and 500 nm, with main peak at 450 nm, explains the blue color observed on the elytron, and at $\theta=60^\circ$, the reflection band is extending between 150 nm and 400nm, with main peak at 380 nm. This indicates a violet color. Thus, for piece impregnated, at $\theta=15^\circ$, the band extending is between 500 nm to 580 nm (main peak is 548 nm), the color is green, and for $\theta=60^\circ$, the band extending is 400 nm to 480 nm (main peak is 450 nm), the color is blue. It is observed that the angle of incidence increases, the main reflection peak moves to smaller waves length. This is the case of the violet Color. The main peak moving in the spectrum shows the existence of a multilayer and also the phenomenon of iridescence. In the remainder of the study in our study, we will focus in single incidence angle 15°.

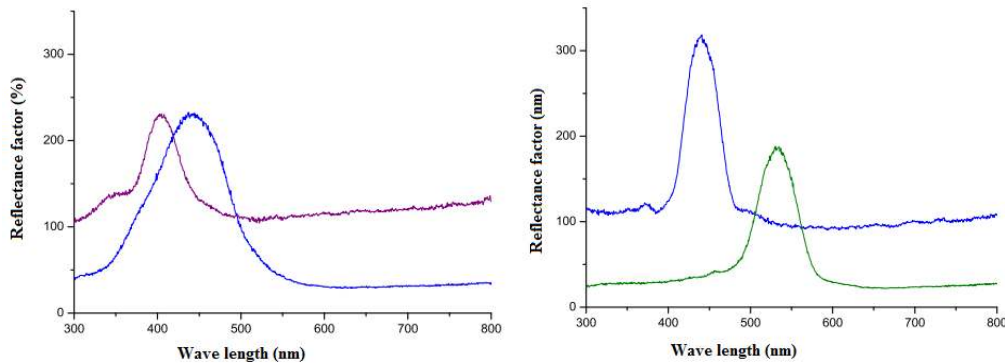


Fig. 2. Reflectance spectrum of elytron *Necrobia rufipes*, left side is the dry structure, the right side structure is impregnated with water, measured for the angles of incidence of 15° and 60°

3. ELYTRON INVESTIGATION

We use JOEL SEM 7500F type for investigation. All equipment is maintained under vacuum, which avoids the diffusion of the beam of electron. The sample of size of 0.5 x 0.5 cm the dorsal elytron of the *Necrobia rufipes*. Then, this sample is broken into two parts in liquid nitrogen at very low temperature, to maximize the risk of a complete break.

The image of Fig. 3 confirms existence of a multilayer. Indeed, the alternation is observed a dozen homogeneous layers composed of chitin and mixed layers formed of chitin and voids (air). SEM pictures also help determine the multilayer parameters. The thickness of a chitin layer is estimated to be 35 nm, and that of a chitin-layer air to 140 nm. Thus, the period (a) of the multilayer is at 175 nm. The structure responsible for the reflectance blue color of the dorsal elytron is a very thin layer of chitin. It is possible to determine the dominant wavelength reflected from the multilayer by the formula [11]

$$\lambda = \frac{2a\sqrt{\bar{n}^2 - \sin^2\theta}}{m} \quad (1)$$

Note that $\theta=15^\circ$ is defined as an angle of incidence relative to the surface of the multilayer. The period is determined by using SEM images $a=175$ nm. We use the values of thicknesses supplied by the SEM images and the dielectric constants found in the literature for air and chitin. In practice, we doesn't proceed with the refractive indices, but with dielectric constants ($\bar{n} = \bar{\epsilon}$ is average dielectric constant) $\bar{n} = \sqrt{\bar{\epsilon}}$, $\bar{n} = 1.32$. Very often in biological systems, $m=1$ (m is integer). The wavelength is estimated at $\lambda=448$ nm, and remains in the area of the blue color. λ is in good agreement with the measured spectrum to $\lambda=450$ nm. The calculation of the dominant wavelength in reflection gives a result that is fairly close to the results of measurements. It only allows us to account for the main peak of the reflectance spectra, and beyond this value no wave reflection is possible; it is also called the Bragg mirror.

