

## **Chemistry and colorimetry: preliminary investigation on chromogenic motion picture film**

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### **Abstract**

Color fading due to the degradation of the dyes is the main concern regarding the conservation and restoration of photographic and cinematographic materials. The intervention on the physical support is most of the time unsatisfactory and insufficient for restoration, which makes the digital conversion and digital restoration the only means to recover the film content. However, missing the non-degraded version of the support, the restoration is still dependent on the subjectivity of the operators that perform the work, even being experts. In this context, colorimetric studies are necessary in order to formulate hypotheses on the real evolution of the degradation process of the dyes as a function of time, with the purpose of obtaining information about the original appearance in respect to the analog materials. Different materials mean indeed different gamuts that lead to different colorimetric coordinates.

The existence of a wide number of different films makes the conservation and restoration process very challenging. Indeed, in the photographic and cinematographic history, not only several supports (cellulose nitrate, cellulose triacetate and polyester) have been used, but also many techniques of coloration or color development (from early cinema to chromogenic motion films) have been employed, as well as many emulsions, dyes and couplers. In this scenario, knowing the material that composes the physical part of the film object could help the experts in all their work, from conservation to restoration.

Unfortunately, the leading production companies have always been reluctant to divulge the compositions of the used compound due to the competitive logic that has always governed the film industry. Moreover, with the decline of the film market, the technical datasheets of films are harder and harder to find. This scenario is even worsened by the fact that a very limited number of studies have been reported on the identification of coloring substances of film materials.

In this work, we want first to make the reader aware of the difficulties and problems we have encountered on this topic, highlighting the importance of scientific research on this cultural object that would otherwise be lost. Finally, we want to show the preliminary results that make Raman spectroscopy, and especially SERS (Surface-Enhanced Raman Spectroscopy), a promising method to individuate the dyes of motion picture films, revealing a new potential application of this technique in the field of conservation science.

**Keywords:** SERS, Raman, Chromogenic films, Color films, Film dyes.

### **Introduction**

Photographic and cinematographic materials have enriched our cultural heritage over the past century. Unfortunately, with the advent of digital technologies and streaming platforms, analog film support is no longer a technology used today. However, there still exists a wide cultural heritage printed on these supports. Despite being quite recent, film materials rapidly deteriorate in function on the environmental condition when not monitored, depending on humidity, temperature and exposure to light. Besides the degradation of the supports (being them nitrates, acetates, or polyesters), in color motion picture film the color fading due to the degradation of the dyes is the main issue since it can also occur in the dark without the presence of light, making the films stored in our archives and film libraries difficult to preserve.

In this work we consider only chromogenic films which are the most common in the color motion picture field. Before continuing, it is important to recall first the mechanism under the formation of dyes in chromogenic films. In this type of films, there are three separate layers of emulsion, respectively responsible for the development of magenta, cyan and yellow. Each of these layers contains the same developing agent (p-phenylenediamine derivatives) that oxidizes in the presence of light and then reacts with three different color couplers (one for each emulsion layer) to form the dyes as shown in Figure 9. The color coupler can be connected to several functional groups that enhance the features of the dye: *ballasting groups* stop dyes from moving across layers; *leaving groups*, often referred to as coupling-off groups, both optimize the coupling rate and encourage the direct synthesis of the chromophore.

