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Lippmann photography: history and modern replications of the elusive structural colour

Elizabete Kozlovska, Susanne Klein, Frank Menger, Centre for Print Research, University of the West of England, Bristol, United Kingdom

Abstract

In 1908 physicist Gabriel Lippmann won the Nobel Prize for creating a true colour process using standing waves. This paper reviews the historic process of creating Lippmann plates and applies them to recreate the process with modern materials. The optics of the created samples are reviewed, comparing results to Lippmann's own research and modern attempts by other researchers to recreate or improve the process.

Introduction: a review of what Lippmann himself has done and what has happened since

French inventor Nicephore Niepce is widely considered to be the father of photography, with his 1827 discovery of heliographs which formed on asphalt coated with lavender oil [1]. Whilst these are some of the first images considered to be true photographs, attempting to create true colour photographs has been a goal for scientists even before monochrome images became mainstream.

Many before Niepce had attempted to capture the world in colour. Either the experiments failed to capture the illusive colours in full spectrum and hue, or they faded with lack of fixing [2]. Even German philosopher Goethe dipped his toes into colour photography at the start of the 19th century [3]. Other famous names in European photography circles, such as Talbot, Herschel and Becquerel continued his efforts, with fleeting success. Meanwhile in the USA, rev. Levi Hill claimed to have created his own colour photographic process which he named Hillotypes [4]. The validity of his results was widely disputed and did not convince his peers, in part because of the inaccessibility of the process [5]. However, in 1908, a French mathematician and physicist by the name of Gabriel Lippmann won the Nobel prize for creating colour photographs in a way no one else had attempted before: by using standing waves to create interference patterns that record full colour images.

Born in 1845 in Luxembourg, Jonas Ferdinand Gabriel Lippmann moved to Paris with his father and mother, where he pursued various fields of education, until discovering his passion for physics [6]. The young man's scientific endeavours expanded from working at home with borrowed equipment to obtaining a position at the Sorbonne University. Later he became chair of mathematical physics at the Faculty of Science, where he taught for 40 years. Inspired by German scientist Zeker's theories on reflection holography, and Maxwell's electromagnetic theory, Lippmann delved into creating true colour photographs without the use of dyes [7].

The mathematician briefly explained his process in some of his lectures before giving his Nobel Prize speech in 1908. In 1896 he claimed that there are only two conditions necessary to create colour: transparent film and a mirror on the back of the film during the exposure [8]. These physical conditions were seen by the scientist as far more important than the chemistry of the photographic emulsion, which Lippmann described as secondary.

He describes the method as follows: '*A plate is covered with a sensitive transparent layer that is even and grain-less. This is placed in a holder containing mercury. During the take, the mercury touches the sensitive layer and forms a mirror. After exposure, the plate is developed by ordinary processes. After drying the colours appear, visible by reflection and now fixed*.'[9]

He continued to explain that interference happens during the exposure process, when the incident rays of light interact with the waves reflected by the surface of mercury. This causes interference fringes to form half a wavelength apart. These fringes are recorded in the emulsion and form a latent image (**1** a)). To view the plate white light is reflected by a semi- transparent mirror onto the Lippmann plate (**Figure 1**). The observer is on the far side of the semi-transparent mirror. The

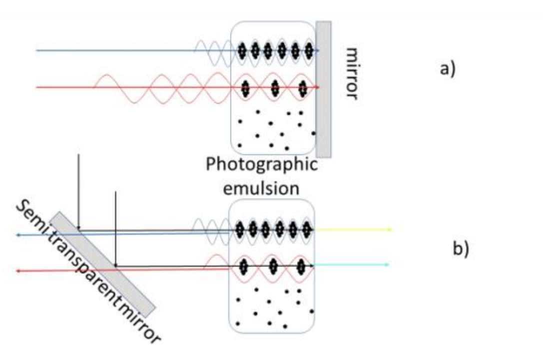

***Figure 1**: The principle of Lippmann photography. a) recording b) viewing*

standing wave in reflection reconstructs the original colour. Complementary colours are transmitted. In short, interference colours are produced when a thin film, such as Lippmann emphasizes in his work, reflects light in a way that light waves overlap and cause extinction of certain wavelengths by destructive interference [10].