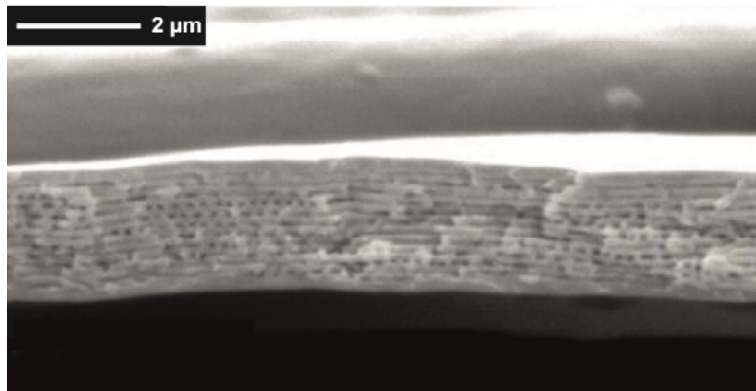


Fig. 3. SEM image showing the multilayer the origin of blue reflections of the elytron of *Necrobia rufipes*

Now, the empty areas of multilayer are replaced by water, refractive index 1.33. The application of the formula (1) gives $\lambda = 506$ nm (measured spectrum $\lambda = 548$ nm), with $\bar{n} = 1.47$. This value is in good agreement with the main peak of the impregnated structure. The Fig. 2 shows the variation of the coloration of the elytron insect gradually as the water evaporates. This leads to a decrease of the contrast of refractive index.

4. NUMERICAL MODELING METHOD

We use the method of transfer matrices to numerically reproduce the reflectance spectrum of the blue color of the elytron of the *Necrobia rufipes*. We consider a multilayer N period formed by the alternation of two types of thickness d_1 and d_2 , dielectric constants ϵ_1 and ϵ_2 . The z axis is the direction to the interfaces of the layers that is to say that the value of the dielectric constant varies along the z axis [12].

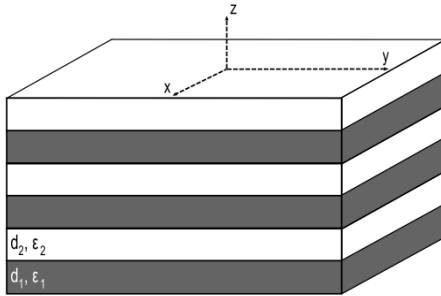


Fig. 4. Schematic representation of the multilayer

It is assumed that the medium is without charge density or current; and relative permeability magnetic unit $\mu = 1$. Maxwell's equations can be written:

$$\vec{\nabla} \cdot \epsilon(z)\epsilon_0 \vec{E}(\vec{r}, t) = 0 \quad (2)$$

$$\vec{\nabla} \cdot \mu_0 \vec{H}(\vec{r}, t) = 0 \quad (3)$$

$$\vec{\nabla} \cdot \vec{E}(\vec{r}, t) = \mu_0 \frac{\partial \vec{H}(\vec{r}, t)}{\partial t} \quad (4)$$

$$\vec{\nabla} \cdot \vec{H}(\vec{r}, t) = \epsilon(z)\epsilon_0 \frac{\partial \vec{E}(\vec{r}, t)}{\partial t} \quad (5)$$

Where: ϵ = dielectric constant, ϵ_0 = medium dielectric constant, μ_0 = magnetic permeability, $\vec{E}(\vec{r}, t)$ = Electric field, $\vec{H}(\vec{r}, t)$ = Magnetic field.

The multilayer has a translational invariance in the x and y direction. Then the component k_x

and k_y of the wave vector is kept the passage of each interface. This shows that we can find fields in the form of a monochromatic wave of angular frequency ω , propagating in the y direction, amplitude modulated by a vectorial function z :

$$\vec{E}(\vec{r}, t) = [E_x(z)\vec{e}_x + E_y(z)\vec{e}_y + E_z(z)\vec{e}_z] e^{ik_y y} e^{-i\omega t} \quad (6)$$

$$\vec{H}(\vec{r}, t) = [H_x(z)\vec{e}_x + H_y(z)\vec{e}_y + H_z(z)\vec{e}_z] e^{ik_y y} e^{-i\omega t} \quad (7)$$