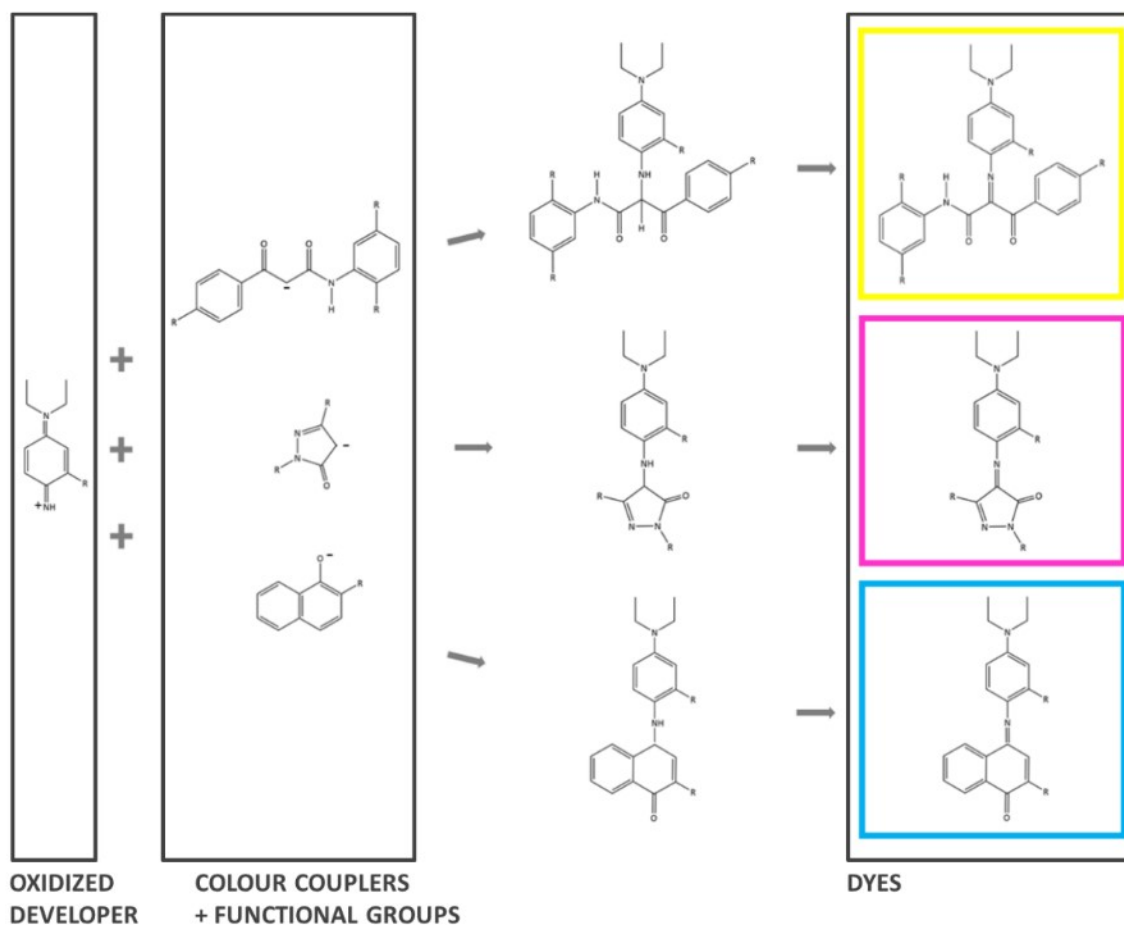


Figure 9 - Schematic representation of yellow, magenta and cyan dyes, resulting from the coupling reaction with benzoylacetyl, pyrazolone and substituted naphthol type of color coupler, respectively (Silva, 2019)

The type of coupler, ballasting groups, and the developing agent will determine the precise nature of the final dye. The knowledge of this nature is important because the degradation processes that must be taken into account when conserving and restoring the films are connected to the molecular classes to which the dyes belong (Di Pietro, 2007). However, throughout the history of photography and filmmaking, a variety of supports, including cellulose nitrate, cellulose triacetate, and polyester, as well as a wide range of emulsions, dyes, and couplers were indeed utilized. Different materials are used depending on the film type and stock (negative, print, reversal film, and intermediate). However, even within the same category, the chemical nature of color couplers and dyes has changed significantly throughout time for finding dyes with more saturated colors, greater stability, increased grain size and sharpness, and lower costs. It is clear that, in this context, conservation and restoration are made difficult

and challenging by the availability of such a wide variety of materials, and scientific support and diagnosis are paramount for the correct treatment and process of this type of cultural heritage.

### **PhotoFire2 and Colorimetric analysis**

The first step we did in this direction is the creation of *PhotoFire*<sup>2</sup>, an online and open-source database both for cinematographic and photographic films. For a more in-depth presentation of the database and the relative webpage (<https://mips.di.unimi.it/photofire/>), the readers can refer to (Sarti *et al.*, 2022). The database collects physical data of the film stocks and the technical datasheets released by the producing companies at the time.