Lippmann's discovery created waves in the scientific community, leaving an especially prominent impact on a Spanish counterpart, a neurologist by the name of Santiago Ramon Y Cajal. He went so far as to include a chapter in his monograph on colour photography (1912) [11]. One of Cajal's main goals was to understand the structure of Lippmann's photographs. His method for this was examining the structure of the optical layers, or laminae, as called by Zenker, under a microscope. A few more prominent figures endeavoured to examine these layers through microscopy, such as Lehman, Neuhouss, and Ives [12].

Sadly, the process did not prove as popular amongst beginners and amateur photographers, who quickly switched to 3 colour processes instead, such as the Kromskop by Frederic Eugene Ives [13] (the diffraction process of colour photography, R. Wood), or the Lumiere Autochrome, which used dyed potato starch to create colour [14]. Soon enough Lippmann's unique process was commercially overtaken by simpler processes.

Nevertheless, the issue of creating true colour photography without the use of dyes has been continuously pursued throughout the 20th century. Some names that followed up on Lippmann's process have already been mentioned, however, the idea of interference imaging persisted throughout the century.

For example, the Hungarian-British physicist Denis Gabor used optical interference fringes to improve images taken by an electron microscope. In 1948, Gabor coined the term 'hologram', using the Greek word 'holos', meaning whole, to describe the optical information stored in the resulting image [15]. The physicist took inspiration from Bragg's theory, which later was used by other like-minded scientists. In 1961 W.G. Burgers from Delft published an article in the renowned journal NATURE, using Lippmann's photographic process as an example of Bragg's Law [16]. (Optical Demonstration of Bragg's Law) Burges focused on the spacing between the wave lengths, similar to Cajal and Zenker before him. He found that introducing moisture into the sensitive gelatine layer by breathing on it causes a colour shift depending on the angle of the reflected wave lengths. This knowledge proved essential to practical experiments conducted by the author.

A year later Yuri Denisyuk was inspired by Lippmann's colour photographs, and created single-beam reflection holography, which he named after himself [17]. Born in the Soviet Union, Denisyuk's goal from the start of his career was 'to develop image display devices which could reproduce and absolute illusion of the presence of the objects displayed'[18]. Unlike Gabor, Denisyuk did not use microscopy for his experiments, but rather appropriated Lippmann's practical method by applying a convex mirror to create a spherical wave front. The resulting image he called a 'wave photograph', which he later adapted with the focus of recording wave fields in space [19].

In the meantime, Lippmann's ideas continued to develop in a completely different way. In the 1950's physicists Emmett Leith and Juris Upatnieks worked at the University of Michigan, where they initially were involved with battlefield surveillance system development. Nevertheless, the optical processing research conducted by both lead them to a different branch of imaging, using the classified universities research background to rebrand their work as a type of photography by showcasing 3D images created by their method. This was called 'lens-less' photography, by the American Institute of Physics [20].

As the connection between holography and interference photography kept developing, more and more professionals engaged with the concept. Hariharan drew a direct connection between Lippmann photography and Holography in 1998 [21]. Similarly, Hans Bjelkhagen dove into the subject; by 1999 he had reviewed the Lippmann colour process and aimed to improve it with modern techniques [22].

Modern research

Some of these scholars continue their work well into the 21st century, researching both the history and applications of Lippmann's work. The Royal Society of London has taken an interest in Lippmann's work, recording the history of interferometric colour photography, and collecting as much detail about the process and the man behind it as possible [23].

In the meantime, Hans Bjelkhagen has continued his work and has written several publications and a book on imaging in collaboration with David Brotherton-Ratchcliffe. Bjelkhagen's body of work somewhat dominates the field of interference imaging, yet others have also contributed with investigations of the subject and Lippmann's process.

Reviewing the history of holography and the connection to Lippmann photography has been widely looked at by Sean F. Johnston, who has curated an array of expansive articles on the historic figures in the field and their practice [24]. William Alshuler in the California Institute of the Arts looked into the practicality of the Lippmann process and its problems [25]. He attempted to use parts of the process for various applications, such as archival recording, large scale projections, and security applications, the latter of which has also been explored by Bjelkhagen [26]. Other significant discoveries have been done unofficially, by practicing the 100-year-old photographic method and experimenting with it.

