Bioinspiration in Printmaking – Routes Toward Structural and Pigmentless Colour

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INTRODUCTION

Colour arises most prominently in the world from subtractive processes. For instance, if a material is dyed with a pigment, when a light is shone upon it, the pigment absorbs portions of the electromagnetic spectrum that the base material does not. This translates directly into a colour, that is, our eye's interpretation of one small portion of the electromagnetic spectrum, known as the visible spectrum (which are waves with a wavelength between 380 – 780 nanometers). For example, in general (though with some notable exceptions) leaves are green because the chlorophyll in them strongly absorbs the red and blue portions of the spectrum, leaving the green to be reflected, irrespective of factors such as viewing angle. It is interesting to recognize that the colour we assign to an object is in fact the colour which is 'rejected' by the material composition, as opposed to anything 'accepted' by it.

This concept of subtractive colour is so ubiquitous in printmaking that it doesn't often merit discussion. Subtractive colour pigments are the de facto method of colouration because they are widely accessible, easily manufactured and, most of all, cheap. However, as manufacturing methods become more complex and these pigments in turn become more accessible, we can begin to imagine colouration that is far more complex.

One benchmark of complex colouration or pigment-free colouration (more widely known as structural or iridescent colour) is widely seen in multiple natural systems. Species including insects, flowers, mammals, birds and marine life have all shown an aptitude for producing these colours and with varying evolutionary reasoning [1]. In these systems, the colour is produced by micro- and nano-scale structures that are small enough to interact with portions of the electromagnetic spectrum that larger structures normally wouldn't. The wavelengths, and therefore the colours that are interacted with, are specific to the size, spacing, structure and viewing angle involved. These factors can be tuned by tweaking these parameters, giving the material its iridescence: defined here as a colour that changes with viewing angle. This gives rise to the concept of biomimetics or bioinspiration in printmaking and art [2, 3, 4], taking inspiration from nature to design new materials and structures. In this article, we highlight three natural systems, increasing in complexity, that produce colour without the presence of pigment. We discuss exactly how these colours arise from internal material structure, before ending with brief

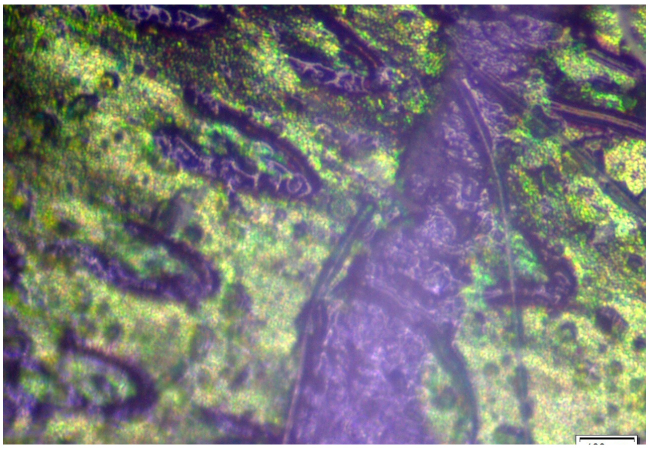

Figure 1

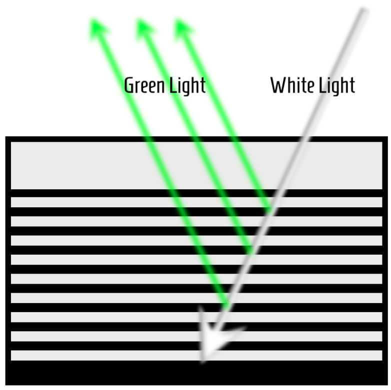

Figure 2

Figure 1: Microscope images of the Rose Chafer (Cetonia Aurata) (a) Underbelly and (b) Elytra (wing casing). Images are taken with a simple optical microscope and highlight the structural colour arising from the cuticle. Specimen provided by Niamh Fahy
Figure 2: Multilayer reflector that defines the generic beetle colouration struc- ture. White light enters, green light is selectively reflected and the remaining light is absorbed by a dark pigmented substrate

discussion of the current state-of-the-art in fabricated structural colour, effect pigments and the limitations on such colours.