This type of information can support the work of the experts both for conservation for choosing the best-storing condition and restoration for obtaining a faithful retrieval of the cultural object to the original materials and period of time. Unfortunately, in the case of digital restoration (that most of the time is the only option left since the original colors cannot be chemically restored), the analog supports are often not even considered by the operator that performs the restoration since the main focus is given to the movie or the photography contents. Nevertheless, every image is the direct outcome of the radiation-matter interaction between the light and the film substance and this means that the fundamental qualities of each image are determined by the physical and chemical characteristics of the material making up the analog stock. Among other features, this can lead for example to a different set of colors that a particular film can or cannot reproduce (i.e. the color gamut).

Figure 10 shows a comparison between two reversal films to give an example: Fujichrome Provia 400X Professional [RXP] by Fujifilm and Kodachrome 64 by Kodak. From the spectral dye density found in technical datasheets of the film stocks (Figure 10a), we were able to extract the color gamut following the Neugebauer and Demichel equations (Oleari, 2015), whose representations in the CIE xyY Chromaticity plot and in the CIE L\*a\*b\* space are reported in Figure 10b. Then, applying the ICC profiles to the same image with an absolute colorimetric intent leads us to the color reproductions in Figure 10c, supported by the  $\Delta E_{200}$  map that indicates the pixel-wise color difference between the two reconstructions. With this study, we had proven that the differences in the material composing the films reflect the difference in the color gamut and, consequently, the variation in the appearance of the content printed on the supports.

It is clear that the availability of film technical and sensitometric data will make the preservation and restoration process easier and, above all, more objective. Tone and color rendition errors can be avoided and some film properties and features may be supported by mathematical and physical models. From the film's spectral sensitivity and spectral dye density curves, specific algorithms can be developed not only to reconstruct the color gamut but also to obtain other colorimetric data, such as the creation of a dye degradation model starting from the original data sheets of the film materials. Although some attempts have already been made to achieve this aim (see for example (Gschwind and Frey, 1997; Rizzi *et al.*, 2008)), much improvement is still needed to faithfully reproduce the perception of color film.