Practical experiments looking into optical properties of Lippmann photography

The objectives of the practical experiments are as follows:

- Recreate Lippmann photographic process as close to the original concept as safely as possible.

- Investigate optical properties of Lippmann plates.

- Investigate modern applications for creating Lippmann plates.

Before any of these can be achieved, samples of Lippmann colour plates must be created for further analysis.

Preparation of sample plates.

For practicality, the interferometric photographs were created on pre-made commercial holographic Slavich plates from the Lithuanian provider Geola. Thirty-four plates sized 63x63mm were prepared and exposed under white light. The plates were mounted in a Hasselblad SWC medium format camera with a 39mm Biogon lens. The images were mounted with the emulsion facing away from the lens, using a 12 mm air gap behind the plate as a replacement for the reflective mercury surface [27]. The back of the holder was covered with black velvet to absorb light. Loading of the plate was performed in appropriate conditions under Kodak #3 Dark Green Safelight in the darkroom. 4 different exposure and development tests were performed.

1st 10 plates:

Images of a pink tea-rose bush taken during bright sunshine outdoors in May 2020. Exposure was ISO 400, 1/500th second, f4. Exposure times:

1st plate 5 minutes
2nd plate 10 minutes
3rd plate 15 minutes
4th plate 20 minutes
5th plate 40 minutes
These plates were processed with Geola commercially

provided SM6 developer and PMB bleach according to the provided instructions.
Plates 6 to 10 were exposed for 20 minutes. Bleaching was omitted from the process.

2nd test: plates 11 to 20

The commercially provided Geola developer was replaced with Lippmann's developer recipe, also known as Lumiere developer, which was described by Hans Bjelkhagen [28].

Based on the previous tests, and with an improved plate holder design, the exposure was kept at 20 minutes as this seemed to achieve the correct visual density for the image.

Materials used for developing were a formalin hardener and Lumiere developer.

Plates no. 21 and 22 were discarded due to being exposed the wrong way round. Pates 23 to 27 were exposed between 20 and 40 minutes, hardened for 6 minutes (except for plate no.26, which remained unhardened), and developed for 3 minutes.

4th test
Plates 28 to 34 were developed with a different variation of the Lumiere developer, with the following recipe:

Solution A: Pyrogallol 1g

Distilled water 100 ml Solution B:

Potassium Bromide 15g Ammonia (saturated) 30ml Distilled water 150ml

To use, mix 3ml part A and 6ml part B plus 100ml water Development time 1 to 3 minutes [28].

The environment was changed: the last batch was created outdoors in bright sunlight. Exposure parameters were ISO 100, 1/250 second, f5.6. Exposure time for these plates was between 10 and 40 minutes. Development time was 3 minutes, and neither of the plates were pre-hardened.

Results of photography:

1st batch:
No visible images resulted on the plates, apart from baseline fog.

2nd batch:
The omittance of bleach retained the silver image, however, only negative images were visible. Example of plate No. 12 can be seen in figures 2 and 3.

3rd batch:
Both negative and positive images can be seen depending on the viewing angle. Images appeared to be overdeveloped and fogged. Most images appear to have a red hue and did not show accurate colours.

4th batch:
More accurate colour representation, yet still biased towards a red hue. Images are faint. Prolonging exposure time for longer than 20 minutes did not change image quality. After exposure, the plates tank and treated as follows:

Pre-hardening of the plate Celsius.

Formula for hardener:

Distilled water 750 ml Formaldehyde 37% (Formalin) Potassium bromide 2 g Sodium carbonate (anhydrous) Add distilled water to make 1 l

were transferred to the processing for 6 minutes at 20 degrees

10 ml (10.2g) 5g

Developing of the plate: 6 minutes at 20 degrees Celsius Formula for developer:

Solution A: Pyrogallol 1 g

Alcohol (propanol) 100 ml Solution B:

Potassium bromide 10 g Water (distilled) 100 ml

Working solution: Mix 20 ml solution A + 30 ml solution B + 140 ml water. Add 10 ml ammonia (s.w. 0.960 at 18 degree C) just before using. Use only once. Use at 15 degrees C. Wash and dry, no fixing or bleaching (Curtesy of Hans Bjelkhagen, 2016, and his comment on Lippmann Facebook group).