BEETLES – CETONIA AURATA

Beetles are a particularly common example of structural colour. Their shiny metallic appearance has fascinated artists and scientists for centuries. Thomas Young was the first to explain the phenomenon fully in 1804 [5]. He suggested that the colour arose from the reflection of light from thin transparent films and that this reflection would change with viewing angle. Though this is by no means the only form in which structural colour arises in beetles, it is indeed the most common.

The chitin fibres that comprise the cuticle readily form into these thin films [6] and stack; a cross-sectional look at the exocuticle reveals this stacked structure. This can be seen in Ref. [7] and [8], and a rough diagram can be seen in Fig. 2. The depth of these films and whether they are all the same or vary determine the apparent colour reflected, and in turn gives us the vast visual differences between beetle species. Thinner films are perceived as blue and thicker films are perceived as red, while yellow and green lie somewhere in between. This relation is also cyclical: an increase or decrease of the thin films will reproduce the initial colour. This colour order has the same distribution as the visible part of the spectrum, going from low wavelength blue (470 nm) to green (530 nm) to yellow (580 nm) to longer wavelength red (700 nm). Other colours have been observed, arising from similar but more complex structures, including gold [9] and white [10] which are both common but distinctly different in their origin.

One example of this effect can be seen in the Rose Chafer (Cetonia Aurata) [8, 11], a beetle common in central Europe, the United Kingdom and Hong Kong. They display a striking metallic green colour, as can be seen in Fig. 1. Upon further inspection under the microscope, certain portions such as the underbelly can be seen to display tones of yellow, orange and red – as in 1a. This suggests local variations in the thicknesses of the chitin layers. Zooming in even further, markings on the surface can be seen revealing a black pigmented layer – this is crucial in ensuring these reflected colours are seen, otherwise they would be drowned out in the ambient white light.

To give these lengths a proper sense of scale, an average screenprinting mesh of 55T contains holes of a 105 microns in size. The fine, colour-providing layers within the cuticle of the Rose Chafer have a depth of roughly 550 nanometers (nm) per layer. This is 200 times smaller than the screenprinting mesh hole… or the difference in scale between an ant and an anteater.

SEASHELLS – GIBBULA UMBILICALIS

Though not as immediately obvious as a source of iridescent colour as the beetle shell, one particular example is widely known. The iridescent properties of pearls and Mother of Pearl have been treasured by

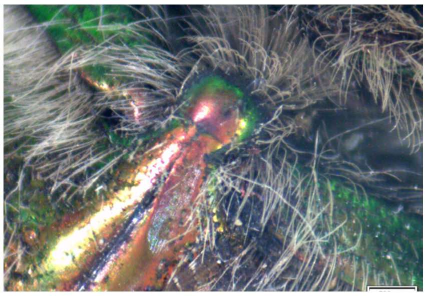

Figure 3

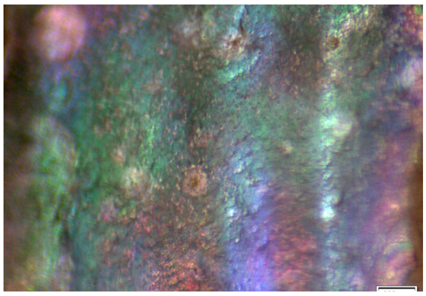

Figure 4

Figure 3. Microscope images of the Rose Chafer (Cetonia Aurata) (a) Underbelly and (b) Elytra (wing casing). Images are taken with a simple optical microscope and highlight the structural colour arising from the cuticle. Specimen provided by Niamh Fahy
Figure 4. Flat top shell (Gibbula umbilicalis). The layers of coloured nacre are more obvious under a bright white light and when viewed from an angle, sections of green and blue can be clearly identified. Capturing the silvery texture is difficult due to the smaller length scales we are observing – it arises from the combination of the 'brick and mortar' structure in bulk and is therefore more easily seen with the eye

society for centuries for their beauty. Pearl oysters, for instance, famously have an inner shell layer of a similar structure, that displays a silvery/metallic sheen that varies with viewing angle and displays hints of monochrome colours (red, green, blue etc.) under specific lighting angles and conditions [12]. In other species, this shift between silver and more specific colours varies prominently across the shell structure due to changing layer thicknesses [13].