By combining eq.6 and eq.7 to the Maxwell's equations (eq.2- eq.5). We write the following equations:

$$ik_y \epsilon(z) E_y(z) + \frac{d}{dz} [\epsilon(z) E_z(z)] = 0 \quad (8)$$

$$ik_y H_y(z) + \frac{dH_z(z)}{dz} = 0 \quad (9)$$

Equation (3) can be divided in three equations:

$$ik_y E_z - \frac{dE_y}{dz} = i\mu_0 \omega H_y \quad (10)$$

$$\frac{dE_x}{dz} = i\mu_0 \omega H_y \quad (11)$$

$$k_y E_x = -\mu_0 \omega H_z \quad (12)$$

Equation (4) can be also divided in three equations

$$ik_y H_z - \frac{dH_y}{dz} = -i\omega \epsilon_0 \epsilon(z) E_x \quad (13)$$

$$\frac{dH_y}{dz} = -i\omega \epsilon_0 \epsilon(z) E_y \quad (14)$$

$$k_y H_x = \omega \epsilon_0 \epsilon(z) E_z \quad (15)$$

The method involves solving eight equations, which reveals a possible separation of the field components. The first group contains only E_x , H_y and H_z . And the second involves only H_x , E_y and E_z . In the first case, the electric field is reduced to its component E_x perpendicular to the plane of incidence $\theta = 15^\circ$. This is an Electric Transverse Mode (ETM). In the second case, the magnetic field is reduced to its component H_x that is perpendicular to the plane of incidence $\theta = 15^\circ$. This is a Magnetic Transverse Mode (MTM). This separation is important because it allows you to search the polarization modes ETM and MTM. Then we can write the wave equations on each of the mode.

$$\text{ETM: } \frac{d^2 E_x}{dz^2} + \left(\epsilon(z) \frac{\omega^2}{c^2} - k_y^2 \right) E_x = 0 \quad (16)$$

$$\text{MTM: } \epsilon(z) \frac{d}{dz} \left(\frac{1}{\epsilon(z)} \frac{dH_x}{dz} \right) + \left(\epsilon(z) \frac{\omega^2}{c^2} - k_y^2 \right) H_x = 0 \quad (17)$$

The complete description of the transfer matrix method based on solving the Maxwell equations has been the subject of a recent by Ouedraogo I et al. [13].

5. NUMERICAL RESULTS

The numerical results of the calculations are shown in Fig. 5. The main peak was estimated at 447 nm for dry piece and about 506 nm for impregnated piece, which is within the range of blue and green color [14].

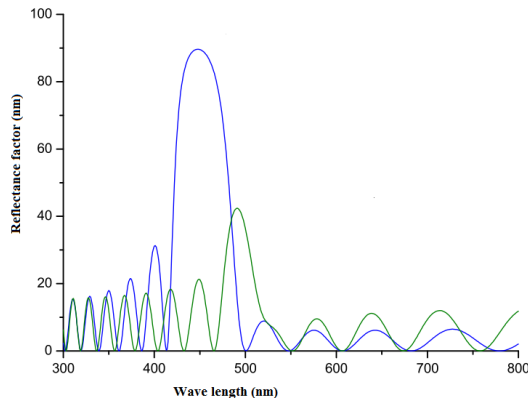


Fig. 5. Reflectance spectrum calculated according to the parameters of the multilayer observed on the elytron of *Necrobia rufipes*. The blue curve corresponds to the dry structure, the green curve in the impregnated water structure. The spectrums were simulated under of incidence of 15°

We compare the experimental and numerical results. The difference can be explained by the uncertainty angle incidence and also, the disorder present in the real structure, responsible for the variation of thickness and refractive indices of the multilayer. The numerical calculation of spectra reflects the decrease in intensity and refinement of the peak in the case of the impregnated layer.

The simulated spectrum also shows an appearance of small oscillation of the reflection band of the impregnated structure. These oscillations are due to interference of the multilayer.

6. CONCLUSION

In conclusion the results of the measurements show a main peak at $\lambda=450$ nm for dry structure and at $\lambda = 548$ nm for impregnated structure. The numerical results show a main peak at 447 nm and 506 nm. In Both reflection bands correspond to the blue and green color. SEM image can confirm the existence of a multilayer, composed of a dozen of chitin layers and mixed layers chitin-empty areas. This multilayer shows that the elytron of the *Necrobia rufipes* have interesting photonic structure. The empty areas of multilayer are too small to cause diffraction of light waves, enabling to modulate the mixed layers reflectance. The results of the measurements also show that when angle of incidence increases, the main reflection peak moves to smaller waves length for both the dry an impregnated structure. When changing the air refractive index of water at the impregnated structure of the multilayer, there is a color change.

This property of the multilayer can be used in the food industry (for example pellets which change color when the cold chain is interrupted) to regulate temperature. Also, structures that change color depending on the relative humidity content are called hydrochromic materials. This type of material allows a qualitative measurement for some highly degradable foodstuffs. They easily identified with the naked eye the color change.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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