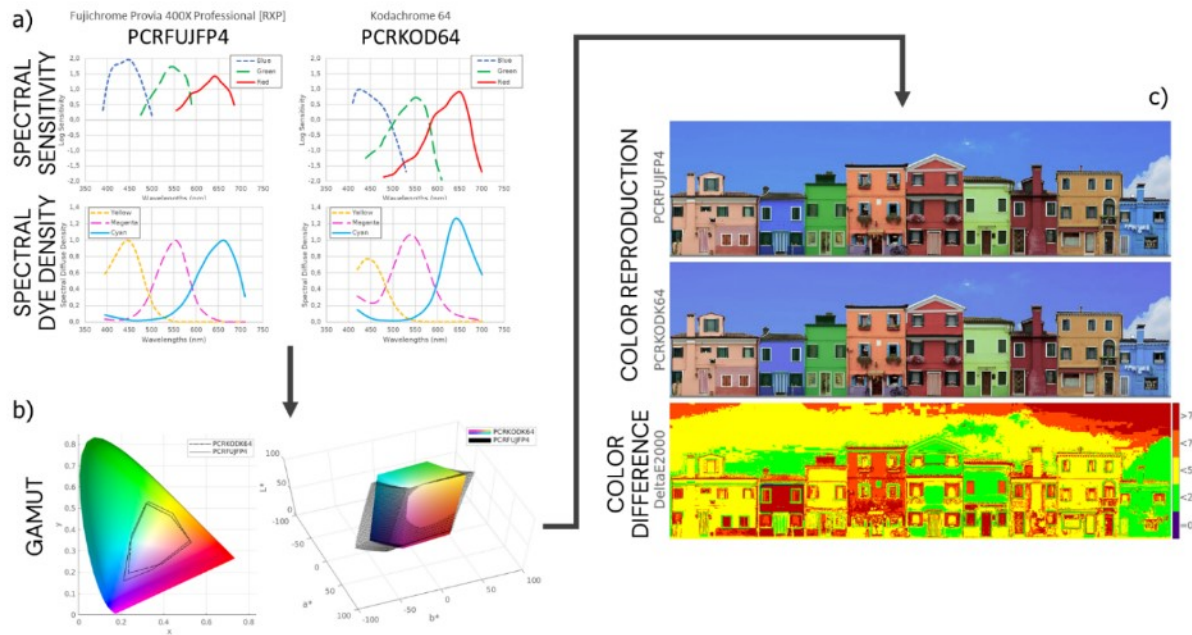


Figure 10 – Comparison of the two reversal film stocks: Fujichrome Provia 400X Professional [RXP] (PCRFUJFP4) by Fujifilm and Kodachrome 64 (PCRKODK64) by Kodak: (a) Spectral sensitivity and dye density, (b) 2d and 3d representation of the gamut of the two films and (c) color reproduction (Sarti et al., 2022)

Up to this publication, we have collected 601 photographic and cinematographic films (233 with technical datasheets) produced by 22 production companies and datable from 1935 to 2018. However, this is an ongoing project and the database is designed to grow.

### Chemical analysis

The second step we made in this direction is the chemical analysis. Although there are several books and manuals about the nature of the couplers and developers (see for example (Bergthaller, 2002a, 2002b, 2002c; Rogers, 2007)), the literature search about the analytical technique that can be used to gather information about the molecular structure of chromogenic dyes leads us to only two works: (Di Pietro, 2007) and (Silva, 2019). According to these contributions, there are three different possible ways to examine the chromogenic dyes.

The first one is using an analytical method that allows for non-destructive layer selection, such as confocal Raman spectroscopy. This technique allows indeed to select the depth from which the signal is taken, however the film materials have a high fluorescence response (probably deriving from the gelatin binder and/or impurities within the emulsion layers), which hides the characteristic signals of the dyes and makes ineffective the application of this technique in this field.

The second strategy consists in cutting the film with a microtome for a thin section and then examining the layers separately. Since each layer has a thickness between 5 and 10  $\mu\text{m}$ , the analytical method must have a measurement area with a diameter of 5  $\mu\text{m}$  or less, such as micro-Raman or micro-FT-Raman spectroscopy. This approach is interesting but is limited by the technical difficulty of preparing thin sections in which the layers are clearly distinguishable.

Finally, the last method involves chromatographic separation. This involves a first step in which the dyes are extracted from the emulsion, after which the separation can be done in two ways: in the case of High-Performance Liquid Chromatography (HPLC) coupled with Mass Spectrometry (MS), the samples separated in the liquid chromatography column end directly to the mass spectrometer; in the case of Thin-layer Chromatography (TLC), the isolated compounds can be then analyzed with further and suitable diagnostic techniques such as Fourier-transform infrared spectroscopy (FTIR) or Raman spectroscopy.

Both (Di Pietro, 2007) and (Silva, 2019) conclude that although some of the tested analytical techniques have shown promising results, the identification and assignment of the dyes to a specific family of chromogenic compounds was not possible due to the lack of reference databases, both for Raman and IR spectroscopies and MS.

Based on these considerations, we studied and proposed the application of Sequentially Shifted Excitation (SSE<sup>TM</sup>) and Surface-Enhanced Raman spectroscopy (SERS), whose methodology and results are deeply described in (Longoni *et al.*, 2022). In this work, we inspected a 35mm Fujicolor Positive Film Eterna-CP 3513DI with PET support, printed with the trailer of the animated movie *Happy Feet* (Warner Bros, Burbank, CA, USA, 2006).

The fluorescence emission associated with organic compounds makes standard Raman spectroscopy unsuitable for detecting such molecules. However, the recent introduction of the SSE<sup>TM</sup> technique has improved the ability to overcome this problem (or at least minimize it) in various analytical fields (Conti *et al.*, 2016). We applied this technique to the three emulsion layers preventively carefully isolated with a scalpel (Figure 11a). Since this technique does not use a conventional Raman spectrometer but relies on a technology that reduces the fluorescence, the results in Figure 11b show flat background spectra with intense and well-defined signals of the dyes, very different from the gelatin spectrum.