These colours all arise from a 'brick and mortar' structure known as nacre, that wraps inorganic structures in an organic binder. It is comprised of aragonite building blocks, typically hexagonal thin discs that are 10 – 20 μm in diameter and 500 nm thick. These are bound by an elastic polymer, usually chitin, lustrin or otherwise. This structure not only provides colour but also general mechanical strength. The aragonite building blocks are again of the size order required to interact with the light that strikes it. The mechanism by which the light is reflected is a combination of the multi-layer reflectors that defined the beetle cuticle previously discussed, and a more complex interaction known as diffraction [14].

A common, and particularly interesting example, is that of the Flat Top Shell (Gibbula Umbilicalis). It can be found commonly on the western shores of the UK and western Europe, but also in some areas adjacent to the Mediterranean sea. They are known for the distinctive markings on the shell which show alternating pale yellow/green and dark purple/black in quick succession. These markings actually cover up the structural colour previously mentioned. However, if some of the outer layers of the shell are lost due to wear and tear from the ocean movement, the distinctive nacre structure is revealed beneath – suggesting that this structure may have evolved more for its strength and mechanical stability than for any colour effect. Fig. 3 shows this nacre structure under the optical microscope: the effect of zooming in diminishes the silvery texture one might expect, and instead reveals patches of reflective colour.

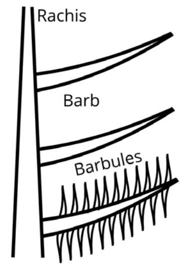

Figure 5

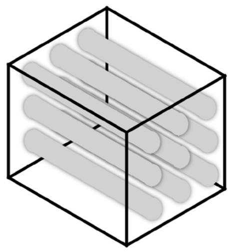

Figure 6

FEATHERS – PAVO CRISTATUS

Perhaps the most famous example of intense structural colour is that of the plumage of birds. Thought to be a sexual signal [15], large areas of pristine structural colour indicate high feather quality and thus a healthy individual. The mechanisms by which this occurs vary greatly between species [16], and occur in everything from regal peafowl [15] to the common magpie [17], and as such we will focus on one particular example.

The peafowl is known for its extravagant tail feathers that mix tones of green, yellow and blue into a distinctive 'eye-like' feature. The main body of the bird also displays a more uniform but still iridescent blue. The structure of the feather consists of a main stem or rachis, from which barbs span. From these barbs, barbules emerge – Within these barbules is a structure similar to that of the nacre structure previously discussed. However, instead of plates, there are rod structures

Figure 5. Toy diagram of the 'levels' of a generic feather structure, showing the main stem or rachis and the barb and barbule structures extending from it
Figure 6. Toy diagram of the feather structure – melanosome rods contained in a keratin matrix

(melanosomes), 1 μm in length and 150 nm in diameter, embedded in a keratin matrix [18]. These have a regular form and are stacked into a rectangular lattice, in which similar rod-like cavities are also embedded. The size and spacing of all these elements is what determines the output colour and this varies throughout the feather structure, between blue, green and no visible reflected colour.

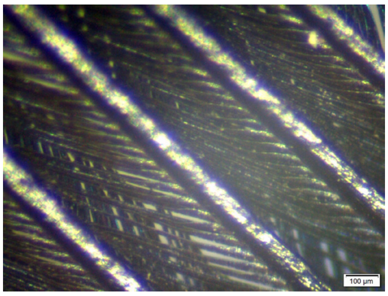

Figure 7

Figure 8

FABRICATION OF STRUCTURAL COLOUR

As seen in the previous examples, structural colour arises from complex and intricate forms that produce vibrant and distinctive colours. However, the unfortunate truth is that these structures are far too small for us to assemble by hand. State-of-the-art print techniques can be modified to produce structural colour through a combination of extremely precise ink deposition and formula- tion [19, 20, 21]. Alternatively, rather than attempting to build the structure directly, a process of self-assembly could be used, where the nano-structures required for colour are formed and built by the ingredients themselves. This only happens under certain conditions and so therefore requires careful tweaking of the ingredients and environmental conditions [22, 21]. Great care must be taken with systems of this type however, that are not pre- formulated for general use in print, due to the complex reactions that underpin them. Some of the constituent chemicals involved may be toxic/irritant and by extension dangerous, if not handled with care. These are an insight to the work being done at the cutting edge and therefore a glimpse into the future of what will be available, as methods of manufacture become more complex. The hope is that this increased complexity will allow for a finer resolution of structure and will allow us the breach the nano-scale architectures that produce so many vibrant colours in nature.