***Figure 2**: Geola exposed plate no.12 viewed at a 90-degree angle in plain light.*

Plates 11 to 20 exposed same as the previous batch: ISO 400, 1/500th second, f4. Exposure time remained 20 minutes.

3rd test:

For the final test, the same Hasselblad medium format camera was used. Photographing took place indoors, during daytime, with exposure measurement ISO 100, 1/15 second, f5.6. Lighting used was a softbox without a diffuser with 4 fluorescent bulbs.

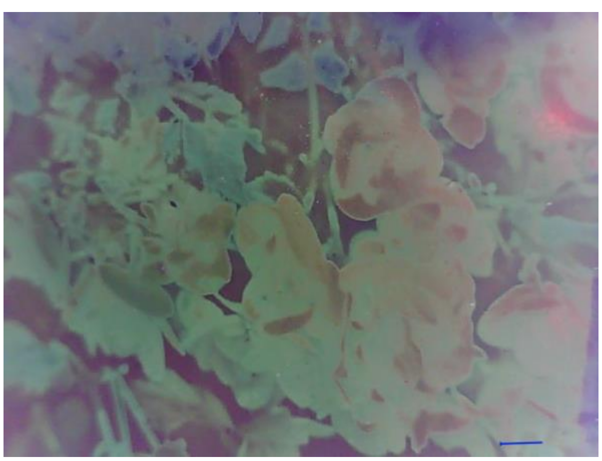

***Figure 3**: close-up of Geola plate viewed from approx. 30-degree angle in plain light. Magnification x55*

Discussion and Analysis

All the holographic plates that have been developed and show a visible image encounter the same issue: a visible bias towards a red hue. Six plates were examined under UV Spectroscopy to assess differences of captured wavelengths within the plates. All the plates proved to be within the 550 – 750 nm range on the visible spectrum, concurring that mainly the red light was captured. Example spectra can be seen in figure 4.

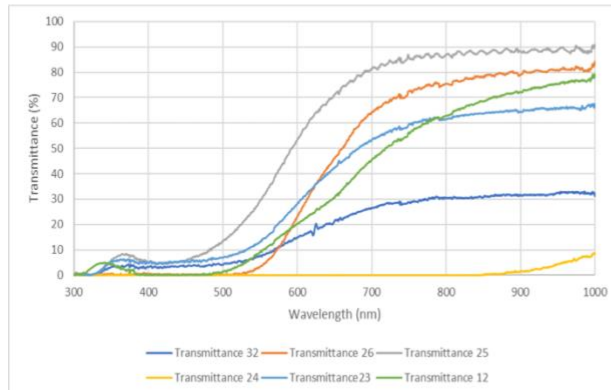

***Figure 4**: UV spectroscopy results comparing transmittance (%) of plates 32, 26, 25, 24, 23 and 12.*

These same plates were examined with SEM, to observe the gelatine layer and what can be seen there. Various layers can be observed in the emulsion, which raised the suspicion of visible optical layers, or how they have been referred to in earlier texts, Zenker's Laminae [29]. Examples of the SEM images can be seen below in figures 5 and 6.