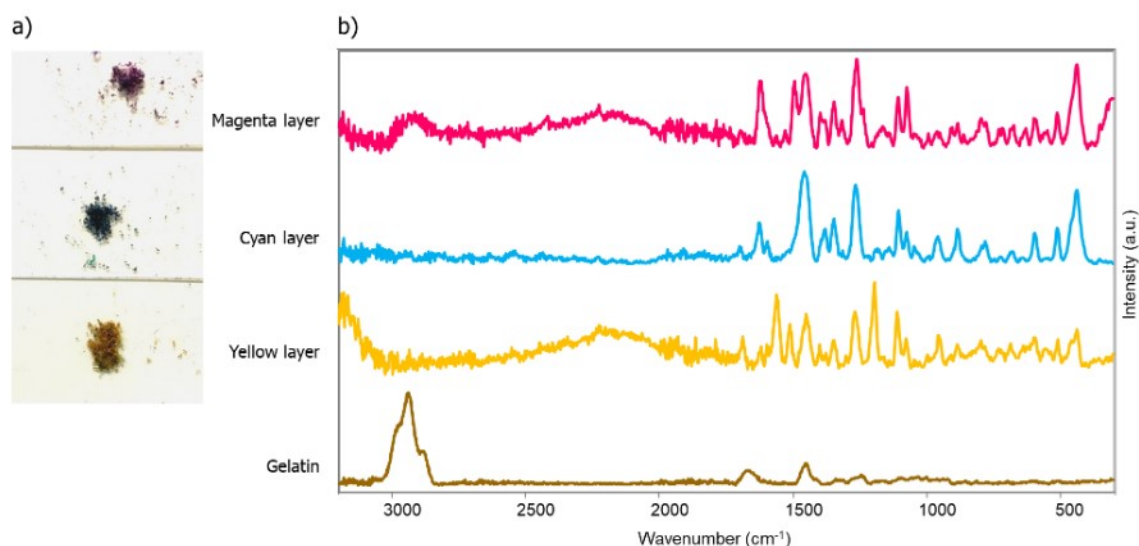


Figure 11 - (a) Powdered cyan, yellow and magenta emulsions of the Fujicolor Positive Film Eterna-CP 3513DI and (b) their SSE<sup>TM</sup> Raman spectra compared with the gelatin spectrum.

Furthermore, we wanted to investigate the SERS response of the dyes. Although, as far as we know, nobody ever applied it to film materials, we believe that this technique could have enormous potential in this field. The great enhancement of the Raman signal (up to a factor of  $10^8$ ) when the analyte is absorbed or is in the proximity of a rough metal surface (Fleischmann, Hendra and McQuillan, 1974) allows the detection of analytes even at very low concentrations, meaning that a small quantity of dye is required. Moreover, the quenching of the fluorescence photons emitted by organic molecules determines its wide application in the analysis of natural dyes in cultural heritage in the past 20 years (Pozzi and Leona, 2016). First, we used TLC to isolate the dyes (Figure 12a), which were then scratched away from the plate and prepared for the SERS analysis by extracting the analytes by sonication in ethanol. The spectral responses were compared with those of three reference compounds, previously reported by some of us (Longoni *et al.*, 2022). These compounds, whose structures are shown in Figure 12b, derived from the most common families of couplers used in films: a *substituted phenol* for cyan; a *benzoylacetanilide* for yellow; and a *pyrazolone* for magenta. Figure 12c shows the SERS spectra

of the three dyes and the three respective reference compounds. Due to the aforementioned functional groups, the film dyes are significantly more complicated molecules than the synthesized ones, as demonstrated by MS analyses (data not shown). Nevertheless, the similarity of the spectral patterns in terms of signals due to the molecular core indicates that the film dyes are members of the same chemical families as the reference ones.