A far more efficient and safer method of fabricating a pigment-less colour is in the use of pre-formulated effect pigments. Typically described as lustrous and angle-dependent in response, these types of pigments are widely utilized in the fashion, automotive and cosmetic industries [23], but are relatively underused in printmaking. They are specially formulated for general use, providing a reflective, pigmentless colour. They usually involve the production of disc-shaped objects that act as a collection of tiny reflective mirrors. These discs are scattered randomly within the substrate, but tend to orient with their faces pointing upward, due to general rough stacking. If oriented randomly, usually by suspending in a medium, the lustrous effect is lost and instead the discs glitter. Coatings added to the discs can further affect the colour properties, depending on the material and thickness used. Examples of coatings include titanium dioxide and bismuth oxychloride, the latter of which was used as a component of cosmetics dating back to ancient Egypt. Their under-utilization in printmaking may lie in the fact that many of these pigments have relatively subdued and subtle colours, in contrast to the sharp and strong colours that traditional pigments can provide. (Stronger structural colours, such as those previously described in natural systems, are achievable, however this relies on constructing extremely ordered nano-structures.)

Figure 7. Peafowl (Pavo Cristatus) feather, from the main body of the bird, under the optical microscope. The largest structures seen here are the barbs. The fine barbules that extend from them and provide the structural colour can be seen in both, however the colour itself is hard to capture under the microscope. Specimen provided by Lorraine Leech
Figure 8. Toy diagram of the nacre structure – solid bricks of aragonite held together by long biopolymer chains that act as the mortar. The light that enters interacts with both the bricks and the mortar

The most common of these effect pigments is mica, a group of silicate minerals that exhibits a stacked plate-like or laminar structure with a strong tendency to cleave into thinner sheets [24]. Commercial versions of these pigments have been wide-spread for decades, used mostly for their glittering effects rather than for a particular shade of colour, and therefore can be applied in a less ordered way. The pigments themselves are relatively cheap and abundant and can be chemically altered in order to affect their colour properties, making them great candidates for iridescent colour. Although not a direct recreation of the structures previously defined, they can provide a similar effect. Due to mica being a mineral pigment, it has been historically more widely used in ceramic artefacts [26].

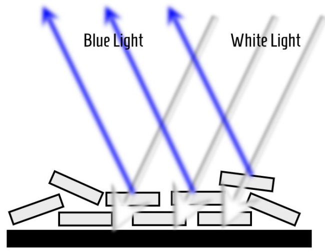

Figure 9

In printmaking, mica also has a fascinating history, having been used in Japanese woodblock printing [25]. Primarily used in ukiyo-e, a Japanese genre of printmaking from the 17th century to present day, a technique known as kirazuri was popular in prints by artists such as Sharaku and Utamaro. In this technique, mica powder is mixed into either the printmaking ink or more commonly dusted onto the print with a gelatin binder, or onto rice paste, resulting in a shimmering effect.

O¯tani Oniji III in the Role of the Servant Edobei by Sharaku is one particularly famous example of this technique in which the image is given a lustrous kirazuri background – however this optical effect is difficult to convey in digital images of the print and hard to appreciate on the computer screen.

Other more complex formulations exist that more closely mimic the structure of the beetle shell. These rely on the properties of cholesteric liquid crystals which self-assemble into stacked thin films that selectively reflect specific colours [2]. Industrial formulations of these types of inks exist, however they can be expensive and require careful application in order to achieve intense colours.

The use of effect pigments and more complex structural colours present an interesting conundrum for printmakers seeking to include them in their work. As previously described, they allow for colours that shimmer and vary depending on the lighting and viewing angle and provide an interactive optical effect that is immediately noticeable. However, the trade-off here is that these effects are impossible to capture completely in a single digital image and it can therefore be difficult to appreciate without a physical artefact in hand. (This could be considered a positive in terms of supporting the ownership of images with subtle materiality, in comparison to interacting with a digital representation of it.) Furthermore, the issue of colour intensity of effect pigments is something that should improve with time. Ink formulations will increasingly allow for greater degrees of accuracy with the structures they intend to self-assemble. Using technology such as 3D printing may allow for more precise layering, selective deposition and patterning in printmaking in the future.