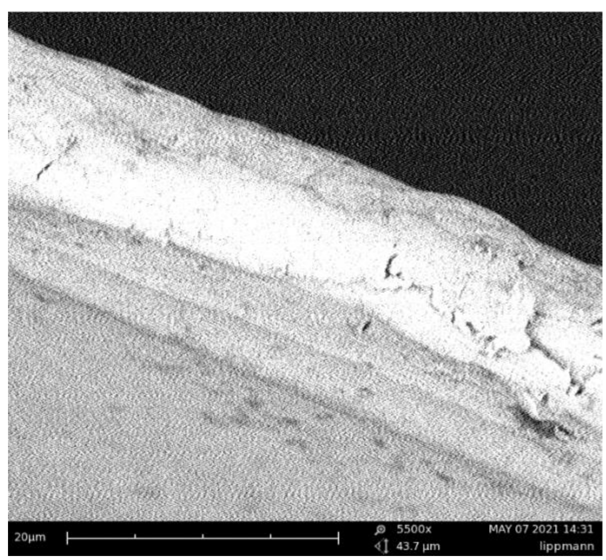

***Figure 5**: SEM of commercial Geola Lippmann photograph, magnification x5500*

The obvious shift towards the red end of the visible spectra can be for various reasons. However, one option in particular seems viable in this case: The creator of the plates mentions the importance of recognizing the emulsion layer and tested the plates by breathing onto them. The same method has been mentioned by Burges in 1961, when demonstrating Bragg's law using Lippmann plates. The author physicist breathed on the emulsion to slightly swell the gelatine, causing significant colour shifts, which was assumed to be because of the changes in the spacing of the wavelengths [30]. Therefore, the SEM served to examine whether the optical layers of the emulsion can be observed with the magnification ranging between x5000 and x7000.

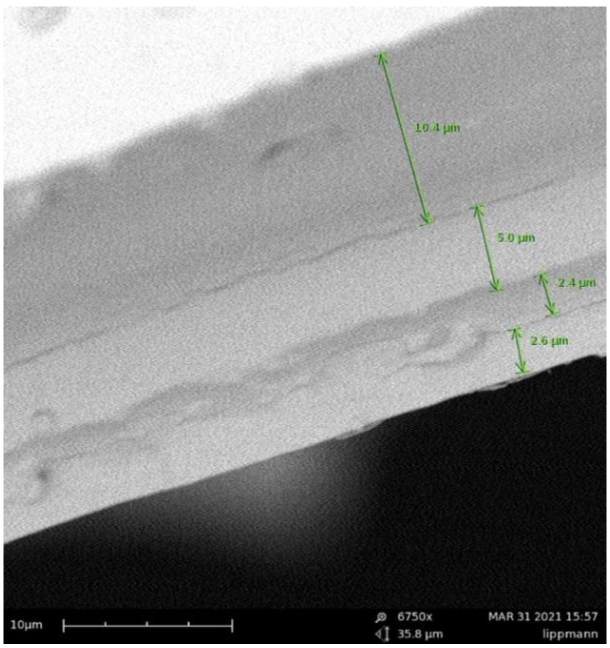

***Figure 6**: SEM of commercial Geola plate Lippmann photograph. Layers are observed in the emulsion, that are measured and compared. Magnification x6750.*

Whilst some layering can be observed within the gelatine layer, there is no certainty of these layers being the so called Zenker's optical laminae. A certain symmetry can be observed as seen in figure 3, however a comparison with a standard black and white emulsion layer under the same magnification may serve well to compare the structural differences and determine the nature of the layers.

In the meantime, there are 30 more Geola holographic PG3c plates to be exposed and developed. The conclusion after developing the first 34 colour plates is to use a variation of the Lumiere developer with the use of hardening. A new variable will be introduced in the form of Relative Humidity (RH), to see if maintaining this variable constant will prevent swelling of the gelatine layer, especially between exposure and developing. Different equipment will also be used for exposing the plates: whilst previously a medium format Hasselblad camera was used, a medium format slide projector will be tested for its effectiveness in the process. Because of the slow exposure times, there is no need for a fast-acting shutter. This will serve to examine the possibility to adapt Lippmann's photographic technique for simpler use taking in account safety of the materials without compromising the quality of the colour photographs.
The next step after using commercially available holographic plates would be to create custom emulsions in a controlled environment. With the freedom to adapt the chemistry of the sensitive layer, more control can be exerted over the results. This can also help examine Lippmann's claim that any photographic method with a fine grain emulsion and a clear film can produce structural colour. A review of such photographic methods during Lippmann's time at the end of the 19th century would be necessary to conduct practical comparisons. Therefore, there is still much to be done in order to fully understand the nature of interference photography and structural colour.

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Author Biography

Elizabete Kozlovska studied her BSc in Conservation from Cardiff University, and obtained her MA in History of Art at University of Bristol. Since then, she has worked in the conservation department at Historic England Archives, before obtaining a Research Associate position at the Centre for Fine Print Research, University of the West of England, Bristol. Her work focuses on historic photographic processes and their application in modern print technology.