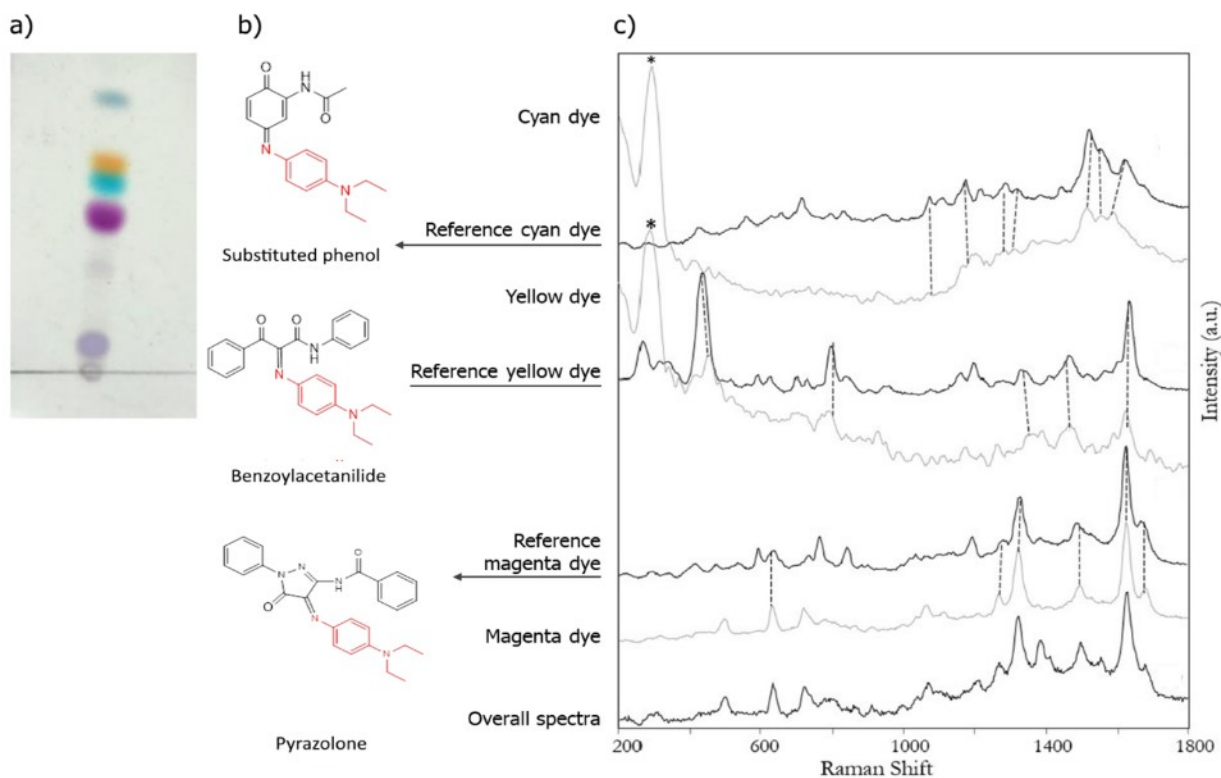


Figure 12 - (a) TLC of the Fujicolour Positive Film Eterna-CP 3513DI; (b) synthesized molecules for dye references; (c) SERS spectra of the isolated cyan, yellow and magenta dyes and the respective reference molecules (Longoni et al., 2022). The asterisk marks a band involving

the Ag nanoparticles.

## Conclusion

The purpose of this contribution is to increase awareness of the value of scientific data among film experts and restorers since it is essential for proper conservation and faithful restoration of the film content to the time it was printed. To overcome the need for technical information, we introduced PhotoFire2, our scientific, open-access and growing database.

From the colorimetric point of view, we have demonstrated how variations in the dye density of the films affect the color gamut and the appearance of the final image.

From the chemical point of view, Raman spectroscopy and especially SERS, as opposed to other molecular analysis methods like infrared spectroscopy, in the preliminary investigations had revealed itself as a promising method to individuate and classify the dyes of motion picture films. In future developments, we want to deepen these investigations, including a wider range of reference compounds, representative of additional coupler types and dyes extracted from films of various brands and dates.

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