Figure 9. Toy diagram of selectively reflective mica pigments. Due to their disc-like shape, they work best when all laid flat on the substrate. However, stacking faults are inevitable and can cause the intensity of the colour to be reduced

CONCLUSION

The origins of colour in nature are surprisingly complex and provide endless fascinating test cases to unravel. Ref. [27], in particular, provides a much more comprehensive overview on the wide range of structures that have evolved. I have discussed have picked a handful of examples and attempted to define both the structures and the colour that arises from them. In addition, I have discussed state-of-the-art research into structural colour in an attempt to provide a glimpse into the future of complex pigments, and highlighted some types of pigments that are currently available which could be easily integrated into the printmakers' toolkit.

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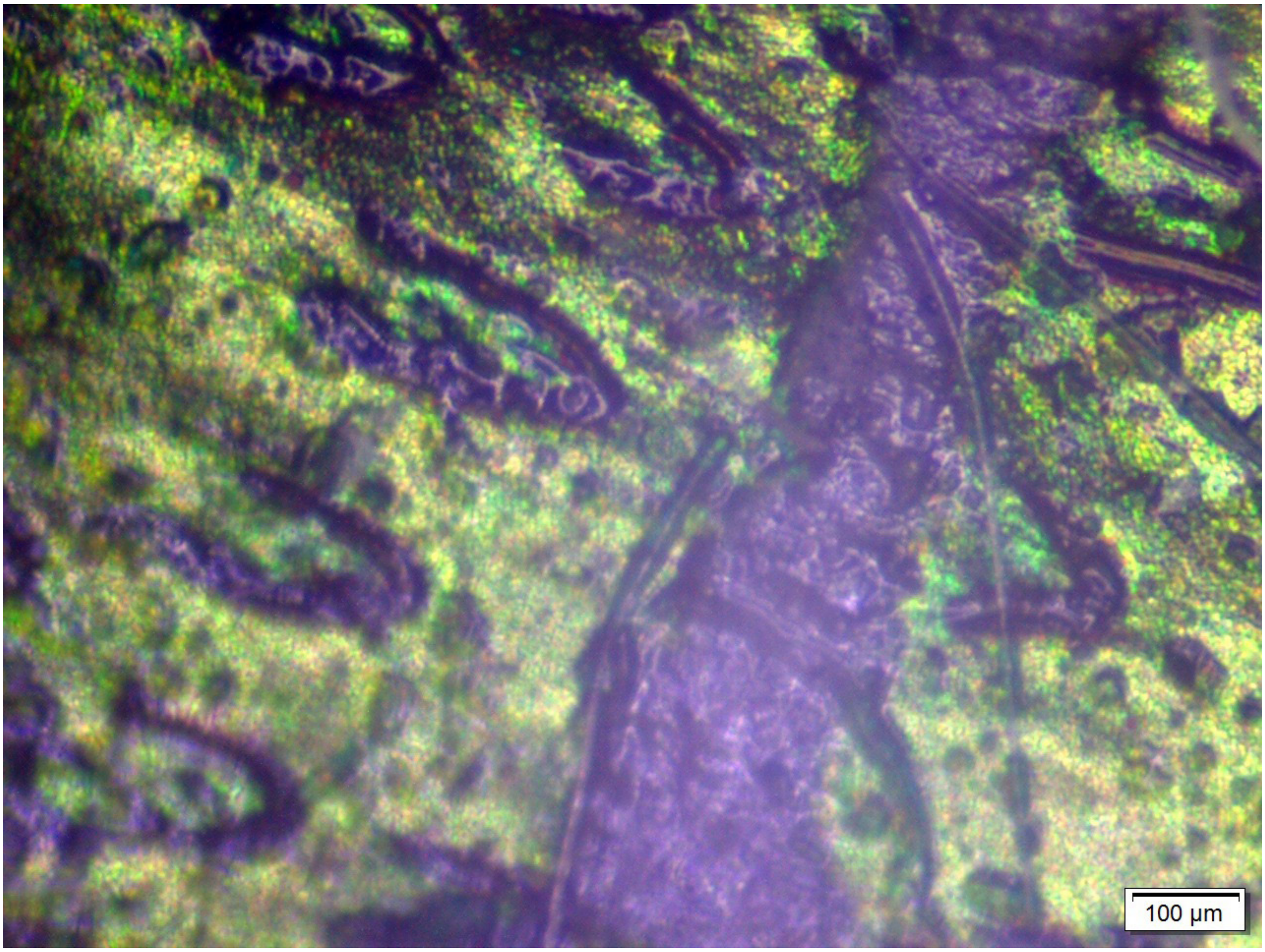
Damien Leech is a research fellow within CfAM, University of Nottingham, working on digital manufacture for new medicine development with a background in physics. He undertook his PhD on theoretical van der Waals heterostructures of 2D materials, such as graphene and silicene, at the University of Bath. Following that he joined the Centre for Fine Print Research within UWE Bristol, working with a variety of engineers, scientists and artists on a range of projects including resurrecting forgotten 19th century printing processes, 3D printing soft gel materials, ceramic extrusion and printing anti-microbial surfaces.

IMAGE GALLERY



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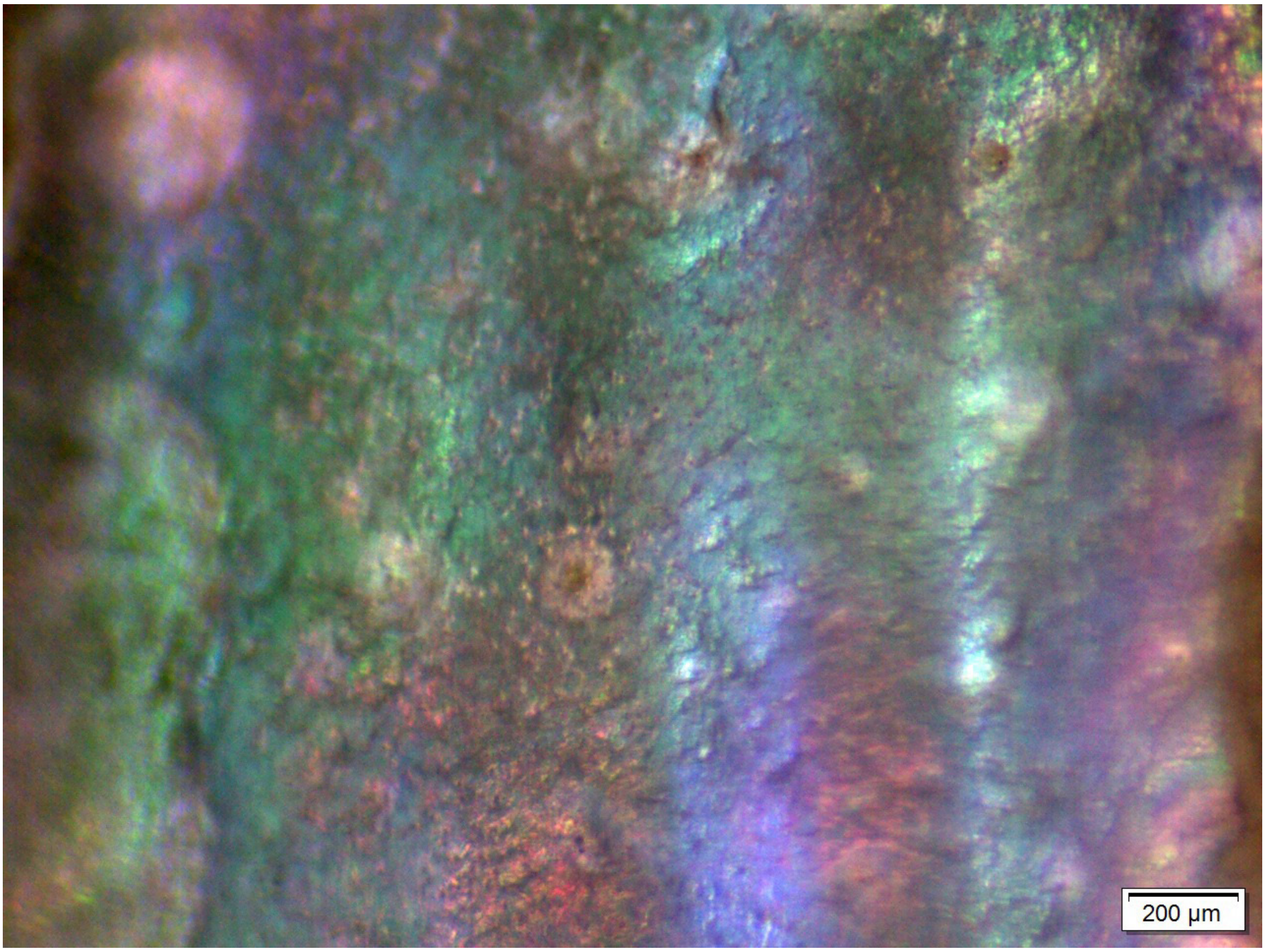

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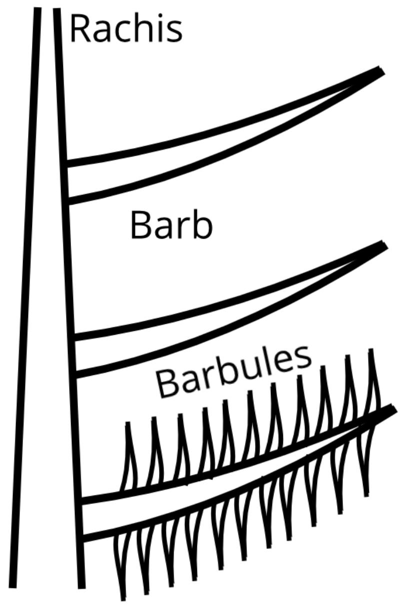

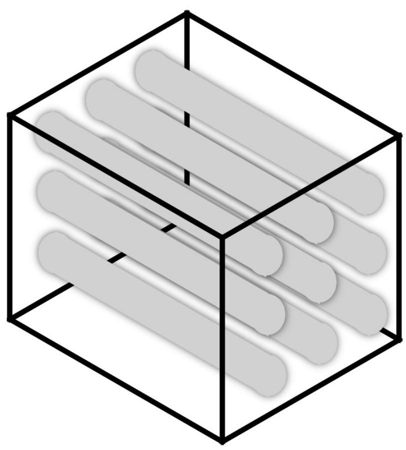

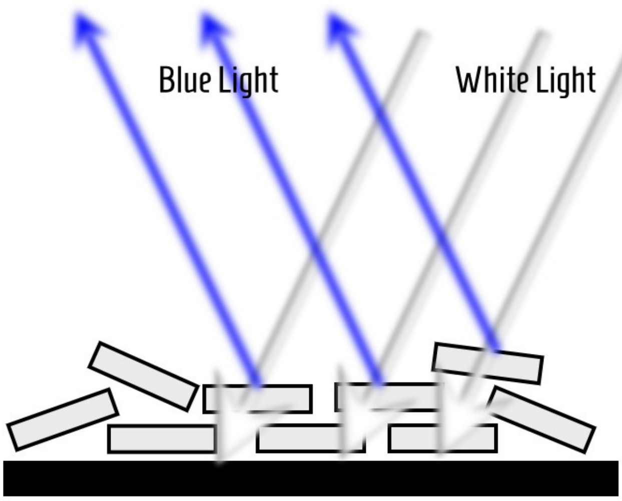

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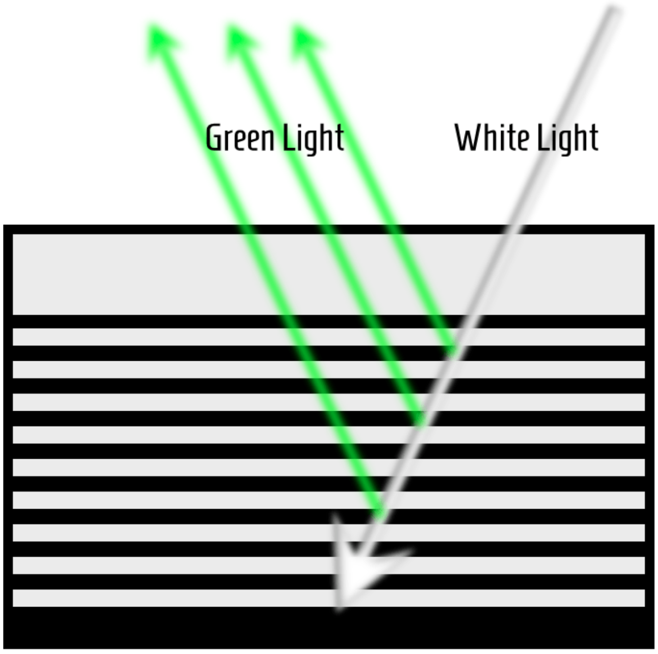

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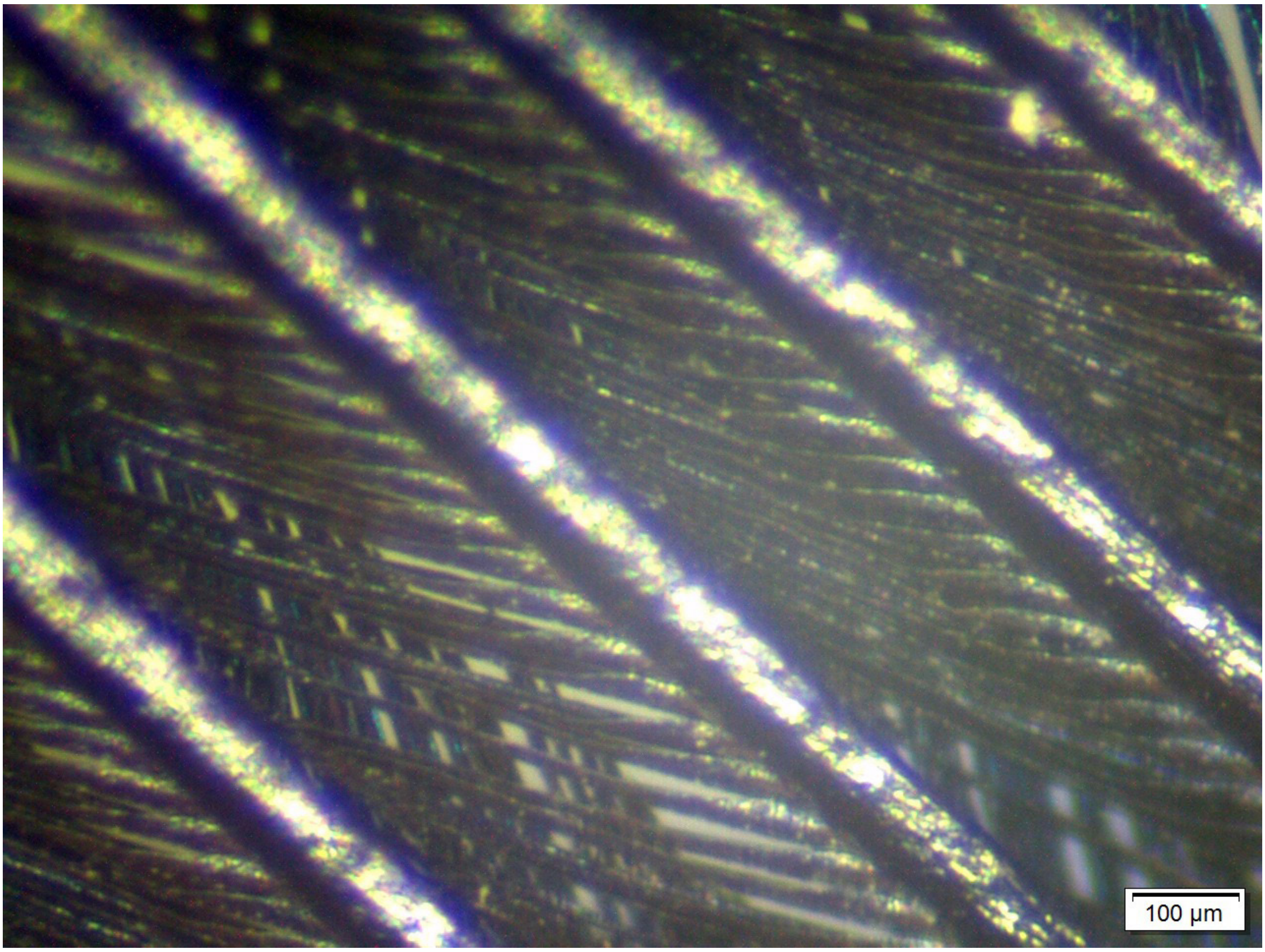

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